ADVANCES IN ATOMIC SPECTROSCOPY

Editor: JOSEPH SNEDDON

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PREFACE

Volume 4 of *Advances in Atomic Spectroscopy* continues to present cutting-edge reviews and articles in atomic spectroscopy as the previous three volumes in this series.

Chapter 1 deals with electrostatic precipitation in electrothermal atomization atomic spectrometry. Electrostatic precipitation has been extensively used in industrial hygiene to remove dust and particulate matter from gases before entering the atmosphere, since its invention and development in the 1920s. Giancarlo Torsi and his group have combined electrostatic precipitation with electrothermal atomization atomic absorption spectrometry for the direct collection and determination of metals in air.

Chapter 2 of this volume is devoted to recent advances in the area of chemical modification in electrothermal atomization atomic absorption spectrometry. Chemical modification involves the in situ treatment of a sample to allow a more accurate measurement and quantitation of a low concentration of an analyte in a (frequently) complex matrix.

Chapter 3 involves a review of seven selected papers in 1996 which, in the opinion of David Butcher, deal with significant advances and use of electrothermal atomization atomic absorption spectrometry.

Chapter 4 deals with recent developments in flow-injection atomic spectroscopy by M.D. Luque de Castro and colleague. In the first volume of this series published in 1992, flow-injection techniques in atomic spectroscopy was presented by Julian

Tyson. The rapid progress in this field in the intervening years has led to a need to introduce this rapidly developing and changing field. The advantage of flow-injection techniques is the increased throughput of samples coupled with the possibility of a significant reduction in sample and reagent consumption. After a general introduction, the chapter focuses on increased sensitivity and selectivity, improving precision, speciation, and indirect determinations.

Chapter 5 describes the use of various atomic spectrometric techniques for the determination of mercury, with a particular emphasis on fish samples. A general overview of mercury is followed by a presentation of the various atomic spectroscopic techniques available for the determination of mercury, including cold-vapor atomic absorption spectrometry, cold-vapor atomic fluorescence spectrometry, electrothermal atomization atomic absorption spectrometry, inductively coupled plasma-mass spectroscopy, and inductively coupled plasma–atomic emission spectrometry. Finally the determination of mercury in fish including sample collection, preservation, and preparation is presented.

Joseph Sneddon
Editor

ELECTROSTATIC PRECIPITATION AND ELECTROTHERMAL ATOMIC ABSORPTION SPECTROSCOPY:

A PERFECT COMBINATION FOR THE DETERMINATION OF METALS ASSOCIATED WITH PARTICULATE MATTER

Giancarlo Torsi, Clinio Locatelli,
Pierluigi Reschiglian, Dora Melucci, and
Felice N. Rossi

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ABSTRACT

Electrostatic precipitation is a well-known and well-established technique for collecting particles in a gas and can therefore be adapted for collecting samples of particulate matter in air with a very high efficiency. In this laboratory, an electrothermal atomizer was developed as the collecting device and accumulator based on electrostatic precipitation, followed by the use of the atomizer for determination of metals using electrothermal atomization-atomic absorption spectroscopy (ETA-AAS). Results have shown that this system can achieve quantitation without resorting to calibration. This is particularly advantageous because of the lack of standards for air particulate matter. For this reason, the subtitle of this chapter is the rather ambitious statement "perfect combination....". The method has been validated by comparison with an official method for lead determination in air particulate matter. It was found that the official method, when implemented with approved commercially available paper filters, gave errors that can be as high as –20% for lead in an urban environment. The data currently obtained are relevant to cadmium and lead in air, but the method can be used for any metal with similar properties and for gases for which the electrostatic precipitation method for capturing particles can be used. It can also be easily automated for a fast analysis.

I. INTRODUCTION

The work reported in this chapter involved two independent directions. The goal of the first line of research was the optimization of a system for collecting samples of particulate matter in air based on electrostatic precipitation and its miniaturization in order to use the system as an atomizer in electrothermal atomization atomic absorption spectroscopy (ETA-AAS). The second line of research was driven by the observation by a fortunate and almost fortuitous coincidence, namely that with the atomizer developed for particles capture in air through electrostatic precipitation absorbance versus time curves were obtained for which absolute analysis could be claimed. This immediately opened up the possibility that the conventional calibration of the method (aqueous standards) could be bypassed and therefore the two lines converged and combined to produce curves for which the simultaneous presence of all atoms injected in the vapor state in the optical beam can be claimed. At the same time, a solution was provided to an almost unmanageable problem, i.e. the preparation of acceptable and accurate standards for particulate matter in air or gas.

The starting point was the realization that electrostatic precipitation is a very efficient method for separating and accumulating particulate matter or droplets present in a gas. The use of electrostatic precipitation in industrial plants to clean gases from particulate matter, with efficiency above 99%, is well established. The first research goal was to miniaturize the electrostatic precipitator to such dimensions that the tube on whose walls the particles were captured, could also be used as an atomizer in ETA-AAS (Torsi et al., 1981, 1982, 1987a, b). The possibility of locating the particles in a small section of the tube, at its center, was obtained by confining the source of charges in one well-chosen point of the collecting device. In this way, the high efficiency of electrostatic precipitation and the high sensitivity and low detection limits of ETA-AAS could be combined. In this case, the sample was not a solution but the captured particles present in the volume of gas that had been passed through the electrostatic precipitation device. Since the beginning, the system designed for these measurements worked very well except for the problem of calibration because the preparation of standards of particulate matter in a gas is very difficult and there is no ground for assuming that a standard made from aqueous solution will give results that can be used for particulate matter unless absolute analysis can be achieved (Locatelli et al., 1996; Torsi et al., 1996).

Absolute analysis was proposed for ETA-AAS by de Galan and Samaey (1970) and L'vov (1978) and recently investigated by Su et al. (1993). However, its application to peak area data obtained with commercial instruments was not easy achieved due to the difficulty of calculating the average time spent by an atom in the optical beam (Torsi, 1995a). In the case of the system constructed in this laboratory, it was found that the design of the atomizer—a graphite tube of small diameter-to-length ratio without the sample injection hole in order to maximize capture efficiency—combined with the focusing properties of electrostatic precipitation could give, when the ETA-AAS measurements were made with an high current power supply, absorbance (A) versus time curves, with a constant value of A for an appreciable length of time. A constant value of A was obtained not only with solutions but also with particulate matter samples and, as far as we know, were never before obtained. These kind of curves fitted a model of atoms vaporization and diffusion in which the constant value of A was attributed to the simultaneous presence of all atoms injected in the atomizer (Falk 1978, Falk and Schnürer, 1989).

If this was the case, then the absorbance value is independent of the atomization and diffusion mechanisms, which are responsible for the different results obtained in the case of solutions and particulate matter samples (Torsi et al., 1987). More important, if the experimental conditions are such that it can be claimed that all the atoms injected are simultaneously present in the atomizer, any matrix effect should be absent opening up the possibility and probability of absolute analysis. Conventional quantitative ETA-AAS (in keeping with all atomic spectroscopic methods) depends on the comparison of signal obtained from real samples with those obtained from standards of (usually aqueous) known composition. Absolute analy-

sis refers to the situation where quantitative results can be obtained directly from the measurement of the real sample without the use of standards.

In this chapter, the instrumentation specifically designed for measuring, without requiring the use of standards, the level or concentration of metal associated with particulate matter in air and experiments performed to validate the proposed method are presented.

II. ELECTROSTATIC PRECIPITATION

Electrostatic precipitation can be defined as the capture on a conducting surface of charged species through an electric field. The charging can be made in different ways according to the type of sample and scope that is pursued. One of the most widely used methods for charging particles in air is to exploit the corona discharge. In fact, in the presence of a corona discharge, there is formation and separation of charges at a conductor/gas interface. The geometry for the corona discharge chosen in the system used in this laboratory can be seen in Figure 1. In the graphite tube or electrothermal atomizer is inserted a tungsten needle with a sharp tip. The needle (1 mm in diameter) is centered coaxially in the tube with the tip at half its length. The tube dimensions are: 36 mm in length, and 3.2 and 4.5 mm internal and external diameter, respectively. It is manufactured by Ringsdorff Werke (GMBH, Bonn, Germany) from RWO-grade graphite and is pyrolitically coated. The needle is connected to the negative pole of a direct current (dc) source (SPD Model PS 325 SPD-Pasadena, CA) while the graphite tube is grounded. The gas, whose particles must be captured, enters the graphite tube in the opposite direction of the needle. In the presence of an electric field of increasing strength, there is a drift of the charges present in the gas toward the electrode of opposite polarity with passage of a current called "dark current." At higher potentials, depending on the geometry of

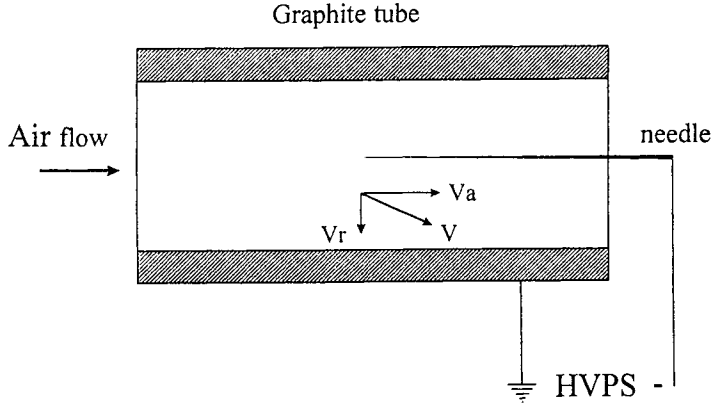

Figure 1. Schematic diagram of electrostatic precipitator.

the system, there is an increase of current by the creation and separation of charges at the tip of the conductor because, here, the electric field is at its highest value. The separation of charges is accompanied by excitation of the molecules of the gas which emit light from a volume around the tip in the form of a torus or corona. This phenomena is called a corona discharge.

The current is not continuous (Figure 2) but is composed of spikes of practically equal shape and height. By increasing the potential (and therefore the current) only their frequency is increased. The most plausible interpretation is that the initial event—which can be an accelerated charge already present in the gas, a tunneling, an energetic photon, or other events—starts a process of multiplication of charges in the vicinity of the tip of the needle where the electric field is at its highest value. The multiplication of charges goes on as long as the field, which has an exponential decay with distance from the tip in the geometry adopted, is high enough, in relation to the mean free path of the species involved, that the production of new charges is feasible. Moreover the charges so created and separated by the electric field decrease the field strength up to a point where no more charges are in effect produced. When the spatial charge has disappeared or reduced and the electric field has recovered, a cycle can start again. At a certain point when the electric field is high enough, this process form a continuous path between the two conductors with a drop, practically to zero, of the resistance, and the generation of a spark. With even higher potentials, the process can be continuous not only in space but also in time with the production of an arc (Nasser, 1971). In the case of electrostatic accumulation, sparks and arcs are to be avoided because very high absorption signals are then obtained. A spark probably damages the graphite surface exposing new and not yet cleaned material which in the subsequent measurement releases the analyte present on the newly formed surface. This situation is not different from what occurs with new graphite tubes before conditioning for use.

The type of geometry used for the electrostatic precipitator with a well-localized point of charges production was chosen because, by doing so, all particles are accumulated in the same section, i.e. the central section of the graphite tube. In a real case, a particle has the average velocity of the gas in which it is entrained so that the point where it impacts into the graphite tube wall and is captured is given by the combination of many factors, among which the most important are the field strength, the mass of the particle, and the charge acquired (Liu and Dasgupta, 1996). An experimental verification that the section of the graphite tube where the particles are captured is at the center was obtained by capturing an aerosol with a radiotracer (^{32}P) added and then measuring the quantity present in the different sections of the graphite tube (Torsi et al., 1986). The comparison of droplets from an aerosol obtained with a flame nebulizer (Perkin-Elmer Model 460, Perkin-Elmer Corp., Norwalk, CT) with atmospheric particles is rather crude because the size of air particles is smaller than those obtained with the above-mentioned nebulizer, and are therefore more easily captured. Even under those somewhat unfavorable conditions and comparison, the analyte was present only in the central section of the

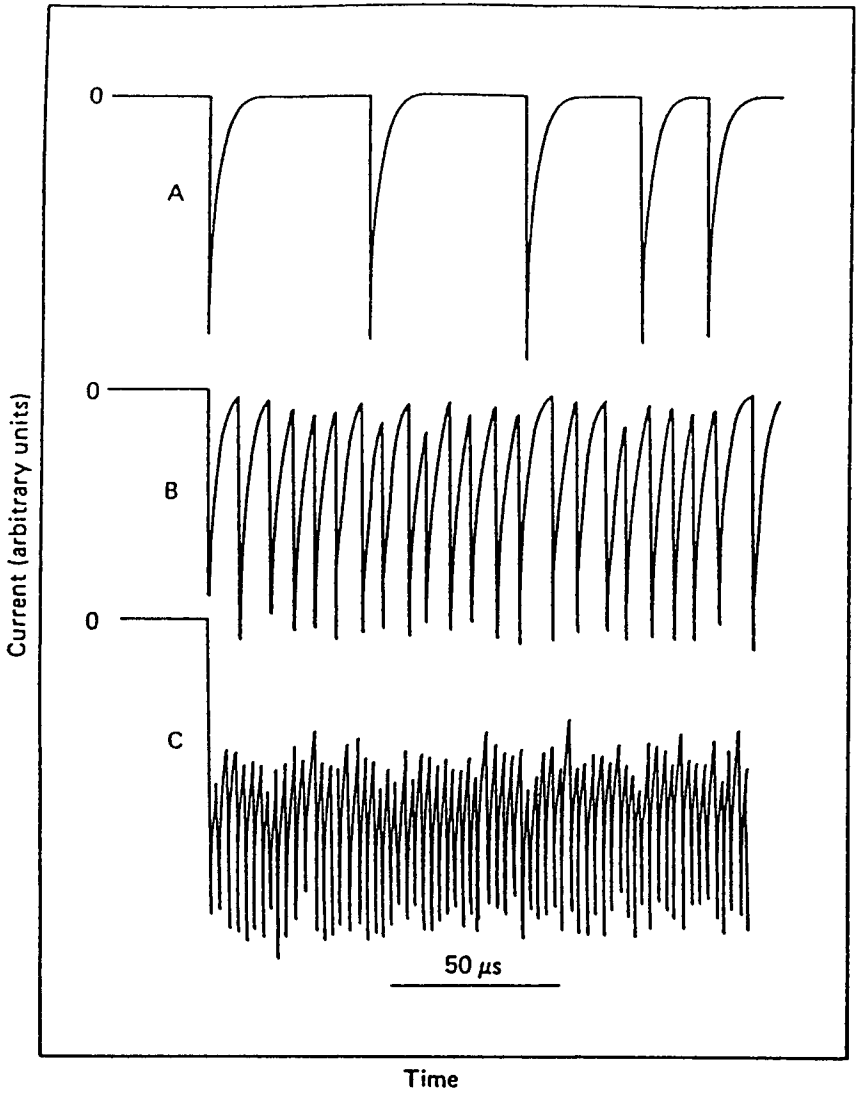

Figure 2. Current pulse trains at three different average currents: A-1; B-10; and C-50 μA. Reprinted from *Spectrochimica Acta* **1986**, *41B*, 257; Torsi G., Palmisano, F. (with permission by Elsevier Science, 1986).

graphite tube. Of course, the gas velocity must not be too high otherwise both the probability of charging and capturing a particle in a section near the needle tip is reduced. The flow rate generally used in these experiments is around 1 cc/s but it has been verified that the capture efficiency is practically 100% up to 5 cc/s (Torsi et al., 1986).

Table 1. Capture Efficiency of the Electrostatic Precipitator[a]

Aerodynamic Diameter (~m)	*Current (μA)*		*Capture Efficiency (%)*	*Conditions*[b]
	Off	*On*		
0.3–0.5	$(125 \pm 8) \times 10^3$	45 ± 5	99.96	A
0.5–0.7	$(290 \pm 10) \times 10^2$	10 ± 4	99.96	
0.7–1.4	$(100 \pm 5) \times 10^2$	8 ± 3	99.92	
1.4–3.0	$(48 \pm 3) \times 10^2$	6 ± 3	99.87	
>3.0	(180 ± 10)	2 ± 1	99.89	
0.3–0.5	$(22 \pm 2) \times 10^3$	20 ± 8	99.91	B
0.5–0.7	$(50 \pm 3) \times 10^2$	5 ± 3	99.90	
0.7–1.4	$(189 \pm 8) \times 10$	2 ± 1	99.89	
1.4–3.0	$(200 \pm 10) \times 10$	0 ± 1	100.0	
>3.0	(98 ± 4)	0	100.0	

Notes: [a]Reprinted from *Spectrochimica Acta* **1986,** *41B,* 257.
[b]A: Flow rate: 2.7 L/min, average velocity: 540 cm/s; B: Flow rate: 0.43 L/min, average velocity: 86cm/s.

The efficiency of the electrostatic capture—the ratio between particles captured and those present in the gas—is very high. With the system described here, efficiency measurements are very simple because one just needs to interpose particles counter between the capturing device and the pump. Tables 1 and 2 are

Table 2. Capture Efficiency of the Electrostatic Precipitator[a]

Current (μA)	*Counts cm^- at C1*	*Counts cm^{-3} at C2*	*Capture Efficiency (%)*	*Conditions*[b]
0	60,300	36,600	39.30	A
20	60,300	70	99.88	
10	60,500	93	99.85	
6	60,200	1500	97.51	
20	60,500	80	99.87	
40	60,000	38	99.94	
10	60,400	100	99.83	
0	60,000	36,500	39.17	
0	60,500	40,500	33.00	B
20	60,200	100	99.82	
40	60,200	100	99.83	
10	60,200	240	99.60	
6	60,400	140	99.77	
20	60,500	100	99.83	
0	60,700	40,000	34.10	

Note: [a]Reprinted from *Spectrochimic. Acta* **1986,** *41B,* 257.

taken from published results and demonstrate that the efficiency is practically 100% for particles from 40 nanometers to a few microns.

Sneddon (1990) describes the theory and use of electrostatic precipitation of an air or aerosol (gas or liquid particles in a gaseous medium) sample on a tungsten rod and injection of this rod into a graphite tube for subsequent atomization from the rod and quantitation by ETA-AAS. The system was subsequently applied to the determination of several metals in laboratory air (Sneddon 1991).

Analysis of air particles previously charged and electrostatically captured on special surfaces can be made by total-reflection X-ray fluorescence spectrometry (TXFS) (Dixksen et al., 1993).

Capture of particles, present in the atmosphere or in other gases directly on an atomizer exploiting impaction instead of electrostatic precipitation is being actively pursued by Baaske and Telgheder (1995) and Sneddon and coworkers (Lee et al., 1996a,b).

III. PARTICLES PRECIPITATION DEVICE AND ATOMIZATION SYSTEM

The above mentioned system, whose part is the graphite tube, must work as an electrostatic capturing device and subsequently as an atomizer for ETA-AAS measurements.

The different parts of this system are shown schematically in Figure 3. Figure 3A is a cutaway of these parts forming what is called the furnace. The metal blocks (c and e) are tightly connected by three stainless screws (m). These screws pass into holes machined in e and are screwed in c. The head of the screws is larger than the holes and the screw can be insulated from the metal block e by small rings (1) of insulating material that can resist to moderately high temperatures of the order of 500 °C. A bigger ring of the same material (d) separates the two metal blocks c and e. In this way, a piece formed by two metal blocks is electrically separated but mechanically tightly connected. The separation of the two blocks is not made in the center because three radial holes (n) at 120°, are machined; one for handling the furnace (this hole and the handle are conveniently threaded), one for a light path to the temperature sensor, and all three for letting a free circulation of the gas between the graphite tube and the metal blocks. The graphite tube is fixed at the center of this device by two graphite cylinders. One cylinder (f) slides inside the metal block c and is kept in position by a metal disk (b) which in turn is fixed to c by a threaded lid (a) screwed to c. The second graphite block (h) has the same dimensions as f but instead of a smooth surface is threaded outside so that it can be screwed in e and, when the graphite tube is inside, force it against b. The two graphite blocks h and f are machined inside in order to have only a small contact surface with the graphite tube because in this way the temperature is more homogeneous along the tube and its length is fully exploited. The metal disk b gives a minimum of elasticity to the system necessary for the small expansion of the

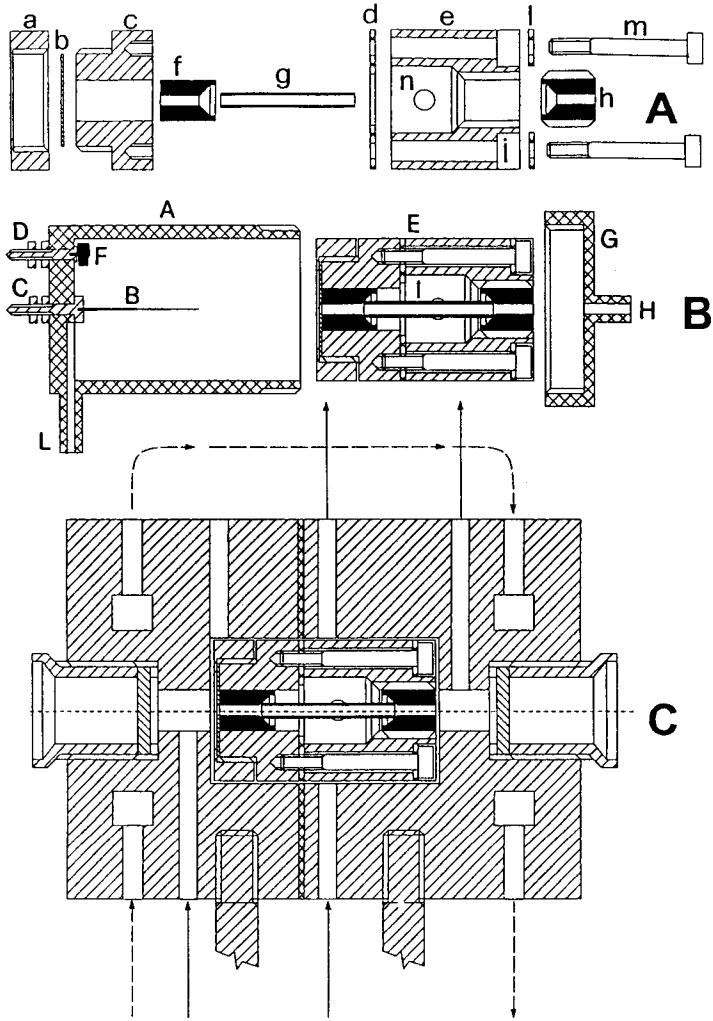

Figure 3. (**A**) Parts (section) that form a furnace. (**B**) Assembled furnace with the cup for particle capture. (**C**) Atomization box with the furnace inserted.

graphite tube when brought to a high temperature during the atomization stage (ca. 2200°C).

The assembled furnace can be inserted in a Teflon cup (Figure 3B) which serves for the electrostatic capture and accumulation of samples. At the base of the cylindrical cup, at its center, the tungsten needle is fixed. When the furnace is inserted in the cup, the tungsten needle is positioned inside the graphite tube with its sharp tip at the center. On the same side of the cup, an electric current contact is inserted to connect the furnace to the second lead of the power supply. In this way,

the graphite tube or furnace and the needle can work according to the scheme shown previously in Figure 1. At the bottom of the cup, a hole is machined for a tube fitting to connect the cup to a pump. A screwed lid fixes the furnace in the cup. A washer between the lid and the furnace allows the gas to pass only inside the graphite tube. The flow in the system is very easily controlled and maintained constant with a simple needle valve and flowmeter between the sampling device and the pump. No particular care is needed in the control of flow rate with time because there is no change in the flow resistance during samples collection as in the case of filtration through paper. Moreover, the pump can be inexpensive. If very precise measurements must be made, the temperature must be determined and the volume sample reduced to standard conditions.

At the end of the sampling step, the furnace can be stored and subsequently transferred to the laboratory or immediately inserted in what is called the atomization box (Figure 3C). This box is obtained from two brass or aluminum blocks assembled with the same components, with different form and dimensions as those used for c and h to obtain the same result. This is a mechanical block with opposite sides electrically separated. In the block, a void volume is obtained by removing part of the bulk to create a chamber where the furnace is inserted. The furnace is fixed in a well-defined position by two stainless steel clamps, one in each block, of the type used for dry batteries. The clamps are screwed to the wall in front of the atomization box window. When the furnace is inserted, the insulation sheet sandwiched between the two metal blocks matches the corresponding insulating ring of the furnace. Two windows of amorphous silica are positioned, with normal screws and O-rings, at opposite sides of the box in order to let the beam of an atomic spectrometer (actually the light from a hollow cathode lamp) pass inside the graphite tube. There are also four holes for electrovalves—two in the center and two with openings in the space between the windows and the furnace in the upper and lower side of the atomization box—to control the path of the gas inside and/or outside the graphite tube. A fifth hole is machined to see the central part of the graphite tube when the furnace is inserted, keeping the handle horizontal. This hole is threaded to tightly screw in it a Teflon cylinder with its bottom closed by a silica window. In this cylinder, a pyrometric sensor (TIL 99 from Texas Instruments) is inserted. As already mentioned, the position and the direction of the cylinder is such that the light from the central portion of the graphite tube can reach the pyrometer. If a more precise geometry is required, or a reduction of light is desired, a field stop can be added before the transistor. The two blocks of the atomization box are connected to the power supply leads. A Plexiglas window is screwed to the front side in order to allow measurements in a controlled atmosphere above or below the atmospheric pressure. Water cooling can be obtained by canals inside the blocks. The box must be positioned in the spectrometer sample compartment with a device in such a way that the spectrometer beam is well-centered inside the graphite furnace. In the case described in this chapter, the burner mount supplied for flame measurements with an adapter was utilized.

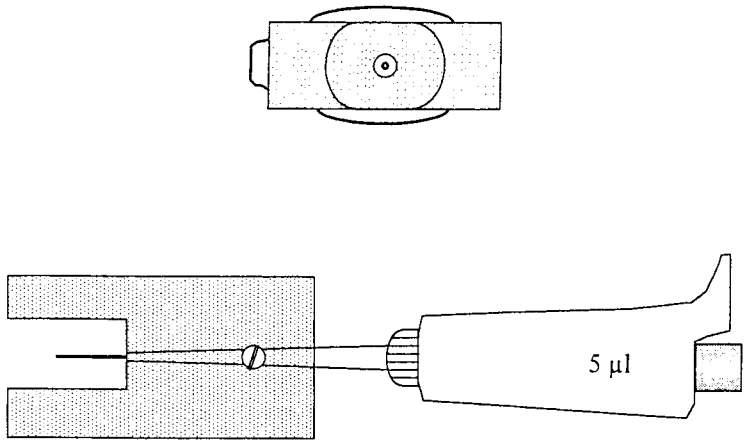

Figure 4. Schematic diagram of solution delivery system.

The sample introduced in the case of particulate matter has been described. It must be pointed out that no manipulation is necessary to obtain the absorbance data, therefore the errors of a measurement is not increased by intermediate steps for sample preparation. In conventional ETA-AAS, a solution is introduced through an injection port at the center of the graphite tube. If a solution is to be analyzed with the current system, then it must be introduced at the graphite tube center through the open extremities of the furnace. This is because there is no injection hole in the graphite tube.

The design of this device is shown in Figure 4. It is a plexiglas slab at one end of which, at its center, a hole is drilled in such a way that the furnace can slide in it rather easily. In the other side of the slab, another hole is drilled in which an hand-held pipette can be fixed. The pipette has, instead of the usual tip, a Teflon tubing of 1 mm outside diameter at its end. The pipette is fixed to the slab in such a way that when the furnace is slid into its compartment, the Teflon tubing tip is at the center of the graphite tube. The pipette used is a 5 microliter Gilson pipette. With this volume of solution, the drop will completely detach from the hydrophobic surface of the Teflon tip.

IV. STANDARDLESS ANALYSIS

The usual method of quantitation in most instrumental techniques including ETA-AAS is through calibration in order to find the relationship between the signal and the concentration or the quantity of analyte in a sample of known composition (standard). In mathematical form:

$$S = f(x) \tag{1}$$

The most common and most desired results is a linear function or relationship between the signal, S, and the quantity x. In ETA-AAS measurements the signal is the absorbance (A) and the quantitation is made by measuring the signal as peak height or peak area. If the function in Eq. 1 is well known with all constants derived from first principles, then we can obtain x from a single measurement. In this case, according to de Galan and Samaey (1970) and L'vov (1978), the analysis can be defined as an absolute analysis. If the constants present in the above given function are not obtained from first principles, but are sufficiently stable, reliably, and reproducibly measurable and, in particular, are not dependent on the type of matrix, then we call this analysis a standardless analysis because a quantitative datum can be obtained from a single measurement. An analytical apparatus with these characteristics need a calibration only to check that everything is working properly.

The Lambert–Beer law is particularly suitable for this type of analysis because is very simple and there is only a spectroscopic constant, if the length of the cell is taken for granted. In fact we have,

$$A = ebc \tag{2}$$

where c is the concentration (mole/L), b (cm) the cell optical path, and e (L cm^{-1} $mole^{-1}$) the molar absorbtivity of the analyte. A and e refer to a specified wavelength. Assuming that the wavelength and absorbance scales are well-calibrated, from a single measurement of A the concentration c can be obtained without calibration if e is known. Equation 2 is valid for homogeneous solutions, but it can be used in the case in which the analyte is distributed inhomogeneously along the optical path. In this case, it is sufficient that the analyte is homogeneously distributed in planes perpendicular to the optical path (Paveri-Fontana et al., 1974). Equation 2 can then be written as,

$$A_t = K N_t / S_c \tag{3}$$

where the subscript t indicates a time variable, K (cm^2/atom) is a spectroscopic constant, N_t (atom) the number of atoms present in the graphite tube with distribution as defined above, and S_c (cm^2) the graphite tube cross section. It is assumed that the atoms are stable only inside the graphite tube and that S_c is constant.

In a model described in literature (Falk and Schnürer, 1989) it was assumed that all the atoms injected are brought instantaneously to the vapor state and are homogeneously distributed in a central section of a cylindrical atomizer. From this moment they diffuse from the center of the cylinder to its extremities where they disappear. In this case, all atoms injected are simultaneously present inside the graphite tube and their distribution satisfies the condition of homogeneity in planes perpendicular to the optical beam from the vaporization moment to the moment in which the first atoms reach the extremities of the graphite tube where they disappear.

From what has been said above in this interval of time, A should be practically constant. The average time spent by atoms in the optical beam is given by the equation,

$$t_1 - t_0 = [(1/\pi^2) * \ln(4/\pi) - (1/24) * (dL/L)]\, L^2/D \qquad (4)$$

where t_0 and t_1 (s) are the times of the beginning of the atomization and the moment in which the first atoms disappear at the extremities of the graphite tube, dL (cm) the section in which the atoms are homogeneously distributed at t_0, L (cm) the length of the graphite tube, and D ($cm^2\ s^{-1}$) the diffusion coefficient of the analyte.

The form of the absorbance versus time curve, in this case, should be like the one schematically shown in Figure 5A. The form of the experimental curve obtained with cadmium in well-chosen experimental conditions with the atomization system described in this review, also shown in Figure 5B, is a good indication that the experimental conditions for obtaining all atoms injected simultaneously present in the optical beam, has been reached.

Another indication that this goal has been reached is the constant nature of A with decreasing heating rate; that is the rate of vaporization of the analyte atoms (Torsi et al., 1996). Now Eq. 3 can be written in the form,

$$A_0 = K\, N_0/S_c \qquad (5)$$

where A_0 is the average value of A in the time interval in which it is constant (the plateau of Figure 5) and N_0 the total number of atoms present at the start of the atomization step. If no analyte is lost in preatomization steps, then N_0 gives the atoms present in the sample.

The spectroscopic constant K can be theoretically derived (L'vov, 1978), therefore an ETA-AAS measurement in these experimental conditions can give an analysis of the absolute type. However the theoretical calculation of K is not easy because there are factors, e.g. the force constant (Doidge, 1996) and the overlap integral between the source and the absorption line, that are not well known. Moreover the lineshape of the source (a hollow cathode lamp) can change with the lamp manufacturer, its history, and the current used. For these reasons it is preferable to measure K by calibration with aqueous solutions of known concentration. However, it is not to be excluded that in the future the problems mentioned above can be solved by technical improvements or by new types of sources such as inexpensive tunable lasers, as shown by Groll et al. (1994). The K spectroscopic constant obtained is independent of the spectrometer if the absorption and wavelength scales have been calibrated. It should be independent of the matrix except for spectroscopic interferences which are rarely encountered and well documented in absorption atomic spectroscopy.

In this case, the type of analysis is called a standardless analysis. In this laboratory the value of K for cadmium and lead has been measured with two types of material: graphite and vitreous carbon for over three years without changes in the average

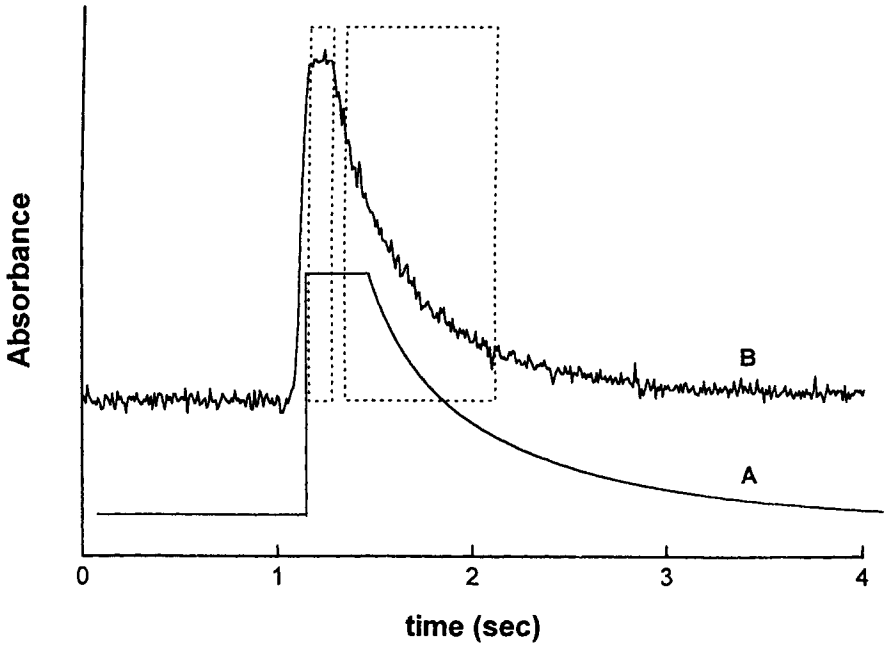

Figure 5. Absorbance versus time curves. (**A**) Theoretical. (**B**) Experimental (obtained with cadmium).

value and with a standard deviation around 5%. The spectrometer was always the same (Perkin-Elmer Model 1100 B) with different hollow cathode lamps of the same manufacturer. The K values measured are always lower than those theoretically calculated from literature data (Torsi et al., 1995b).

V. POWER SUPPLY, MEASUREMENTS CONTROL, AND SIGNAL ACQUISITION SYSTEM

As previously noted, the use of Eq. 5 for standardless analysis is possible only if the experimental conditions are strictly controlled because only in this case all the atoms injected can be considered simultaneously present in the atomizer. The most important conditions that must be met are: (1) the absence of the injection hole, because otherwise there is a very fast path for analyte escape (Falk and Schnürer 1989), and (2) a very fast rate of atoms formation compared to the diffusion of the atoms outside the atomizer. In the Falk and Schnürer model, the atomization is assumed to be instantaneous. A fast atomization can be obtained with high heating rates and a final temperature which is as high as possible (ca. 3000 °C). Up to now only the most volatile elements have been studied for two reasons: first is the

possibility of obtaining atomization rates sufficiently fast, and second is more easy cleaning of the graphite tube (Torsi et. al., 1995b). The necessity of using a very clean atomizer material, often not available, derives from the low linear dynamic range of the calibration curves typical in atomic absorption spectroscopy. The high heating rates required for these measurements cannot be obtained with common power supplies that basically use a step-down transformer because the impedance of this system does not permit a full power delivery at the beginning of the atomization step when the maximum power is needed. The best choice in this respect would be the use of a bank of capacitors as described by Chakrabarti et. al. (1980) and Chakrabarti et al. (1981). In this case, the maximum power is delivered at the closing of the circuit. However for the atomization system used in this work, the power required was too high for a manageable solution of this type. Therefore it was decided to use commercial batteries with a fast, solid-state switch which is both inexpensive and delivers maximum power just a few microseconds after the switch is closed (Torsi et al., 1995a).

From the absorbance versus time curve of Figure 5, it can be seen that a few microseconds have no influence on the atomization rate because the transients are of the order of milliseconds. The instrument that forms the atomization and signal acquisition system is composed of batteries (12 V, 400 A commercial batteries) and a solid-state switch (SKM 450 A 020 mosfet with its driver SKHI 20 from Semikron Int. (Nuremberg, Germany)). The circuit for the driver control is based on board 8253 (clock) and 8255 through a homemade interface. Through these PC-driven interfaces, all the functions needed for an ETA-AAS measurement can be carried out through an ad hoc program. A measurement is composed of various steps which are very similar for all these types of measurements. Each step is characterized by its duration, the percent of power delivered, the temperature level, and the status of the electrovalves. There is also a command for the start of data acquisition whose duration is also software controlled. The most important function of the PC program is the control of the temperature level. The problem has been solved with the usual feedback method. A pyrometric sensor is placed at the position already described. The signal, conveniently amplified, is compared with a DAC level and the output is used to close or open the circuit through the electronic switch. The temperature level is chosen in a scale 1–1020. The percent of power is obtained by blocking the switch for the corresponding percent of time with 500 Hz frequency.

The small intervals between on and off switching permit a good control of the temperature as can be seen in Figure 6. Here the variation of the level of temperature and the corresponding voltage of the driver signal are shown in two different conditions: (1) 100% power, that is the maximum heating rate, and (2) maximum temperature (9000–10,000 °C/s and 2100 °C, respectively) (Figure 6a) and 50% power with 700 °C as maximum temperature (Figure 6b). A more detailed picture of what is happening in a cycle (2 ms) can be seen in Figure 7 in which the output signal of the comparator through which the driver control status of the solid-state switch at points A and B of Figure 6b are enlarged on the time scale. In the first

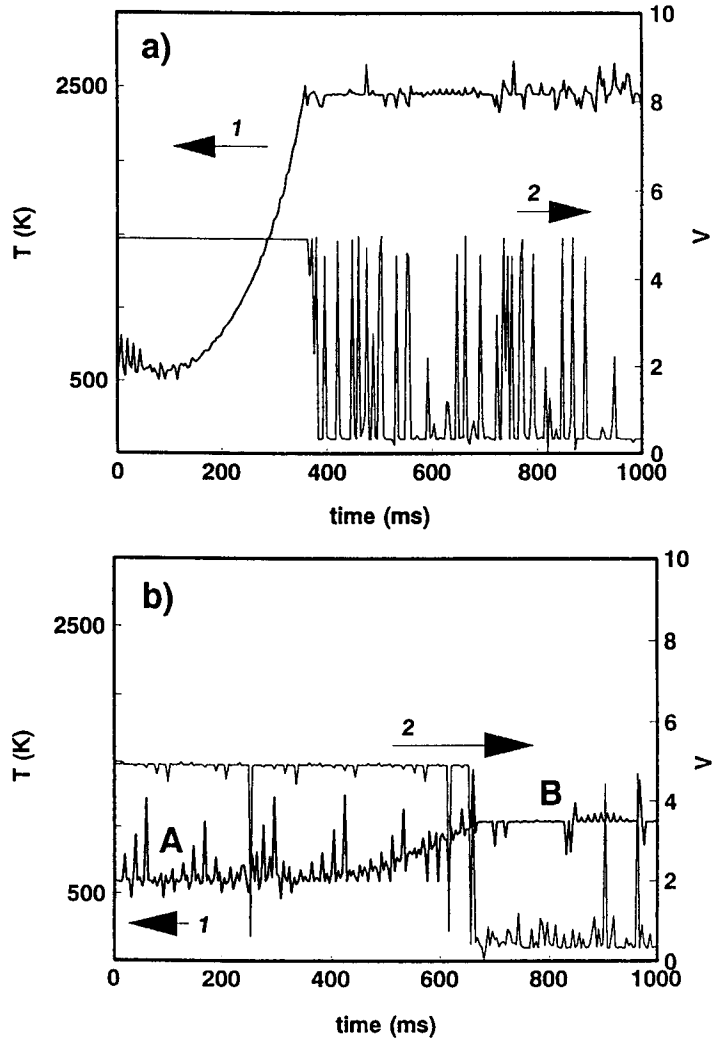

Figure 6. Temperature and comparator output versus time. (**A**) 100% power and 2100 °C final temperature. (**B**) 50% power and 700 °C final temperature. Reprinted from *Review of Scientific Instruments* **1997**, *68*, 1609.

50% of time, the switch in blocked while in the remaining 50% the power is always on in A because the temperature is below the programmed level (trace A) while it is freely switching on and off when the temperature programmed has been reached (trace B) except of course during half of the time cycle.

The temperature scale has been obtained (Torsi and Bergamini, 1989) through a calibration of the pyrometric sensor, by measuring at constant temperature the output of a Pt/Pt/Rd 13% thermocouple inserted in the center of the graphite tube

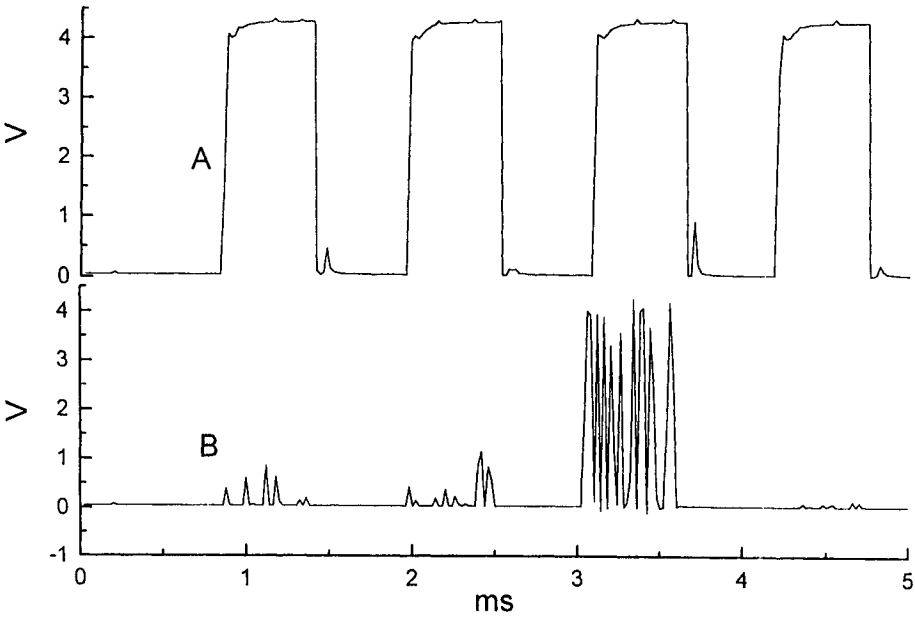

Figure 7. Expanded time scale of the output of the comparator voltage. (**A**) The comparator voltage with time obtained in point **A** of Figure 6B when the temperature is always below the programmed level. (**B**) At point **B** of Figure 6B when the programmed temperature has been reached.

and the level of the DAC. By plotting the log of the DAC level, or the corresponding value of its output in volts versus $1/T$, a roughly linear relationship is obtained in the 300–1100 °C interval according to the Wien law. Temperatures above 1100 °C were obtained by extrapolation. The lack of accuracy in temperature measurements and control is not particularly important because both from theoretical calculations and experimental measurements K and therefore A changes very little with temperature (Torsi et al., 1993) in the temperature interval of ETA-AAS measurements.

The absorbance data are stored by the spectrometer. The acquisition time of one point is about 9 ms and can be valued by the vertical straight lines in the fast increase of absorbance at the beginning of the atomization step in Figure 5. It can be seen that the acquisition rate is sufficiently fast to follow without distortion; the absorbance variation also is the more critical moment. At the end of the atomization measurement, the data stored by the spectrometer are transferred through the serial RS232 port to the PC memory, translated into raw data, and displayed on the screen. They can then be saved for further treatment. The experimental curve of Figure 5 shows the number of points averaged in that particular curve for measuring A_0. Both the number of points and the region where this operation is performed are chosen by the operator and displayed as a dotted frame for better control.

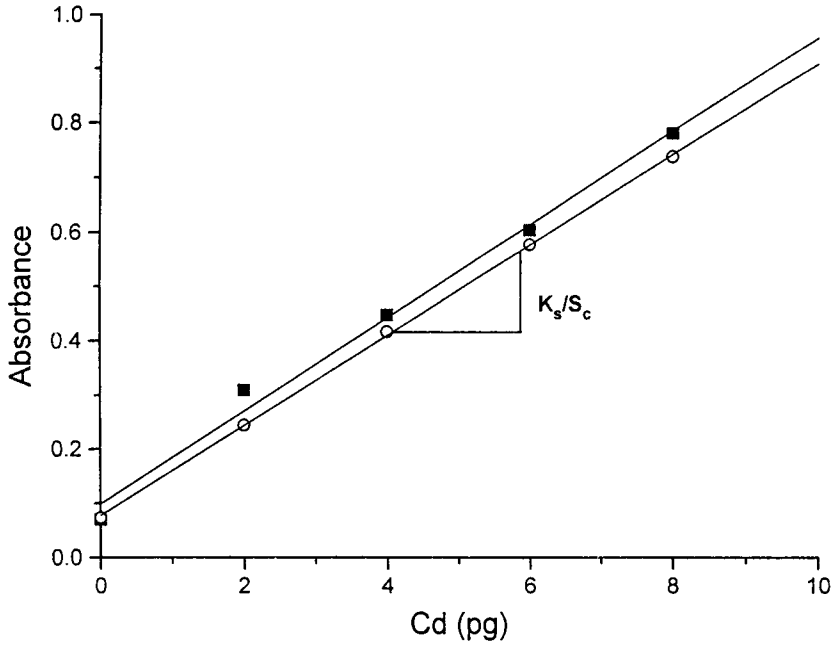

Figure 8. Calibration curves for the determination of K: cadmium at 228.8 nm, ■ graphite, and o vitreous carbon tubes.

The spectroscopic constant K is measured from the slope of calibration curves. An example is shown in Figure 8 for two types of material—graphite covered with pyrolitic graphite and glassy carbon. The nonzero value of the intercept is due to the presence of the metal in the atomizer material and not to blank solution.

VI. STANDARDLESS ANALYSIS OF METALS ASSOCIATED WITH PARTICULATE MATTER IN AIR

It has been previously established that standardless analysis is possible if all atoms injected are simultaneously present in the graphite tube for a sufficiently long time that A_0 can be easily measured. We claim that these conditions have been reached in our atomization system with solutions because the form of the absorbance versus time curve is in agreement with a theoretical model which foresees a very rapid increase of absorbance followed by a constant signal. By increasing the heating rate after a certain value no increase is observed because the saturation stage has been reached. Therefore, above a certain atomization rate A_0 is constant (Torsi et al., 1995b).

It has been experimentally found that the same form of atomization curves are obtained with samples accumulated with electrostatic capture (Torsi et al., 1996)

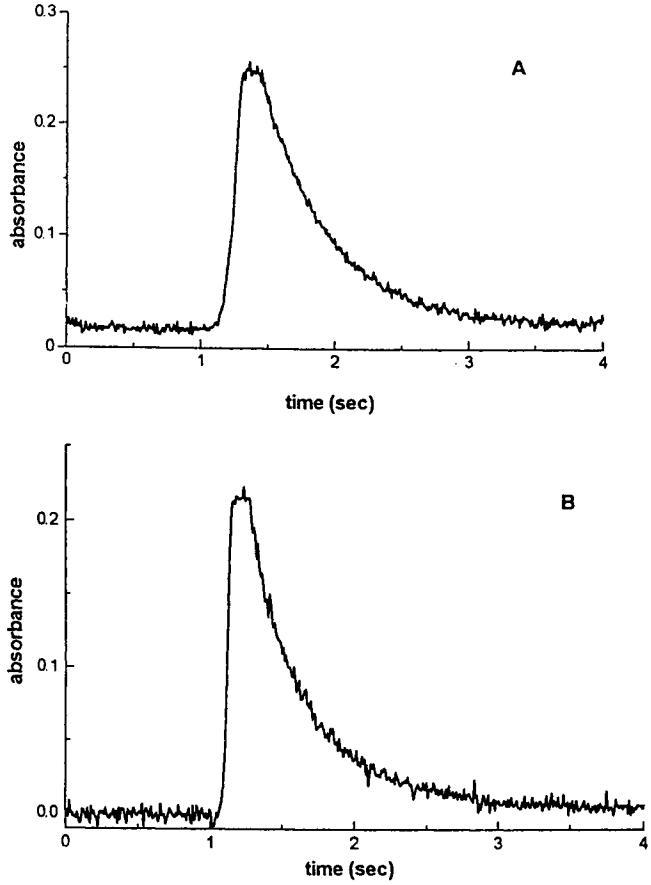

Figure 9. A versus time curves for lead. (**A**) solution. (**B**) aereosol.

(Figure 9). This finding was not unexpected because, as shown before, the particles, captured with the geometry of the electrostatic precipitator used, are concentrated in a small central section of the graphite tube. Moreover with an analyte imbedded in particles of low diameter the atomization rate is higher than with solutions, therefore the plateau relevant to A_0 is more easily reached. These facts, together with the experimentally proved high capture efficiency of the system, are supporting evidence to the claim that the system has reached the experimental conditions for standardless analysis for elements associated with particulate matter in air. All experimental data presented here are relevant to cadmium and lead in air because, at this point of research, there is more interest in the general aspects of the method. However it should be possible to extend the method to all metals, for which standardless analysis can be applied, and gases in which a corona discharge, with the same characteristics of that in air, is possible.

The combination of standardless analysis in ETA-AAS measurements with electrostatic precipitation performed in the same atomization system have many advantages over the classical method of accumulating the particles on a paper filter with subsequent analysis of the samples with the array of analysis techniques available to the researcher.

The most important are:

1. no manipulation of the sample;
2. very short analysis time;
3. no need of standardizing the method except for an occasional check on K with aqueous solutions.

The possibility of making an analysis without manipulation of the sample is a very convenient feature of the method because not only can one pass directly from the sampling step to the analysis step but also because any chance of blanks or other type of error associated with the sample preparation for the analysis is avoided.

The analysis time for ETA-AAS measurements is of the order of 1–2 min (typically dry for 30 s, ash for 30 s, atomize for 1–6 s, and cool down for 30 s, etc.), thus the major time for an analysis is generally given by the sampling time. This can be very short because the limit of detection of the ETA-AAS technique is very low. As an example we can assume that the noise on the absorbance is around 3×10^{-3}, and therefore we have a limit of detection for a quantity of analyte which will give the value of A_0 equal to 10^{-2} (signal-to-noise = 3). From Eq. 3 with a value of K of 10^{-13} cm^2/atom for lead and S_c around 0.1 cm^2, N_0 should be equal to 10^{10}. This is equal to less than 4×10^{-12} g for lead. If we are sampling air in a low-polluted area, the level of lead is around 100 ng/m^3. Therefore we reach a quantity of lead for a limit of detection just by sampling 40 cc of air. Our sampling flow rate is from 1 to 2 cc/s and therefore the sampling time is of the order of minutes. It can be said therefore that the method will give the level of lead in real time (or at least in near real time). The possibility of making a measurement in a very short time can be a big advantage when an action must be taken immediately in order to avoid poisoning or other dangers.

Another real bonus is given by avoiding the calibration which in the case of particulate matter in gases is particularly difficult and prone to errors (Mitchell, 1992).

VII. VALIDATION OF THE METHOD

The method proposed here has been validated by comparing the results obtained for lead in air with those obtained with the official method, the same used in European countries and North America. The method fixes the type of filter and the experimental conditions for the sampling of particles and the subsequent preparation of the sample (in the form of an homogeneous solution) for analysis. As

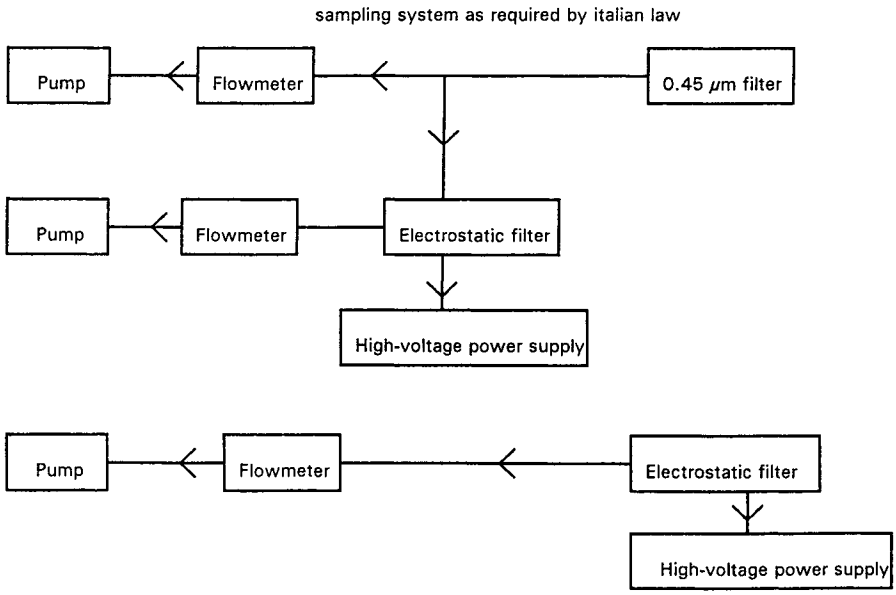

Figure 10. Scheme of the experimental set up for validating the proposed method.

mentioned above, the linear range of absorbance versus the analyte quantity is small—typically 2 to 3 orders of magnitude above the detection limit—and therefore the quantity that can be accumulated with an electrostatic filter is different from the quantity which can be accumulated with a paper filter. The comparison has been made by setting up a sampling scheme shown in Figure 10. A sampling line is directly measuring the level of lead in the atmosphere with an electrostatic filter. The second sampling line as been added with an electrostatic filter below the paper filter. This addition, in principle, is not necessary. However, in practice, it was necessary because it was observed that there was a systematic difference between the level of lead found with the two methods (Torsi et al., 1995b, 1996). In this way, if a fraction of lead escapes the paper filter, it will be collected and measured by the electrostatic filter. The presence of lead in the filtered air was considered to be quite disturbing and was initially ascribed to the electrostatic system not functioning caused by a release of lead from the filter paper or from the walls of the tubing. However, any artifact was excluded by sampling air without lead. In this way there was three samples: (1) Pb_1, the lead captured on the filter paper according to the experimental conditions; (2) Pb_2, the lead escaped beyond the filter paper; and (3) Pb_3, the lead captured directly from air.

The difference in sampling time were normalized by making the measurements with convenient sampling times. The level of lead in the intervals between these

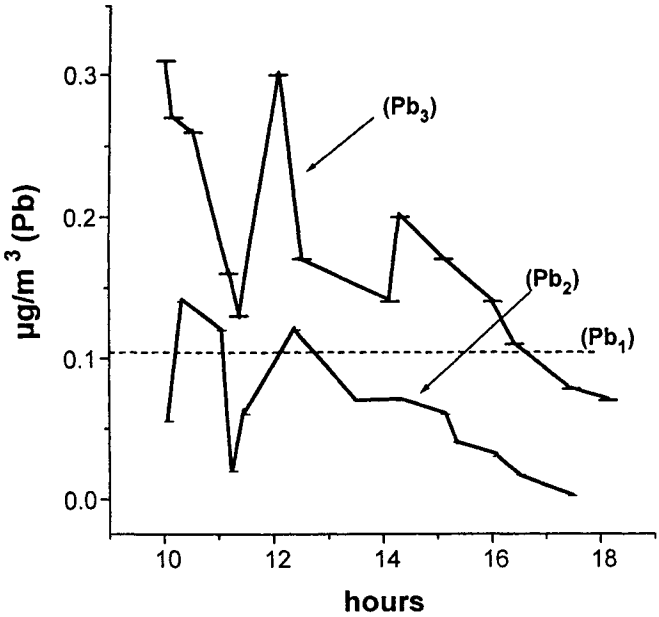

Figure 11. Data relevant to lead determined with the experimental set up of Figure 10 positioned on the windowsill of the authors laboratory (April 3, 1995 in Bologna, Italy).

data were mediated assuming a linear variation as shown in Figure 11. The samples of Pb_1, were analyzed in three different laboratories with three different techniques: the one described in this work, a conventional ETA-AAS measurements and anodic stripping voltammetry (ASV). The last two measurements techniques were performed with commercial instrumentation. It was straightforward to see, if the systematic errors were small, that:

$$Pb_1 + Pb_2 = Pb_3 \tag{5}$$

Table 3 gives the results of these type of measurements. It is clear that the paper filter used (Sartorious 0.45 micron pore size) in the experimental conditions used are not perfect. The data with 20% loss or more of lead were all obtained in the same whether conditions (clear balmy days in may 1995 in Bologna, Italy) in which the loss was particularly high. The loss can also be measured by simply measuring Pb_2 and Pb_3 without measuring Pb_1, which requires long sampling time and sample treatments. With this configuration, one can easily measure the two fractions of the particulate, the first above the cut-off and the second below it. The information can be very important because the adverse effects on health can be quite different according to the particles dimensions. From measurements performed over many

Table 3. Mass Balance ($Pb_3/Pb_1 + Pb_2$) and Lead Lost by the Paper Filter[a]

Measurement	Pb_2/Pb_3	$Pb_3/Pb_1 + Pb_2$
1	0.33	0.84
2	0.23	0.97
3	0.28	1.17
4	0.33	1.17
5	0.23	0.93
6	0.29	0.98
Mean	0.27 ± 0.05	0.99 ± 0.11

Note: [a]Sartorius leadless (Pb_2/Pb_3).

days on different seasons, it appears that the loss decreases with decreasing temperature and increasing humidity.

The measurement were made not only by sampling air in the windowsill of our laboratory, located in a zone of limited traffic in downtown Bologna, Italy, but also by measuring the loss of lead in a station for pollution control operated by the pollution control agency of Bologna (Via Vizzani). In this case, both the filters and the pumping system were those normally used by the agency operator. The results were for all purposes the same.

Presently, this laboratory is making measurements on cadmium. The results obtained indicate that the level of cadmium is around 1 ng/m^3 and a loss of 1 to 5% against a loss from 5 to 20% with lead. A possible explanation is the source of the metal particles of different average diameter. Research in this area is in progress.

VIII. CONCLUSION

From the data presented in this chapter, it can be concluded that the combination of electrostatic precipitation and accumulation of particles with the system and geometry proposed, coupled with ETA-AAS measurements using the same device, has several interesting characteristics over the official method for the measurement of the level of metal associated with particulate matter in air. These include the following:

1. High accuracy.
2. Fast response.
3. Possibility of automation (increase in cost will occur but may be offset by other advantages).

4. Possibility of obtaining, with two capturing systems, two fractions and thus a much better definition of the danger in a given situation.
5. Modest cost.

A disadvantage is the large amount of data that, given the poor linearity of the calibration curve, are necessary if an average over extended time intervals are required. The experimental data presented are only for lead and cadmium in air because these two metals have high volatility and are therefore suitable for standardless analysis. This is not an insurmountable obstacle except for metals with very low volatility. The method could be extended to other metals and other gases in which it is possible to obtain a corona discharge similar to that obtained in air.

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REFERENCES

Baaske, B., Telgheder, U.J. *J. Anal. Atom. Spectrom.* **1995**, *10*, 1077.
Chakrabarti, C.L., Hamed, H.A., Wan, C.C., Lee, W.C., Bertels, P.C., Lee, S. *Anal. Chem.* **1980**, *52*, 167.
Chakrabarti, C.L., Wan, C.C., Lee, W.C., Teskey, L.J., Cheng, S.B., Hamed, H.A., Bertels, P.C. *Spectrochimica Acta* **1981**, *36B*, 427.
de Galan, L., Samaey, G.F. *Anal. Chem.* **1970**, *50*, 39.
Dixkens, J., Fissan, H., Dose, T. *Spectrochimica Acta* **1993**, *48B*, 231.
Doidge, P.S. *Spectrochimica Acta* **1996**, *50B*, 209.
Falk, H. *Spectrochimica Acta* **1978**, *33B*, 695.
Falk, H., Schnürer, C. *Spectrochimica Acta* **1989**, *44B*, 759.
Groll, H., Schnürer-Patschan, C., Kuritsyn, Y., Niemax, K. *Spectrochimica Acta* **1994**, *49B*, 1463.
Lee, Y.I., Smith, M.V., Indurthy, S., Deval, A., Sneddon, J. *Spectochimica Acta* **1996**, *51B*, 109.
Lee, Y.I., Indurthy, S., Smith, M.V., Sneddon, J. *Anal. Lett.* **1996**, *29(14)*, 2515.
Liu, S., Dasgupta, P.K. *Anal. Chem.* **1996**, *68*, 3638.
Locatelli, C., Reschiglian, P., Torsi, G., Fagioli, Rossi, F.N., Melucci, D. *Applied Spectrosc.* **1996**, *50*, 1585.
L'vov, B.V. *Spectrochimica Acta* **1978**, *33B*, 153.
Mitchell, J.P.J. *Aereosol. Sci.* **1992**, *23(suppl. 1)*, S289.
Nasser, E. *Fundamentals of Gaseous Ionization and Plasma Electronics*; Wiley Interscience: New York, 1971.
Paveri-Fontana, S., Tessari, G., Torsi, G. *Anal. Chem.* **1974**, *46*, 1032.
Sneddon, J. *Appl. Spectrosc.* **1990**, *44*, 1562.
Sneddon, J. *Analytica Chimica Acta* **1991**, *245*, 203.
Su, E.G., Yuzefovsky, A.I., Michel, R.G., McCaffrey, J.T., Slavin, W. *Microchem. J.* **1993**, *48*, 278.
Torsi, G., Desimoni, E., Palmisano, F., Sabbatini, L. *Anal. Chem.* **1981**, *53*, 1035.
Torsi, G., Desimoni, E., Palmisano, F., Sabbatini, L. *Analyst* **1982**, *107*, 96.
Torsi, G., Palmisano, F. *Spectrochimica Acta* **1986**, *41B*, 257.

Torsi, G., Palmisano, F., Cosmai, G., Kabil, M.A. *Ann. Chim. (Rome)* **1987a**, *77*, 917.
Torsi, G., Palmisano, F.J. *Anal. Atom. Spectrosc.* **1987b**, *2*, 51.
Torsi, G., Bergamini, G. *Ann. Chim. (Rome)* **1989**, *79*, 45.
Torsi, G., Reschiglian, P., Fagioli, F., Locatelli, C. *Spectrochimica Acta* **1993**, *48B*, 681.
Torsi, G. *Spectrochimica Acta* **1995a**, *50B*, 707.
Torsi, G., Valcher, S., Reschiglian, P., Cludi, L., Patauner, L. *Spectrochimica Acta* **1995b**, *50B*, 1679.
Torsi, G., Reschiglian, P., Lippolis, M.T., Toschi, A. *Microchem. J.* **1996**, *53*, 437.

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CHEMICAL MODIFICATION IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Dimiter L. Tsalev and Vera I. Slaveykova

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ABSTRACT

Advances in chemical modification electrothermal atomic absorption spectrometry (ETAAS) are reviewed with an emphasis on the progress made after the publication of the previous extensive review (Tsalev et al., *Spectrochim. Acta Rev.* **1990**, *13*, 225). Among the topics discussed are the useful effects, drawbacks, and limitations of chemical modifiers; thermal stabilization and isoformation effects; the rational integrating of chemical modification in analytical procedures; classifications of modifiers and analytes based on theoretical and empirical approaches; mechanisms; guidelines for selection and optimization of chemical modifier compositions; and the progress made on mixed, composite, and permanent modifiers. The review is supplemented by an exhaustive bibliography of ca. 1000 references covering the period of 1990–1996. This large amount of information is organized in four tables arranged in an alphabetical order of analyte elements for easy reference: non-ETAAS applications of chemical modification in electrothermal vaporization–plasma spectrometric techniques; applications of instrumental techniques; and theoretical approaches for studying mechanisms, recent analytical procedures involving chemical modification, and applications in preconcentration and speciation studies.

I. INTRODUCTION

The concept of chemical modification (CM) is extremely popular in modern electrothermal atomic absorption spectrometry (ETAAS). According to the International Union for Pure and Applied Chemistry (IUPAC) recommendations (Ure et al., 1992): "In order to influence processes taking place in the atomizer in the desired way, reagents called *chemical modifiers* may be added. These can help to retain the analyte to higher temperatures during pyrolysis, to remove unwanted concomitants or improve atomization in other ways." There is an apparent tendency of broadening the scope of this term, starting from the classical and still used term "matrix modifier" (Ediger, 1975); then "matrix/analyte modifier" (Chakrabarti et al., 1980); "instrumental matrix modification" (Fazakas, 1990) to indicate the useful effects of the type, pressure, and flowrate of protective gas or gas mixtures; "internal matrix modifier" (Hulanicki et al., 1989), i.e. matrix constituent(s) that positively affect processes in the graphite atomizer (GA), either by themselves (refractory components) or upon addition of suitable promotors; "permanent modification" (Shuttler et al., 1992) of graphite surfaces with high-boiling noble metals or carbide coatings; and numerous applications of chemical modifiers in electrothermal vaporization (ETV)-inductively coupled plasma atomic emission spectrometry (ICP-AES) or ETV-ICP-mass spectrometry (ICP-MS) (see Appendix 1).

It is not surprising therefore that, despite expectations during the preparation of previous reviews at the end of the 1980s (Tsalev et al., 1990b; Tsalev and Slaveykova, 1992a) that the extensive period in studying modifiers had reached a plateau of around 80–100 publications per year; there is an apparent third wave of increasing number of studies on CM during this reviewed period (Figure 1). Thus about 780 new papers covering the period between 1990 and 1996 are treated in this chapter, while the total number of all CM publications in ETAAS as depicted in Figure 1 already exceeds 1360. The drop in publications for 1996 could be due to incomplete coverage of the literature during the last several months of that year. Chapters in books, conference abstracts, and theses are not cited in the present bibliography.

Papers on CM in ETV-ICP-AES and ETV-ICP-MS are not covered exhaustively, either. The effects of CM in ETV are quite specific with the chemical modifiers acting mainly as vaporizers and physical carriers for the analytes at much lower (nanogram) masses; therefore only selected recent publications on ETV are compiled in Appendix 1, while more detailed information can be found in the original papers, e.g. in particularly informative papers by Ediger and Beres (1992), Gregoire et al. (1992, 1994), and Gregoire and Sturgeon (1993). ETV-ICP-AES and ETV-ICP-MS have also proved useful in studying mechanisms of CM, as reflected in publications by Byrne et al. (1992, 1994a,b) and Goltz et al. (1995a,c) (see Appendix 2).

The large documentation on CM has been organized and discussed elsewhere in several previous reviews and overviews by Ni and Shan (1987) and Matsumoto (1993b), both covering mainly the noble metal modifiers; Tsalev et al. (1989, 1990b); Komarek et al. (1991b); Carnrick et al. (1991); Volynsky (1987) on carbide coatings with 136 references; Sommer et al. (1992) and Volynsky (1995) on organic modifiers. Other relevant information may be found in the reviews on mechanisms of electrothermal atomization (ETA), including experimental techniques for their studying (Styris and Redfield, 1993); radiotracers in AAS methodological studies (Krivan, 1992); catalytic processes in graphite atomizers, with 180 references (Volynsky, 1996); in situ trapping of hydrides on modified surfaces (Matusiewicz and Sturgeon, 1996); shadow spectral imaging of formation and dissipation processes for atoms and molecules and condensed phase species (Hughes et al., 1996b); and the bibliography on CM for the period 1973–1989 with 560 references indexed according to analyte element, modifier, sample matrix, and other keywords (Tsalev, 1991). Citations of pre-1990 literature are confined in this text to only some milestone publications such as the classical paper by Ediger (1975), giving some examples of thermal stabilizers like Ni for As and Se or "matrix modifiers" like NH_4NO_3 for promoting vaporization of NaCl matrix; the early CM papers by Machata and Binder (1973) and Brodie and Matousek (1974); the first publications on palladium (Shan and Ni, 1979) and $Mg(NO_3)_2$ modifiers (Slavin et al., 1982); the introduction of the "reduced Pd" modifier (Voth-Beach and Shrader, 1986,

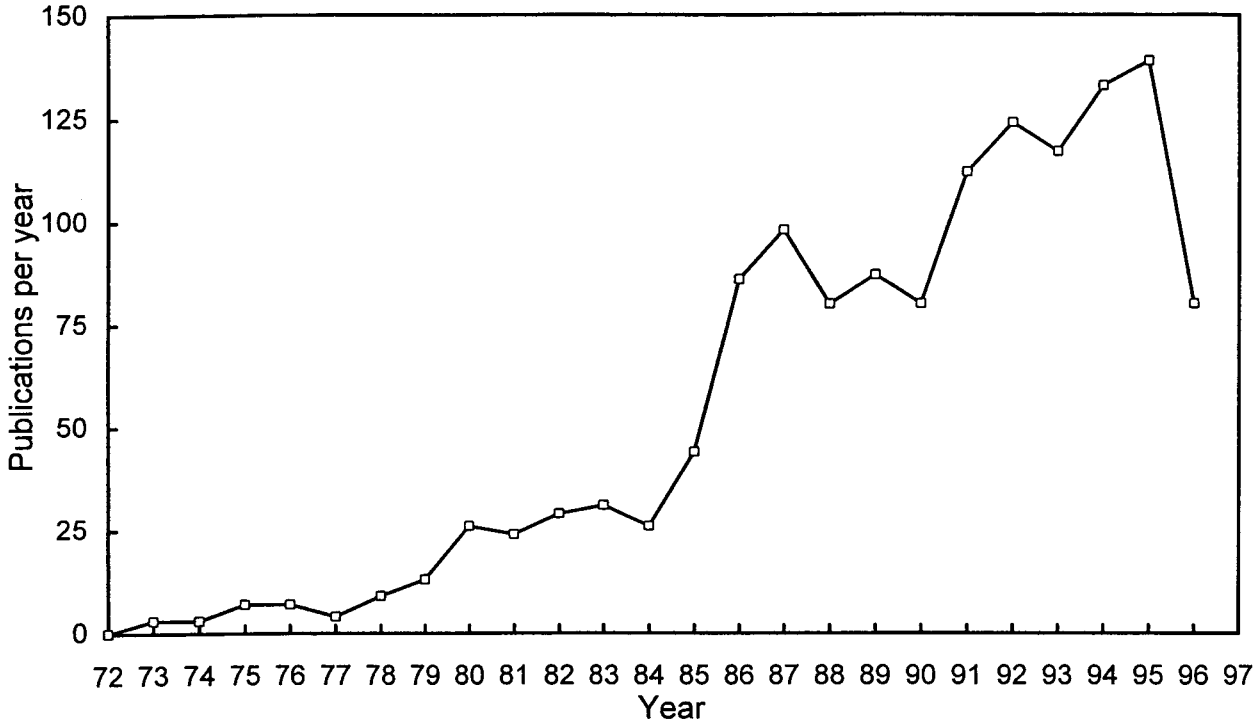

Figure 1. Recent trends in publications on chemical modification in ETAAS. Based on data from bibliography (Tsalev, 1991) and the reference list in this chapter.

1987), and the "more universal" Pd-$Mg(NO_3)_2$ mixed modifier (Schlemmer and Welz, 1986).

Upon addition in large excess to samples and standards, chemical modifiers exhibit complex, multisided and not completely understood effects on all components of the ETA system (the analyte, the matrix, the atomization surface and the gas phase) and affect numerous metrological and technical characteristics of analysis: the temperatures of pyrolysis, vaporization atomization, and cleaning temperatures (T_{pyr}, T_{vap}, T_{at}, T_{cl}, resp.); the accuracy and precision (relative standard deviation, RSD) of ETAAS assays; the characteristic mass for peak absorption (m_p) and (less so); the characteristic mass for integrated absorption (m_o); the limits of detection (LOD); the duration of temperature programs; the lifetime of atomizer; the long-term stability of measurements ("sensitivity drift"); and demands to sample pretreatment stage, sample throughput rates, etc. (Tsalev et al. 1990b). While improved analytical characteristics due to performing an efficient in situ chemistry are aimed in modifier applications, many side and negative effects are inevitably entailed; they will be discussed later as drawbacks and limitations of the CM approach (see Section II).

The most important aimed effects of modifiers are summarized below (Tsalev et al., 1990b; Tsalev, 1998):

1. Efficient thermal stabilization of analytes with high and moderate volatility—over 30 elements, among them such important analytes like As, Bi, Cd, P, Pb, Sb, Se, Tl, Sn, etc.—particularly in matrices with volatility similar to that of the analyte, as discussed in some length in Section III.A.
2. Isoformation of various analyte species such as arsenite, arsenate, monomethylarsonate (MMA), dimethylarsinate (DMA), arsenobetaine (AB), arsenocholine (AC), etc., i.e. leveling off their integrated absorbance (Q_A) signals, owing to transformation to a less volatile chemical form—e.g. in direct ETAAS determinations of the total As in urine, wherein all these species may be present in unknown proportions (see Section III.B).
3. Increasing volatility of unwanted concomitants so as to remove them from the atomizer during the pyrolysis stage; e.g. elimination of the bulk chloride matrix in analyses of seawater or urine by adding NH_4NO_3, dilute HNO_3, ammonium salts of organic additives, or H_2–Ar as alternate gas during pyrolysis.
4. Facilitating in situ ashing rather than charring of organic matrices (oils, sugar, blood, serum, solid or slurried organic matrices, etc.) by using air or O_2 alternate gas during the (low-temperature!) pyrolysis step.
5. Thermal stabilization of some interfering species such as P_2 or PO in phosphate-rich samples (milk, bone, biological fluids) upon addition of noble metals or Ni so as to delay their vaporization during the atomization stage as P atoms rather that molecules. Otherwise, they produce structured background that may not be properly corrected.

6. Transformation of certain interfering compounds into less harmful species; e.g. binding sulfate by mixed modifiers containing salts of the alkaline earth metals, such as Pd-Mg-Ba (Welz et al., 1992a), Pd-Ba (Ni et al., 1994), Pd-Sr (He and Ni, 1996), etc.
7. Modifier action as "volatilizer," i.e. facilitating a low-temperature atomization of the analyte before the bulk matrix [e.g. Cd, Pb, and Zn in seawater in the presence of oxalic acid (Cabon and LeBihan, 1992, 1994, 1995,1996b)] and/or assisting the cleaning stage [e.g. 6% v/v CHF_3 (Freon 23) in Ar as purge gas during the cleaning step at 2700 °C in determinations of Dy in blood serum (Knutsen et al., 1995)]—see also Section III.C.
8. Insuring better contact between the sample and atomization surface by adding wetting agents and/or organic reagents for smooth drying/pyrolysis, thus resulting in efficient multicomponent ("cocktail") composite modifiers—see also Section III.D.
9. In situ speciation; e.g. fractional vaporization of only Se(IV) as volatile piazselenol complex during the pyrolysis step, while Se(VI) remains in the atomizer for selective quantitation (Krivan and Kueckenwaitz, 1992).
10. Increasing sensitivity (?). While very attractive, this aim and (eventually) result of chemical modification may just reflect the situation that conditions for efficient atomization cannot be obtained in the absence of modifiers in many analytical cases; e.g. in determinations of the highly volatile organotins because of premature losses, which can be eliminated or greatly reduced in the presence of organopalladium modifier, $PdCl_2(CH_3CN)_2$ (Katsura et al., 1990, 1991; Matsumoto et al., 1991). Apparent sensitivity increases are also often due to the fact that wall rather than platform atomization and peak height (A_p) rather than peak area (Q_A) measurements are employed or otherwise an improper temperature program is applied. Much smaller is the magnitude of sensitivity increase due to real improvement of the atomization efficiency (ε_A), i.e. the ratio of calculated and experimental characteristic masses for integrated absorbance measurements, $100.m_{o(calc)}/m_{o(expl)}$, in the presence of modifiers; e.g. for Bi and Pb with Pd, being temperature-independent and for Bi, Ga, and Mn with Pd, being temperature-dependent (Yang and Ni, 1995); for Sn with Pd modifier (Gong et al., 1993), etc.
11. Employing modified graphite surfaces (with carbides, noble metals, or both) for trapping volatile hydrides in hydride generation (HG)-ETAAS, as recently reviewed by Dědina and Tsalev (1995) and Matusiewicz and Sturgeon (1996).
12. Better resistance of some carbide-coated surfaces (TaC, WC, NbC) to attack/permeation by acidic digests, organic solvents/extracts, corrosive matrices or modifiers, etc.
13. Providing better conditions for simultaneous multielement assays due to thermal stabilization of volatile analytes to similar T_{pyr} and employing more

uniform temperature programs for groups of several analytes, e.g. As and Se (Garbos et al., 1995); Cd, Cr, Pb, and Ni (Kobayashi and Imaizumi (1991); Cd, Cu, Mn, and Pb (Drews, 1993); Ag, Cd, Pb, and Sb (Latino et al., 1995); Cd, Cr, Cu, Pb, and V (Harnly and Radziuk, 1995); Ag, Cd, Co, Cr, Mn, Mo, Pb, and V (Berglund et al., 1991), etc. Noteworthy, some of these programs rely on "compromise conditions"; thus T_{pyr}, is adapted to the most volatile analyte such as Cd (Edel et al., 1995; Harnly and Radziuk, 1995), while T_{at} should be high enough to insure atomization of the most refractory analyte like V (T_{at} = 2500 °C), albeit some sensitivity loss for the most volatile analyte (Cd) may be entailed (Harnly and Radziuk, 1995).

Some of these aimed effects and ways of improving chemical modifier efficiency will be discussed in the subsequent text, while numerous examples and original references could be found in Appendixes 3 and 4.

II. LIMITATIONS AND DRAWBACKS OF CHEMICAL MODIFICATION

Numerous side effects, limitations, and drawbacks of the CM approach today are better recognized. While some of them can be corrected to a certain extent—others have just to be considered in practice by selection of an appropriate modifier composition, rational sample preparation, and organization of analytical work.

1. Impaired effectiveness of modifiers with real matrices due to their competitive side reactions with or inhibition by matrix and/or solvent constituents. Pyrolysis temperatures often happen to be lower than those established with simple aqueous solutions. Hence, an increased modifier mass (by a factor of 1.5–3) may be required, and the pyrolysis temperature may need be set lower by 100–200 °C than T_{vap} for simple aqueous solutions. Thus, Bozsai et al. (1990) increased fivefold the mass of Mg in the mixed modifier, 15 μg Pd-50 μg $Mg(NO_3)_2$, in determinations of As, Cd, Pb, and Se in highly mineralized waters. Particularly troublesome are chloride and sulfate matrices as well as an excess of acids (e.g. $HClO_4 >> H_2SO_4 > HF > HCl > HNO_3$). This calls for a thorough adaptation of literature data and published procedures to any new analytical task. Faster optimization approaches such as factorial design (Araujo et al., 1994, 1995; Grotti et al., 1996) and simplex optimization (Pergantis et al., 1994; Stalikas et al., 1996) are detailed in the cited papers. Noteworthy, chemical modifiers may prove not as effective with solid and slurried samples as with solutions.

2. Longer temperature programs are typically required in the presence of modifiers because of infavorable kinetics of solid-phase reactions responsible for analyte stabilization and elimination of interfering matrices. Unwanted modifier constituents (counterions such as nitrate or chloride) need also be eliminated, otherwise nitrate may produce undercorrection errors due to their decomposition

products (presumably NO) (Docekal et al., 1991), while chlorides cause "dips" in pyrolysis curves—especially for Ga, In, and Tl (Tsalev and Slaveykova, 1992b) and impaired modifier performance. Temperature programs in the presence of modifiers can be as long as 2 min, thus unfavorably increasing instrumental time and expenses and decreasing sample throughput rates. This situation is in strong contradiction with the current trend of using "fast programs" (< 1 min) by drying at higher temperatures with "hot injections" and eliminating the pyrolysis step, as advocated in an excellent manner by Halls (1995). Hence examples of successful using fast programs with CM are rare, e.g.: Kunwar et al. (1991), Larsen (1991), Hoenig and Gilissen (1993), Lopez-Garcia et al. (1993b, 1996a,b), Zhang et al. (1993a), van Dalen and de Galan (1994), Vinas et al. (1995b,c), Tsalev et al. (1996c), eventually entailing poorer sensitivity than conventional programs (Larsen, 1991). Employing permanent modifiers offers somewhat better potentialities for using fast programs.

3. High reagent blanks applying large masses of chemical modifiers may entail intolerable blank corrections. Therefore high-purity (expensive) reagents are used or otherwise an extra purification step by ion exchange on chelating resins (Dubois, 1991; Bulska and Pyrzynska, 1996) or dithiocarbamate extraction may be required for phosphate-based modifiers. In situ decontamination of Pd based modifiers from volatile analyte impurities is possible by incorporating an extra pretreatment stage for the preinjected modifier at 1100 or 1200 °C for Cd (Buiska et al., 1990; Moreira et al., 1995) or up to 1700 °C for As (Slaveykova et al., 1996a). Radical solutions for decreasing or eliminating blanks are employing permanent modifiers such as noble metals or carbide coatings or otherwise alternative modifier forms with better purity, e.g. triethylphosphite vapors instead of phosphate (Ebdon et al., 1992), $(NH_4)_2PdCl_4$, etc.

4. "Overstabilization" effects (Dabeka, 1992) are caused by the application of copious amounts of modifier (Frech et al., 1992), prolonged pyrolysis times at high T_{pyr}, gradual accumulation of nonvolatile modifiers (V, W, Ir), and migration of modifier to the cooler ends of longitudinally heated atomizers (Frech et al., 1992; Johannessen et al., 1993). Thus atomization peaks are unfavorable delayed and broadened, calling for higher atomization and clean temperatures, which entails sensitivity reduction in peak height (A_p) and less so in integrated absorbance measurements (Q_A). Peak shapes may also be distorted (Rademeyer et al., 1995; Haug and Liao, 1996). Overstabilization is a common effect for some carbide forming analytes on carbide coated graphite tubes (GT), e.g. Mo on WC, as well as for some analytes with low and medium volatility on noble metal coatings, e.g. Mn and V on Ir-sputtered GTs (Rademeyer et al., 1995). Reduced lifetimes of atomizer and memory effects are common consequences as well.

5. The usefulness of some potential modifiers is limited due to their corrosive action on graphite and pyrocoatings, which strongly affects the useful lifetime of atomizer. Among the widely used modifiers, rather corrosive at high concentration levels are HNO_3, NH_4NO_3, O_2 and, air-alternate gasses, phosphate, and lanthanum.

Graphite is penetrated and attacked also by such additives or macro components such as Cr(VI), $FeCl_3$, $HClO_4$, HCl–HNO_3, Sc, Y, Ce, and chlorinated solvents. Most of these oxidants and acids are better tolerated on surfaces treated with metal-like carbides (TaC, WC, NbC, ZrC).

6. Some modifiers (Cr, Mg, Mo, Ni, P, Pd, V, etc.) contaminate graphite parts and surrounding area in an irreversible manner, and cannot be determined at a later stage as analytes.

7. Some modifiers exhibit by themselves high background absorption which calls for efficient (Zeeman) correction: phosphates (Zong et al., 1994; Hughes et al., 1996b; Heitmann et al., 1996), excess of $Mg(NO_3)_2$ (Bozsai et al., 1990; Johannessen et al., 1993; Shan and Wen, 1995), and excess of nitrates at low T_{pyr} (Docekal et al., 1991). Overcompensation errors due to the PO band splitting has been registered even with Zeeman correctors (Zong et al., 1994; Heitmann et al., 1996). More examples and possible remedies have been given in our previous review (Tsalev et al., 1990b).

8. High toxicity or other noxious effects of some modifier constituents cannot be overlooked, either; e.g. modifiers containing Cd (Aller and Garcia-Olalla, 1992), Hg (Aller and Garcia-Olalla, 1992, Garcia-Olalla and Aller, 1992a,b), thiourea (Yang, 1992b; Ohta et al., 1992b, 1993, 1995; Li and Zhang, 1993), CS_2 (Ohta et al., 1990b), etc. cannot be recommended for routine work.

9. Compatibility problems also must be dealt with. In order to avoid hydrolysis and be kept in solution, some modifiers need stabilization by high concentrations of acid (Ir, Nb, Pt, Ta, Ti, Zr) or base (Si, W, Mo, V). Depending on their chemical properties, acceptable stabilizing additives are dilute HNO_3 or HCl, ethylenediaminetetraacetic acid (EDTA), many organic acids, and dilute aqueous ammonia (aq. NH_3), while excess of Cl^- and F^- has to be avoided. Possibility of precipitation or stratification upon mixing the modifier with sample solution as well as upon mixing different modifier components (e.g. noble metal salt + reductant) should also be considered and in situ addition of modifiers or individual modifier components may be required—yet at an expense of somewhat longer instrumental time. Complexed forms and/or water soluble salts of modifiers are often preferred for better stability and more convenient handling of their solutions. Let us note that ammonium forms of modifiers are beneficial, also owing to the positive effect of NH_4^+ cation in ETAAS, e.g.: ammonium dioxalatopalladate(II), $(NH_4)_2Pd[C_2O_4)_2]\cdot 2H_2O$ (Volynsky and Krivan, 1996); Pd(II) + aq. NH_3 (Vinas et al., 1994c); palladium(II) diaminochloride, $Pd(NH_3)_2Cl_2$, and palladium(II) diaminonitrite, $Pd(NH_3)_2(NO_2)_2$ (Popova and Bratinova, 1990); ammonium hexachlororhodate(III), $(NH_4)_3RhCl_6\cdot 1.5H_2O$ (Ni et al., 1996); ammonium hexachloroiridate, $(NH_4)_3IrCl_6$ (Hoenig, 1991); ammonium metavanadate, NH_4VO_3 (Tsalev et al., 1990a; Ma and Wang, 1992; Manzoori and Saleemi, 1994; Huang and Shih, 1995); ammonium paratungstate, $(NH_4)_{10}H_2(W_2O_7)_6\cdot H_2O$ (Slaveykova and Tsalev, 1990; Russeva et al., 1993; Slaveykova et al., 1996b); cerium(IV) ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ (Mandjukov and Tsalev, 1990;

Mandjukov et al., 1991; Tsalev et al., 1987, 1992); ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Tsalev et al., 1989, 1990c); Sahayam and Gangadharan, 1992); NH_4NO_3 (Ediger, 1975); as well as ammonium salts of organic acids (see text on mixed and composite modifiers in Sections III.A and III.D).

10. Partial and nonuniform coating of platform or tube surfaces with permanent modifiers results in "islands" structure with different atomization sites. It is typical for the injection mode of surface treatment with noble metals or carbides and less so for atomizers with electroplated (Bulska and Jedral,1995; Dittrich et al., 1995; Marawi et al., 1995) or sputtered surfaces (Marawi et al., 1995; Rademeyer et al., 1995). Such imperfect coatings entail distortion of peak shapes, peaks with shoulders, and even multiple (double) peaks, as observed experimentally for Ge on Pd-Zr-treated GTs (Ni and Zhang, 1995); Bi and Te on Ir-W-treated platforms (Tsalev et al., 1995, 1996a); and Pd on aged Ir-sputtered GTs (Rademeyer et al., 1995).

11. Ample empirical information and large discrepancies also exist in the literature. Thus several hundred different qualitative compositions of individual, mixed, and composite modifiers have been documented (Tsalev et al., 1990b and Appendixes 2–4) but published results are often in conflict as far as optimum analytical parameters and figures of merit are concerned (T_{vap}, T_{pyr}, T_{at}, m_o, m_p, etc.). The reasons for these discrepancies are numerous and should be born in mind when comparisons of literature data are made and published procedures are adopted. First of all, the ETAAS instrumentation is quite far from unification: many authors do not work under stabilized temperature platform furnace (STPF) conditions (Slavin et al., 1981) and the role of heating times and ramp rates is often overlooked. Among other important factors also are the type (electrographite or pyrolytic graphite), age, and "history" of the graphite surface, the mass of modifier, the presence of other additives (solvent, acid, stabilizer, wetting agent), non-homogeneous distribution of injected samples on the surface and in-depth, etc. Of course, further complications are brought by the presence of sample matrix.

III. OVERVIEW ON THE MAIN EFFECTS OF CHEMICAL MODIFIERS

The most important effects of chemical modifiers will be discussed in some length under this heading. An attempt to list all possible aimed and side effects of modifiers has been made in the previous two sections. Admittedly, such an approach is tutorial to a certain extent, yet helpful in better understanding mechanisms of CM, while in analytical practice modifier compositions are blended in such a manner that diverse useful effects are obtained by a given modifier application. Typical examples are the organic acid modifiers as well as some mixed and composite modifiers.

A. Chemical Modifiers as Thermal Stabilizers

Efficient thermal stabilization of volatile analytes to higher pyrolysis temperatures (T_{pyr}) is an integral part of the popular (and vital) STPF concept (Slavin et al., 1981). The maximum pyrolysis temperatures at which analyte loss becomes significant, i.e. the vaporization temperature (T_{vap}) can be improved by several hundred centigrade and can reach values well above 1000 °C, with only a few exceptions for the most volatile analytes (Cd, Hg, and Zn). The best T_{vap} for over 30 analytes are depicted for easy reference in Figure 2, while more data for individual analytes can be extracted from the monograph by Tsalev (1995) and from Appendixes 3 and 4. Noteworthy, these temperatures may be impaired (lowered) in an unpredictable manner in the presence of real matrices and/or inappropriate solvents.

By applying higher T_{pyr}, both losses of volatile analytes are eliminated and volatile components removed from the matrix which otherwise could interfere during the pyrolysis step in numerous manners (excessive background, premature or retarded volatilization of some analyte species from matrix residues, gas-phase side reactions, etc.). Moreover, atomization peaks are shifted to higher appearance temperatures (T_{app}), when the whole system is closer to stabilized-temperature atomization conditions, thus entailing positive effects on sensitivity (mainly in A_p mode), accuracy, precision, facilitating calibration, etc.

Thermal stabilization effects are rather typical and universal in heated graphite atomizers. First of all, two macrocomponents in atomizer—carbon (the graphite itself) and oxygen (from oxides or added)—are moderate thermal stabilizers. Graphite can be penetrated by liquid sample solutions, especially the porous electrographite (EG) and much less so the pyrolytic graphite or pyrographite coatings. Some analytes (A) like As, Se, etc. are thus stabilized as intercalation compounds, $C_xA_yO_z$. Oxygen-treated ("oxygenated") graphite surfaces, e.g. with 1% v/v O_2 in Ar, are known to provide moderate thermal stabilization for some analytes like Bi, Ga, Ge, In, Pb, Sn, Te, TI, etc. (Byrne et al., 1993b; Eloi et al., 1995a), probably also because of intercalation (Mueller-Vogt et al., 1995, 1996; Brennfleck et al., 1996); thereafter, the analytes are vaporized, mostly as volatile monooxides. These effects, however, have found very limited practical applications, and are more often demonstrating themselves as negatives and complications such as unwanted carbide formation for many refractory analytes (Mo, V, lanthanoids, etc.) and reduced atomizer lifetime. Hence rather the opposite trend—using dense, pyrocoated graphite surfaces and eliminating oxygen residues by applying $T_{pyr} \geq 1000$ °C—has proved more practical in ETAAS. Let us note, however, that oxygen by itself is very reactive and forms strong chemical bonds with many analytes; so, when oxygen is stabilized to higher pyrolysis temperatures, e.g. as a refractory oxide, MgO, it provides useful stabilization effect on numerous analytes.

Many other matrix constituents and additives may exhibit thermal stabilization action. Generally, any macrocomponent that is stable in contact with the incandes-

T°C	$Mg(NO_3)_2$	Pd or Pd +asc. acid	Pd + $Mg(NO_3)_2$	misc. stab. Pd	misc. stab. PO_4^{3-}	misc. modifiers
900		Cd Tl	Cd		Zn	
1000		Ag Pb Se	Ag Tl Zn	Ag	Cd	
1100		Sn Bi	Au	Tl	Pb	
1200	Pd	Au Ga Ge In Te	Bi Sb Se		Ag Li Tl	
1300	Cs	As Sb	Cu Ga	Au Bi	Bi In	Au
1400	B Co Fe Mn Ni	Mn	As Mn Pb P	Ni Sb	Cu Ga Sn	B Fe Pd
1500	Be Rh Ru		Ge In Si Sn	Ge Se Sn Te		Ba Rh Sb
1600	Al Cr V			As P		P Si
1700			Al			Al
1800	Mo					

Figure 2. Summary of the best vaporization temperatures in the presence of various groups of individual and mixed modifiers. Based on data from Slavin et al. (1982); Schlemmer and Welz (1986); Tsalev et al. (1989, 1990a); Slaveykova and Tsalev (1990); Welz et al. (1992c); Shan and Wen (1995).

cent graphite will cause some delay of analyte vaporization, just due to a simple physical mechanism of entrapping the analyte. Furthermore, the analyte would be stabilized better when formation of strong chemical bonds with the modifier or some of its components is taking place—this is the "more chemical" effect of the modifier action. What is important and aimed in practical analysis, however, is to control these effects to an extent that they are taking place in a reproducible manner between different samples and between samples and standards, while insuring high efficiency of thermal stabilization, i.e. high T_{vap} and T_{pyr}. Thus modifiers are applied at large molar excess versus the analyte (10^3–10^5-fold) (so as to favorably shift reaction equilibria and account for the adverse effects of matrix) and their qualitative and quantitative composition is carefully optimized. It is noteworthy, that the ratio of modifier-to-matrix is not as favorable, which is the main reason for an impaired performance in the presence of interfering matrices—cf. 1–100 μg of modifier, typically 20 μg versus 10–500 μg of matrix, typically ca. 100 μg.

Only a few types of chemical compounds can be thermally stable in the GA during pyrolysis at temperatures typically required for the elimination of interfering matrices (800–1500 °C): (1) refractory oxides (MgO, CaO, etc); (2) carbides (Mo, V, W, Zr, etc.); and (3) some (mainly noble) metals (Ir, Ni, Pd, Pt, Rh, etc.). These are actually the most frequently used and most effective modifiers–thermal stabilizers. Brief outlines of their analytical applications are given in Appendixes 3 and 4.

The vaporization temperature (T_{vap}) for simple aqueous solutions in the absence of matrix can be considered as an important quantitative characteristic of the thermal stabilization effect (see Figures 2–4). These temperatures depend on the chemical identity of the analyte and modifier, as well as on modifier mass and chemical form, thus indicating that both chemical and physical effects are responsible for thermal stabilization. The effect of chemical identity of individual analytes is illustrated in Figure 3, which shows some trends in T_{vap} for analytes from the same group of the Periodic Table in the presence of chemical modifiers of an "oxide," "carbide," and "metal" type, as well as for a series of modifiers with increasing boiling points (Ru > Rh > Pd).

The effect of modifier mass has often been underestimated in early studies—the modifier being applied at sufficiently large excess corresponding to the plateau of the T_{vap}/mass function. It has been treated theoretically by Mandjukov et al. (1992, 1995) and Slaveykova et al. (1997c), and experimentally by Docekalova et al. (1991), Frech et al. (1992), Mahmood et al. (1995), and Mazzucotelli and Grotti (1995). Thus, lead was stabilized to 600 and 900 °C at 1:1 and $1:10^5$–10^6 molar excess of W modifier, respectively (Mandjukov et al., 1992). The negative effects of high modifier masses are now better recognized: reagent blanks, increased background, sensitivity drift, overstabilization, etc. (see also Section II), and efforts have been constantly made to improve the efficiency of thermal stabilization by rational designing mixed and composite modifiers and optimization of their quantitative composition.

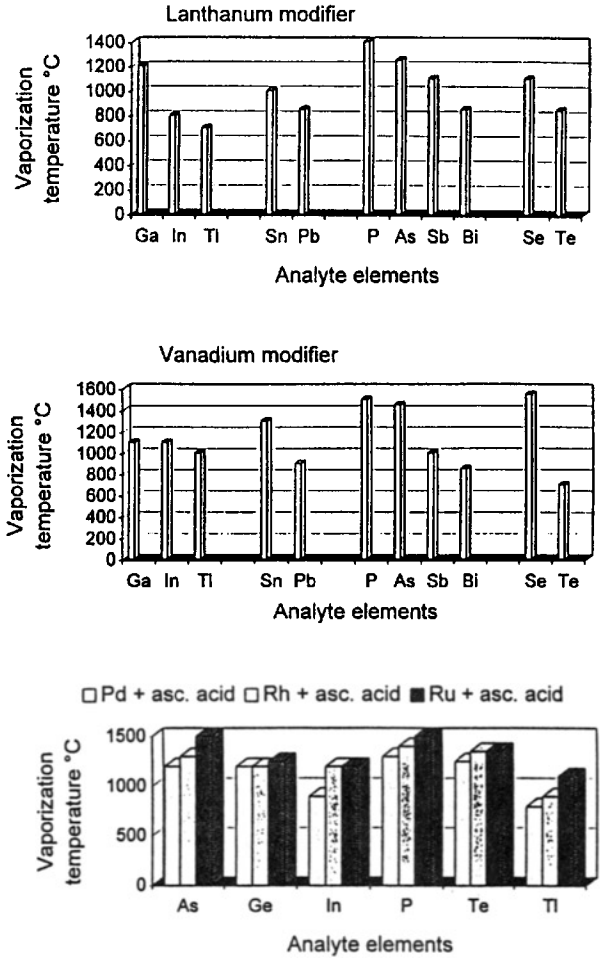

Figure 3. Illustration of certain trends in T_{vap} for some volatile analytes from the same group of the Periodic Table in the presence of individual modifiers of different types: La, V, and noble metals. Based on data from Tsalev et al. (1989; 1990a) and Tsalev and Slaveykova (1992b).

Some guidelines for improving efficiency of chemical modifiers are summarized below:

1. Palladium and other noble metals often perform better in the presence of reductants, resulting in a "reduced Pd modifier" (Voth-Beach and Shrader, 1986, 1987). Common reductants are ascorbic or citric acid (50–200 μg), 5–10% v/v H_2–Ar as an alternate gas during drying and pyrolysis, and (rarer) hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), hydrazine sulfate [$(NH_2)_2{\cdot}H_2SO_4$], oxalic acid

($H_2C_2O_4$), ammonium oxalate [$(NH_4)_2C_2O_4$], and others. Thermal conditioning of noble metals by injection and pretreatment at 1000 °C, followed by cool-down, and then injection of sample solution is also widely practiced. Prereduction of noble metals has proved particularly important (1) for some difficult analytes forming strong bonds with chloride and other halides mainly Ga, In, and Tl, but also for As, Cd, P, Pb, Se, Sn, etc.; (2) in the presence of excess Cl^-, HCl, and HNO_3, aqua regia digests, seawater, sediment, and urine matrices; (3) even more pronounced with some noble metals other than palladium—Ir, Pt, Rh, Ru, and their mixtures. Many examples can be found in Appendixes 3 and 4; only a few most typical recent applications will be mentioned here. These include Tl in sediments in the presence of Pd–$Mg(NO_3)_2$ modifier with drying and pyrolysis steps in 5% v/v H_2–Ar up to 700 °C (Schlemmer, 1996; Schlemmer et al., 1996); As in urine in the presence of 25 μg Rh–1.2 mg citric acid, with T_{pyr} up to 1600 °C so as to eliminate phosphate interference (Ni et al., 1996); Sb in blood and urine with a mixed noble metal modifier containing each of 0.025% Pd + Pt + Rh + Ru combined in the atomizer with 1% ascorbic acid, allowing T_{pyr} up to 1200 °C (Dahl et al., 1994); and Pb and Mn in seawater with Pd–$(NH_4)_2C_2O_4$ modifier (Sachsenberg et al., 1993).

2. Alternative noble metals other than Pd may perform better in certain particular analytical cases, mainly due to their lower volatility (Ir, Pt, Rh, Ru). Thus T_{vap} is higher for the prereduced ruthenium, rhodium, and palladium (Ru > Rh > Pd), in the order given (Figure 3) (Tsalev and Slaveykova, 1992b).

3. Mixed noble metal modifiers (Dahl et al., 1994) may be preferred owing to their lower volatility and higher T_{vap}, e.g. the Pd–Pt–Rh–Ru modifier cited above (Dahl et al., 1994) or the permanent Pd–Ir modifier for in situ collection of hydrides (Shuttler et al., 1992).

4. Mixed modifiers containing noble metals plus "oxide"- or "carbide"-forming element are often not only more efficient as thermal stabilizers but also more universally applicable to larger number of analytes (Schlemmer and Welz, 1996). Typical examples of such type of mixed modifiers are $Pd(NO_3)_2$–$Mg(NO_3)_2$ (Schlemmer and Weiz, 1996), Pd–$(NH_4)_{10}H_2(W_2O_7)_6{\cdot}H_2O$ (Slaveykova and Tsalev, 1990; see Figure 4), Pd–$(NH_4)_2Ce(NO_3)_6$ (Mandjukov and Tsalev, 1990), Pt–$Mg(NO_3)_2$ (Kumpulainen and Saarela, 1992), Ir–$Mg(NO_3)_2$ (Hoenig, 1991; Hoenig and Gilissen, 1993), Rh–$Mg(NO_3)_2$ (Haldimann et al., 1996), and Rh–Re (Thomaidis et al., 1995a). Vaporization temperatures are significantly higher in the presence of mixed modifiers than with each individual component (Figure 4), presumably due to the oxide or carbide matrix provided by the second component, which is thus stabilizing the modifier-"stabilized palladium" or "stabilized phosphate," as given in Figure 4. Indeed, the T_{vap} for Pd is increased from 900 °C in simple aqueous or ascorbic acid solutions up to 1200, 1300, and 1400 °C in the presence of $Mg(NO_3)_2$, $La(NO_3)_3$, and Zr or W, respectively (Tsalev et al., 1989). In $Mg(NO_3)_2$ matrix, the volatization losses of Pd, Rh, and Ru do not start until 1200, 1400, and 1500 °C, respectively. Thus, the second component of the mixed modifier plays the role of "modifier of the form" (Welz et al., 1984) of the noble

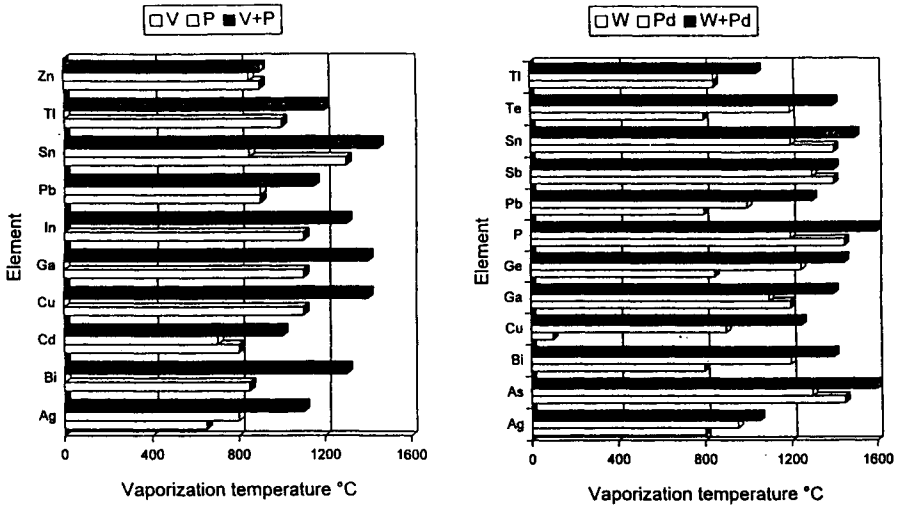

Figure 4. Improved thermal stabilization in the presence of mixed modifiers V–PO_4^{3-} and W–Pd versus their individual components. Based on data from Tsalev et al. (1989; 1990a) and Slaveykova and Tsalev (1990).

metal resulting in (1) better thermal stabilization; (2) more dispersed form of the noble metal, hence smaller droplets formed, resulting in straightforward atomization with higher and narrower peaks (Qiao and Jackson, 1991); and (3) preferential absorbtion of the carbide-forming component on the most active graphite sites, defects, edges of the platform, etc., thus "healing" them and consequently more uniform distribution of Pd is obtained, particularly when organic acid is also added (e.g. Pd-W-citric acid) (Havezov and Russeva, 1993; Russeva et al., 1993). Mixed modifiers containing phosphate are very reactive towards analytes like Ag, Cd, Pb, etc. but are also rather volatile and have to be applied at relatively large amounts (50–200 μg), which entail background and blank problems. Upon thermal stabilization with the isomorphous, nonvolatile vanadate (Figure 4), they produce much better stabilization effects on volatile analytes (Tsalev et al., 1990).

5. (Noble) metal modifiers often exhibit improved efficiency when applied on carbide-coated graphite tubes or platforms, an effect similar yet lower in magnitude than in the presence of their corresponding mixed modifiers—e.g. Ni on ZrC for boron determinations (Luguera et al., 1991; Liu et al., 1994; Gong et al., 1995b); Pd on WC for Sn in seawater (Iwamoto et al., 1993); Pd or Pt (as aminohalide complexes) on WC (Arpadjan et al., 1990; Tserovsky et al., 1992); and Pd-$Mg(NO_3)_2$ for Sn on WC (Osojnik and Drglin, 1993). Both noble metals and metal-like carbides exhibit catalytic properties and may promote the low-temperature reduction of analyte oxides and the decomposition of organoelement compounds (for a review, see Volynsky, 1996).

6. Permanent modifiers, such as carbide coatings (NbC, TaC, WC, ZrC, etc., as extensively reviewed by Volynsky (1987) or less volatile noble metals (Ir, Rh) or

noble metals on carbide coatings (Tsalev et al., 1995, 1996a,b) are becoming more popular. Although these modifiers often show impaired efficiency than modifier additions to each sample, they are very attractive and promising in several analytical cases including (1) on-line coupling ETAAS to separation/enrichment techniques such as hydride generation (HG)–in situ trapping (the best application field so far), FI ion exchange, and HPLC (see Section III.E); (2) when wet modifier additions entail intolerable blanks (e.g. for Ag, Au, Cd, Mn, Pb, Zn, etc.; (3) when certain modifier components (e.g. Cl^- ion) are strongly interfering but cannot be eliminated during the pyrolysis stage because of low T_{vap}, e.g. in Hg determinations; (4) with modifiers exhibiting very low volatility (Ir, V, W), which otherwise cannot be eliminated after atomization and accumulate in the atomizer causing sensitivity drift and other negative effects; and (5) with fast programs.

Limitations of permanent modifiers, as experienced with current technologies for their application, are: (1) imperfect coatings which may eventually result in double or multiple peaks; (2) relatively short lifetimes; (3) limitations imposed on temperature programs (T_{pyr}, T_{at}, and T_{cl} being set somewhat lower so as to avoid excessive loss of modifier); (4) applicability to relatively simple sample solutions, since high-salt matrices and acidic digests may adversely modify atomization surfaces; (5) overstabilization of some carbide-forming and less volatile analytes; and (6) lack of interest of instrumental manufacturers. Therefore, only a few applications of permanent noble metal modifiers to real samples have been documented—e.g. Hg in soil digests with Au–Rh (Bulska et al., 1996); Hg in biological and environmental digests with Ir-modified GTs (Dittrich et al., 1994); and As in sediment and Pb in plant digests with Ir-WC-treated platforms (Tsalev et al., 1996a). For HG-ETAAS applications with in situ trapping, see Appendix 4.

B. Chemical Modifiers as Analyte Isoformers

As a result of improved knowledge and methodology in trace element analysis, today it is better realized that a trace analyte may often be present in various chemical and physical forms in real samples, and that these individual forms (called species or analyte species) may behave quite differently during sample storage, pretreatment, and analysis. Therefore, the ETAAS technique in its direct mode and upon addition of a suitable modifier ("isoformer") should be able to recover completely all these forms, giving information about the total amount of a given analyte. This may be due to the transformation of different analyte species into one single, definite, and thermally stable form (e.g. the highest oxidation state), or otherwise the analyte species may maintain their identity but must anyway yield similar signals in Q_A measurements.

Insuring efficient analyte isoformation is particularly important in analyses of intact biological and environmental samples or extracts and leachates from these matrices, as well as chromatographic effluents. Several analytes are well known for

their presence in different oxidation states and binding forms in these kinds of samples: arsenic (as arsenite, arsenate, MMA, DMA, AB, AC, tetramethylarsonium, arsenolipids, arsenosugars, etc.); selenium (as selenite, selenate, trimethylselenonium, selenocystine, selenomethionine, etc.); tin (as highly toxic alkyltin compounds such as methyl-, ethyl-, butyl-, octyl-, and other derivatives, e.g. in ship paints, antifouling additives, plastic stabilizers, marine tissues, and near-coast waters); mercury (methylated, etc.); and lead (alkylleads in petroleum products), Sb, Te, Cr, etc. (Tsalev, 1984, 1995). Several systematic studies on thermal stabilization and isoformation of these species in biological or environmental samples, paint leachates (Katsura et al., 1990, 1991; Matsumoto et al., 1991), organic extracts (Astruc et al., 1992a), and HPLC effluents (Astruc et al., 1992b; Gailer and Irgolic, 1994; Marchante-Gayon et al., 1996; Slaveykova et al., 1996a) are known for arsenic (Larsen, 1991; Tsalev et al., 1987, 1996a; Gailer and Irgolic, 1994; Pergantis et al., 1994; Slaveykova et al., 1996a); selenium (Welz et al., 1984; Roesick et al., 1991; Docekalova et al., 1991; Radziuk and Thomassen, 1992; Krivan and Kueckenwaitz, 1992; Potin-Gautier et al., 1993; Johannessen et al., 1993; Laborda et al., 1993a,b; Deaker and Maher, 1995; LeBlanc, 1996; Marchante-Gayon et al., 1996); tin (Katsura et al., 1990, 1991; Matsumoto et al., 1991; Ni et al., 1991; Astruc et al., 1992a,b; Dominic et al., 1993; Ide et al., 1995; Erber et al., 1996; Tsalev et al., 1996a); and antimony (Dahl et al., 1994), etc.

Noteworthy, complete isoformation is more difficult to achieve for all organoelement species, even with carefully blended compositions of mixed modifiers and thoroughly optimized temperature programs (Welz et al., 1984; Johannessen et al., 1993; Erber et al., 1996; Li et al., 1996a; Slaveykova et al., 1996a), and it is furthermore difficult with fast programs (Larsen et al., 1991) and permanent modifier coatings (Tsalev et al., 1996a). This is a tempting research topic, especially when related to the increasing interest in speciation studies.

C. Chemical Modifiers as Volatilizers

No doubt, the most promising application field of chemical modifiers as volatilizers is the electrothermal vaporization (ETV) with plasma spectrometric techniques, ETV-ICP-AES and ETV-ICP-MS (see Appendix 2 for examples). In ETAAS, the vaporizing agents are interesting as an alternative to the popular STPF concept; however their application field is still rather narrow, being confined to three typical cases:

1. Determination of a few analytes with high volatility in less-volatile matrices such as seawater, brines, and other high-salt solutions; thus, instead of trying thermal stabilization of Cd (Hoenig et al., 1991a; Cabon and LeBihan, 1992; Sachsenberg et al., 1993), Pb (Hoenig et al., 1991a; Cabon and LeBihan, 1996b), and Zn (Cabon and LeBihan, 1994), which is not particularly efficient, the low-temperature atomization of these analytes is promoted by addition of appropriate volatilizers. Oxalic acid (Cabon and LeBihan, 1992,

1994, 1995, 1996b) or ammonium oxalate, $(NH_4)_2C_2O_4$ (Sachsenberg et al., 1993) or elsewhere alternate gas H_2–Ar during pyrolysis (Hoenig et al., 1991a) have been employed as volatilizers. Upon pyrolysis, and also during atomization, some organic acids give reaction products that change in a favorable way both the atomization surface, leaving more reactive activated carbon, and the gas phase evolving H_2 and CO (Gilchrist et al., 1990; Byrne et al, 1993a). This approach has proved useful also for several analytes with medium volatility (Cr, Cu, Mn), again in a seawater matrix (Cabon and Le Bihan, 1995).

2. Modifiers, promoting low-temperature processes of both pyrolysis and atomization is a rare example described in a paper by Beinrohr et al. (1991) on lead determination in GaAs, wherein the addition of NH_4Cl–$CrCl_3$ promotes both matrix elimination at 600 °C and analyte atomization at 1100 °C.
3. Assisting the cleaning stage for nonvolatile analytes; e.g. Freon 23 alternate gas in Dy determinations (Knutsen et al., 1995).

Additives promoting removal of refractory matrices like metals, silicates, etc., which actually are volatilizers of the matrix, should better not be treated under this heading.

D. Practical Considerations for Blending Efficient Composite Modifiers

Although there is no well-defined borderline between the mixed and composite modifiers, we prefer differentiating between these two types, mainly for methodological reasons. Indeed, because of the large diversity of chemical modifier compositions (Appendixes 3 and 4) it is often confusing to understand the role of one or another constituent in multicomponent mixtures. Thus, some efficient mixed modifiers contain two or more compounds with *similar* mode and aim of action [e.g. $Pd(NO_3)_2$–$Mg(NO_3)_2$, both being thermal stabilizers (Schlemmer and Weiz, 1986), or Pd + Pt + Rh + Ru + ascorbic acid as an efficient thermal stabilizer of Sb (Dahl et al., 1994)], while a composite modifier is a solution or in situ prepared mixture of several components with *different* modes of action aimed at a complex overall effect [containing, e.g. thermal stabilizer + volatilizer of unwanted matrix + acid + surfactant + antifoam agent, etc, e.g.: 4 mM $Ni(NO_3)_2$-50 mM $(NH_4)_2$EDTA-1 mM $Al(NO_3)_3$-0.3 M aq. NH_3 for In in Cl^- containing matrices (Matsusaki, 1990) or 0.2% $Mg(NO_3)_2$-4% H_2O_2-1% HNO_3-8% C_2H_5OH in determinations of Al in carbonized chewing gum by slurry sampling (Vinas et al., 1995c)]. These more efficient "cocktails" are particularly useful in difficult analytical cases, such as analysis of biological materials or organic solutions/extracts, slurries, and solid microsamples.

Wetting agents and antifoam additives with good behavior in the GA which insure smooth pipetting and drying, more uniform spatial distribution of injected solutions/slurries over the platform, and better contact between modifier and

solid/slurried particles are Triton-X-100 (0.005–0.25%), ethanol (≤10% v/v), 5% v/v butanol (Temminghoff, 1990), octanol (Bermejo-Barrera et al., 1990c), triethanolamine (Qian and Yang, 1990, 1991), dilute aq. NH_3 (better ≤1% v/v), and dilute tetramethylammonium (or tetraethylammonium) hydroxide, TMAH, or TEAH, respectively, (better ≤1% m/v but up to 5% m/v tolerated) (Tsalev et al., 1990a, 1993, 1996c; Tan et al., 1996a,b; Zhou et al., 1996). The low surface tension of melts of some organic additives is also part of their useful overall effect (Volynsky et al., 1993).

Dilute nitric acid (0.03–0.2 M, but with tolerance up to 0.5–1 M, depending on modifier) and hydrogen peroxide (4–10% v/v) (Ruekgauer et al., 1995; Vinas et al., 1995a,b,c) are popular in situ "ashing aids" in analyses of biological and organic matrices. Nitric acid exhibits also other useful effects: stabilization of dilute aqueous solutions of digests and modifiers; decreasing the effect of halide interferences due to their early removal as volatile vapors (HCl, HF, etc.); and partial extraction of analyte from slurry particles ("analyte partitioning"). Excess of HNO_3 may be detrimental with noble metal modifiers, while being quite tolerated and even beneficial with Ni-based modifiers. Partial neutralization of acid with aq. NH_3 yielding NH_4NO_3 may prove a good remedy in such cases.

Applying alternate gases as in situ ashing aids together with chemical modifiers may also be considered as a complex approach of chemical modification. Low flow rates of O_2 or air (ca. 10 mL/min) are programmed during pyrolysis (ashing) at 450–550 °C for assisting oxidation and removal of difficult organic matrices (biological fluids, slurries, sugar, oils, and fats). It is particularly important in these cases to add a subsequent step of pyrolysis in Ar atmosphere, so as to expel the chemisorbed and gaseous-phase oxidant before atomization (up to 900–950 °C). Significant reduction of the lifespan of atomizer (by several-fold) may be entailed, depending on T_{pyr}. Some researchers have applied with apparent success T_{pyr} as high as 750 °C (Miller-Ihli and Greene, 1993) or 800 °C (Hoenig, 1991; Granadillo and Romero, 1993c).

EDTA (0.05 M), preferable as diammonium or tetraammonium salt, is an appropriate stabilizer for keeping in solution some strongly hydrolyzable modifiers, analytes, or matrices (Matsusaki, 1990, 1991; Matsusaki et al., 1991b, 1993, 1994; Tan and Liu, 1991; Zheng and Zhou, 1992). EDTA is not only a good conditioner in composite modifier compositions but also a preferred reagent in sample pretreatment as well as interference suppressant for Cl^- and SO_4^{2-} (Matsusaki, 1990; Matsusaki et al., 1991b; Matsusaki and Oishi, 1993). Some other useful complexing agents for stabilizing solutions are citrate and tartrate (see Appendixes 3 and 4).

Hydrofluoric acid is much less ETAAS-friendly but may be resorted to as an additive for in situ removal of certain matrices: silicates (Bendicho et al., 1990b; complex catalysts (Grey, 1990); Lopez-Garcia et al., 1996a,b), boric acid (Tompuri and Tommavuori, 1996).

Clever and rational combination of two types of modifier action in a molecule or complex of a single reagent is also worth mentioning here, although this is not a

composite modifier but rather a modifier with versatile, composite action: noble metal + reductant like $(NH_4)_2Pd[C_2O_4)_2]\cdot 2H_2O$ (Volynsky and Krivan, 1996) or thermal stabilizer + Cl^- interference depressant like NH_4^+ forms of modifiers, as listed in Section II.

E. Chemical Modification as an Integral Part of Analytical Procedure

Numerous examples can be derived from analytical practice showing rational combination of sample pretreatment with ETAAS in the presence of modifiers. Only some most typical and efficient approaches will be discussed here: "internal modification," relevant sample decompositions, coupling with enrichment techniques, and CM in speciation studies.

Internal Modification

Hulanicki et al. (1989) introduced this term in a paper on determination of Mn in blood serum, wherein the dilution of samples with diluted nitric acid leads to the formation of an internal matrix modifier composed of calcium and phosphoric acid. In a broader sense, internal modification can be used to indicate those favorable analytical cases where the matrix by itself or certain matrix constituents play a role of thermal stabilizers or exhibit other beneficial effect on analyte quantitation, either by themselves or upon external addition of solvent, acid, base, or other modifier. Many examples of favorable matrix–analyte couples can be found in Appendix 3; e.g. in analyses of dissolved, slurried, or solid metals (Ag, Au, Cu, Ga, Pd, Pt), alloys (Cu- or Ni-based, etc.), oxides (Al_2O_3, MoO_3, Ta_2O_5, WO_3, ZrO_2), glasses, refractories (carbides, borides, nitrides), bone (Tang et al., 1996), carbonized residues of organic samples, seawater matrix upon addition of 800 μg NaOH, thus stabilizing Cd up to 1400 °C (Lan, 1993), as well as certain concentrates after trace enrichment. Note that in some of these cases the matrix component/internal modifier has to be added only to calibration standards since it is already present in the matrix (de Benzo et al., 1990; Tang et al., 1996); thus more complicated calibration may be entailed. The choice of an appropriate solvent and other additives is also a serious concern.

Rational Sample Pretreatment

The decomposition step should preferably leave the analyte in dilute HNO_3 (0.03–0.2 M) or HCl (<0.1 M); more concentrated acids generally impair modifier performance but may be tolerated after suitable blending of modifier composition. Minimum acid consumption can be insured by applying more efficient sample decomposition techniques such as pressurized bombs, microwave heating, and catalysts of wet digestions (molybdate and vanadate, both being then efficient modifiers by themselves or furthermore when supplemented by Pd) (Tsalev et al., 1989, 1990a). External ashing aids for biological materials and food [MgO, $Mg(NO_3)_2$, or $MgO–Mg(NO_3)_2$] may serve then as efficient modifier components,

just at 5 to 50 μg levels in final injected aliquots, depending on GT volume; higher levels cause increased background absorption and sensitivity drift. Very appropriate media are sample extracts/leachates with organic acids, such as leachates with dilute acetic acid from paints, ceramic vessels, soils, sediments and leachates or digests containing EDTA. Suitable pretreatment techniques for ETAAS are alkaline solubilization of biological tissues and many food items with TMAH or TAAH (Tsalev, 1984, 1995).

Chemical Modification Integrated in Preconcentration Procedures

Ideally, a rational trace element enrichment procedure should transfer the analyte into a small amount of concentrate appropriate for ETAAS quantitation. Unfortunately, most of these procedures (see Appendix 4) are performed off-line and are difficult to automate (extraction, co-precipitation, ion exchange).

A good exception from the above rule is the flow-injection (FI)-hydride generation(HG)-ETAAS technique with in situ collection of hydrides in a graphite atomizer, which offers high analytical potentialities for up to 10 analytes (As, Bi, Ge, Pb, Sb, Se, Sn, Te, etc.)—for reviews, see Dědina and Tsalev (1995) and Matusiewicz and Sturgeon (1996). The hydride collection surface is (best) coated with a permanent modifier, but its physical modification by mechanical removal of the pyrolytic graphite layer, thus exposing a rough, more reactive graphite surface, may also be acceptable for some analytes (Bi, Te). Noble metals (Ag, Au, Ir, Pd, Pt, Rh, Ru), pre-injected and dried/pyrolyzed on the platform or graphite tube (GT), have been used for trapping hydrides and stabilization of volatile analytes. However, applying modifier additions before every hydride trapping run has exhibited some disadvantages and limitations, as noted by Shuttler et al. (1992): complications in the existing hardware and software and increase in the total cycle time when pipetting modifier solution, then thoroughly washing autosampler capillary, performing drying/ashing for conditioning of the modifier, then cooling down the atomizer to an optimal collection temperature (T_{coll}), and then introducing hydrides through the same capillary. Permanent modification (Shuttler et al., 1992) of the graphite atomizer with less-volatile noble metals (Ir, Pd–Ir) or carbides (Nb, Ta, W, Zr) or elsewhere with Ir on WC- or ZrC-treated surfaces (Tsalev et al., 1995, 1996a,b) has proved an efficient and practically useful approach, offering possibilities for an automated HG-ETAAS determination down to pg and pg/mL analyte levels (Appendix 4). The scope of this approach has been extended to multielement techniques such as HG-ETV-ICP-MS (Marawi et al., 1994, 1995; Sturgeon and Gregoir, 1994) as well as to other hydrides and volatile species: the cold vapor technique (CVT) for mercury (Sinemus et al., 1993a,b; Dittrich et al., 1994), cadmium (Bermejo-Barrera et al., 1996g; Goenaga Infante et al., 1996) $Pb(C_2H_5)_4$ generation (Willie, 1994), alkyltin hydrides (Ni et al., 1991; Tsalev et al., 1996a,b), methylarsenic hydrides (Tsalev et al., 1996a,b), and alkylselenium compounds (Zhang et al., 1991a; Jiang et al., 1992), thus promising future developments in speciation studies. It cannot be overlooked that optimum conditions for generation,

trapping, and atomization of organoelement species may differ from those established for their inorganic analogues (Ni et al., 1991; Tsalev et al., 1996a,b). Comparative studies of noble metals versus carbides are scarce (Haug, 1996; Haug and Liao, 1996; Tsalev et al., 1996a), and seem to give preference to noble metals (Ir) because of better sensitivity (Haug, 1996) or lower T_{coll} (Haug and Liao, 1996) or both (Tsalev et al., 1996a).

Coprecipitation with palladium ("reductive precipitation") of Se and Te (Ashino et al., 1994; Ashino and Takada, 1995), Ge, Sb, and Sn (Ashino and Takada, 1996), and Cd, Cu, and Pb (Zhuang et al., 1996) can provide enrichment factors of 50–100. Other appropriate carriers in co-precipitation procedures are: the hydrated Zr(IV) oxide (Mihara and Yokota, 1990; Chen et al., 1993a; Nakamura et al., 1994); $Mg(OH)_2$ (Hiraide et al., 1994); Mg(II) quinolin-8-ol (oxinate) (Atsuya et al., 1990); mixed ligand complexes of Ni(II) with dimethylglyoxime (DMG) and 1-(pyridylazo)2-naphthol (PAN) (Atsuya et al., 1990); and miscellaneous analyte complexes adsorbed on activated carbon (Naganuma and Okutani, 1991; Okutani et al., 1993; Wei et al., 1994; Kubota et al., 1995). These precipitates may be analyzed by slurry (Naganuma and Okutani, 1991; Wei et al., 1994) or solid sampling (Nakamura et al., 1994), with or without addition of another modifier component.

Slurried chelating resins with adsorbed analytes can also be analyzed by slurry sampling, thus providing minor thermal stabilization effect due to delayed vaporization from the charred particles (Sedykh et al., 1994).

Organic extracts are not very conveniently handled in ETAAS because of their low surface tension and viscosity, as well as attacking some autosampler parts (unless special, solvent resistant kits are installed). Chlorinated solvents are rather troublesome and should be avoided as much as possible. Organic extracts behave much better on surfaces permanently modified with carbides: Mo, W, or Zr. Some coextracted components may play a role of thermal stabilizers, e.g. Ag, Cu, Ni, Pd, or Pt, being present in the matrix or added before extraction. Numerous organopalladium complexes (Tserovsky et al., 1992, 1993; Li et al., 1993, 1996; Matsumoto et al., 1993b) and some organophosphorus compounds (Silva et al., 1993; Li et al., 1996a) have been tested as modifiers in organic phases. Modifier mass may need be increased (the more typical case, especially with organohalide extractions) or diminished (Tserovsky and Arpadjan, 1991) depending on each particulate case. Noble metal modifiers (Pd, Pt) exhibit further improvement of their thermal stabilization efficiency on W-treated tubes (Tserovsky et al., 1993). Eventually, back extraction (stripping) of the analyte into a small volume of dilute HNO_3 (Cardelicchio et al., 1992) or other modifier solution may be resorted to (Shintsu et al., 1992; Sachsenberg et al., 1992).

Speciation Studies

The potential of ETAAS for speciation by performing in situ fractionation of different analyte species is very limited. Krivan and Kueckenwaitz (1992) separated

Se(IV) and Se(IV) by preatomization elimination of Se(IV) as volatile piazselenol. Elsewhere, Chen et al. (1993a) coprecipitated As(III) and As(V) with hydrated Zr(IV) oxide; then was fractionally volatilized only $AsCl_3$ upon addition of HCl and pyrolysis within 1100–1400 °C, while As(V) was retained for quantitation. In a series of interesting papers, Yoshimura and coworkers performed in situ differentiation of the oxidation states of several analytes in solid or slurried oxides mixtures in the presence of active carbon ("carbon black"): Fe(II) and Fe(III) (Yoshimura and Huzino, 1990), Ti(II), Ti(III) and Ti(IV) (Yoshimura et al., 1993), Mo compounds (Yoshimura et al., 1992), and Fe, Ti, and Si (Yoshimura and Huzino, 1993). Recently, Wang and Holcombe (1994) utilized the multiple peaks in ETAAS at reduced pressure for studying the spatial distribution of Pb in a Cu alloy; three consecutive peaks were observed at 0.1 torr which could be attributed to different atomization sites: surface, grains, and bulk of the sample, thus revealing prospects for determination of the "near surface lead."

Most other speciation studies rely on off-line separations of analyte species (Appendix 4). Somewhat better potentialities offer the FI-HG-ETAAS coupling and chromatography-ETAAS, both with permanent modification, which are yet to be explored.

IV. CLASSIFICATIONS OF CHEMICAL MODIFIERS AND ANALYTES

This is a theoretical task with potential practical implications. Classification of modifiers and analytes in groups with analogous behavior in ETAAS processes may help to better understand the large diversity of empirical observations and organize literature data in a more accessible way, and, on the other hand, to utilize theoretical schemes for predicting behavior of any new analytical set of analyte–modifier–matrix, and eventually to even design new, more efficient chemical modifier compositions. Several classifications of modifiers and analytes based on theoretical, formal, empirical, and experimental parameters have been described in some detail elsewhere (Slaveykova and Tsalev, 1989; Tsalev et al., 1989, 1990b,c; Tsalev and Slaveykova, 1992a).

According to their chemical nature, chemical modifiers can be found in all types of chemical compounds and all aggregative states (Tsalev et al., 1990b):

1. Inorganic salts (the most popular group), modifiers being both cations of Pd(II), Ni(II), NH_4^+, etc. and anions (nitrate, phosphate, vanadate, tungstate, etc.). The best counter ions for these salts have proved to be NO_3^- and NH_4^+, respectively.
2. Organoelement and complexed forms of modifiers, which are useful when samples or analytes are transformed into organic phase: extracts, leachates, oils, fats, petroleum products, organometallic compounds, etc.; e.g. $Pd(CH_3COO)_2$ (Bhattacharyya et al., 1993), Pd(II) acetylacetonate (Li et al.,

1996b), $PdCl_2(CH_3CN)_2$ (Li et al., 1996b), $PdCl_4$(methyltrioctylamine)$_2$ (Tserovsky et al., 1992), (Matsumoto, 1993b) (see also Appendixes 3 and 4).

3. Inorganic acids (HNO_3, H_3PO_4, etc.) and bases (aq. NH_3).
4. Organic acids (acetic, tartaric, etc.) and bases (e.g. solubilizers of biological tissues like TMAH, TAAH, hyamine hydroxide, etc.).
5. Complexing agents for keeping in solution the analyte, modifier and/or matrix components, e.g. EDTA, citric acid or citrate, etc.
6. Reductants for conditioning noble metal modifiers (ascorbic acid, citric acid, $NH_2OH{\cdot}HCl$, H_2-Ar, etc.).
7. Oxidants for promoting in situ ashing of organic matrices (HNO_3, $Mg(NO_3)_2$, O_2 or air alternate gases, etc.).
8. Reactive alternate gases (H_2, O_2, air, Freons, etc.).
9. Miscellaneous organic additives with complex action (organic acids, organic solvents, surfactants, etc.).

Obviously, some of these single-component modifiers or constituents of mixed or composite modifiers may play more than one role, as discussed in previous text and illustrated in Appendixes 3 and 4.

According to their constitution, three types of modifiers: single-component, mixed, and composite modifiers can be distinguished. Although mixed and composite modifiers were highly praised for their efficiency in Sections III.A and III.D, it should be admitted that there are analytical cases wherein more simple compositions may perform better (Bermejo-Barrera et al., 1995c; Shan and Wen, 1995).

Among gaseous chemical modifiers, alternative and alternate gases can be distinguished. The first group comprises those protective gases which are alternative to argon—e.g. N_2 (no practical advantages vs. Ar) or 5–15% v/v H_2–Ar used with metal atomizers (Mo tube, W ribbon, Ta strip, Pt tube or loop, etc.). The second group, alternate gases, are introduced only during a certain stage of the temperature program: during drying and pyrolysis so as to aid the oxidation of organic matter ("ashing aid" such as O_2 or air) or to condition (pre-reduce) noble metal modifier (5% v/v H_2–Ar) and assist removal of Cl^- as $HCl_{(g)}$ (to a certain extent, hydrogen also promotes atomization at lower temperature); much less popular are alternate gases applied as volatilizers during atomization and/or cleaning stage (CHF_3, CCl_2F_2, CCl_4, etc.)

Elemental chemical modifiers can be classified into three groups on the basis of their expected and prevailing species at the end of pyrolysis stage (Figure 5a) (Tsalev et al., 1989, 1990b,c). The feasible transformations of analytes, generally following the order: nitrate salts–oxides–lower oxides–carbides (or metals) have been evaluated on the basis of thermodynamic calculations as well as literature data on their species identified by instrumental methods. The three groups shown on Figure 5a can be formulated (from left to right) as: (1) oxides–salt-like carbides; (2) oxides–metal like carbides; and (3) metals, with the most popular representatives being $Mg(NO_3)_2$, tungsten, and palladium, respectively. The disadvan-

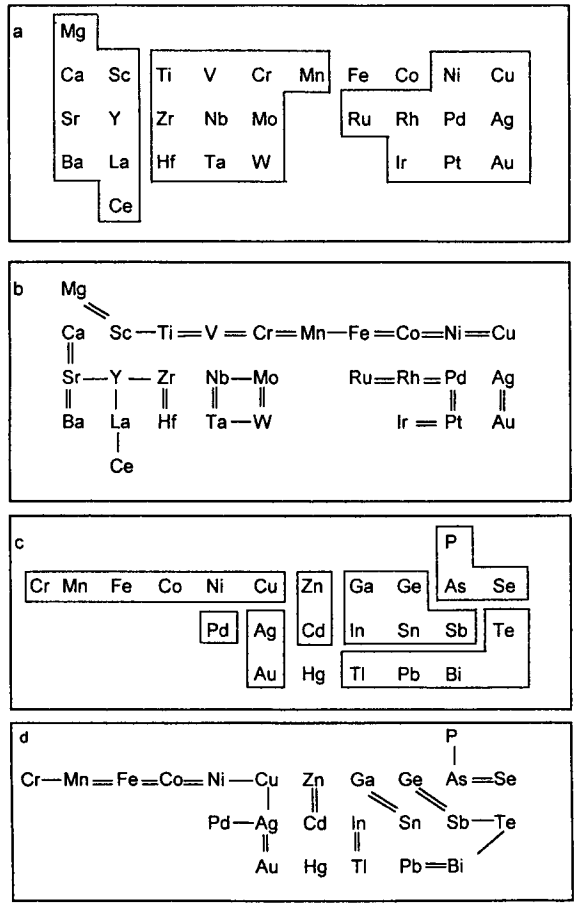

Figure 5. Classification and essential relations between chemical modifiers (**a**, **b**) and analytes (**c**, **d**). (**a**) Three groups of modifiers ("thermodynamic classification") as described by Tsalev et al. (1989; 1990c); (**b**) and (**d**) relations and similarities between modifiers and analytes, the more typical and steady links being shown by double lines; (**c**) "expert classification" of analytes into 7 groups as detailed by Tsalev et al. (1990b). Modified from Tsalev and Slaveykova (1992a) and Tsalev et al. (1990b).

tages of some modifiers from the first group (Sc, Y, La, Ce) are already well documented: their salt-like carbides are easily hydrolyzed by water or dilute acids upon subsequent, repeated additions of sample solutions; gaseous hydrocarbons are evolved which are more corrosive to graphite and may rapidly attack and defoliate pyrolytic graphite coatings, causing sensitivity drift and impaired precision.

Multivartiate methods such as cluster, correlation, discriminant, and factor analysis based on sets of fundamental parameters or experimental data for T_{vap} have been

applied to classify volatile analytes into several groups with analogous behavior (Slaveykova and Tsalev, 1989; Tsalev et al., 1990b; Tsalev and Slaveykova, 1992a). Among the factors used were ionic and atomic radius, atomic volume, electronegativity, ionization potential, ionic potential, polarizability, melting and boiling point of the element, bond energy for element oxygen, heat of melting and of evaporation, and Pearson classification of ions—electronic configuration and character of analyte oxides (acidic, basic, amphoteric). An expert classification of analyte elements into seven groups is shown in Figure 5c, while some essential relations and analogies between the elements–modifiers (Figure 5b) and the elements–analytes (Figure 5d) are represented with double lines and single lines on these figures, indicating the more typical and steady links between pairs by double lines, as detailed elsewhere (Tsalev and Slaveykova, 1992a). Most pairs of these pairs shown in Figure 5b and 5d (except for Bi–Te, Ge–Sb, and La–Y) are isomorphous, which is another criterion of similarity (Tsalev et al., 1989, 1990c).

On the basis of metallographical considerations (Terui et al., 1991a) and phase diagrams of alloys (Hirokawa et al., 1992), these authors proposed the combinations of modifier metals and analyte elements to be classified into three cases: (1) effective modifiers which sinter or alloy with the analyte within a broad concentration range, the melting points (mp) of the resulting alloys being higher than the mp of analytes and T_{pyr} but near to the T_{at}, e.g. Bi, Cd, and Zn with Ni modifier or Bi, Cd, In, Pb, and Zn with Pd or Bi, Pb, Sn, and Zn with Pt modifier; (2) moderately effective combinations, where the presence of eutectic phases or intermetallic compounds with low mp should be considered, e.g. As and Se with Ni modifier or Se and Te with Pd or As and Sb with Pt modifier; and (3) ineffective cases such as no solid solution formation (the pair Pb with Fe) or the mp of alloys formed is ≥ than the mp of the modifier metal, e.g. Cr, Mn, and V with Ni modifier or Cr, Mn, and Ni with Pd, as well as the cases when the mp of modifier is lower than that of the analyte (e.g. Bi, Sb, Sn, Zn being inappropriate as modifiers) (Hirokawa et al., 1992).

V. THE PROGRESS IN STUDYING MECHANISMS OF CHEMICAL MODIFICATION

Today, the general picture of chemical modification is relatively clear thanks to the results of many fundamentally oriented studies. The most important results are briefly outlined in Appendix 2. Valuable information has been obtained recently by some instrumental techniques (for their abbreviations, see the footnote to Appendix 2) and particularly by their combined use: temporally and spatially resolved measurements of atomic, molecular, and condensed species by MAS, MONES, SSDI, etc.; identification of the in-depth profiles and surface-bound intermediate and final species by RBS, SIMS, TPS-SIMS, XPS, XRD, etc.; surface examination by microscopy, SEM, HR-TEM, etc.; MS in vacuum and at atmospheric pressure; and independent quantitative measurements by ETV-ICP-MS, FANES, IC, IR,

Raman spectroscopy, radiotracers, thermal methods, etc. (Appendix 2). Admittedly, there are many discrepancies and contradictions in details, not only for the reasons given in Section II but also because of the large diversity and complexity of the studied physicochemical systems, and limitations on the available instrumental and theoretical approaches. Taking the risk of generalizations, let us try itemizing the most important findings and conclusions on mechanisms of elemental inorganic modifiers (for details, see Appendix 2 and references therein).

1. Interactions between at least four chemical components of the ETAAS system are taking place: the analyte (A), the modifier element (M), oxygen (O), and carbon (C). Complications imposed by modifier counterpartners (Cl or O) cannot be neglected, either. Further complications are brought by the presence of matrix which may be a source of O, Cl, C, etc., and should be excluded in model studies for seek of simplification. This quaternary system may be simplified to a ternary or even binary in certain cases whenever some of these possible interactions are weak or nonessential (e.g. –P–O–Cd– or –In–Pd–systems).

2. The modifier, either in its elemental form (metal) or as a compound (oxide, carbide, oxocarbide) should exhibit certain chemical and crystallographical stability in contact with the heated graphite within 800–1200 °C (or better up to 1500 °C), and should be relatively nonvolatile (say, mp above 1600–1700 °C). If not, an additional component may be required in order to stabilize the resulting mixed modifier to higher temperatures. As a rule, volatile modifiers are neither effective, nor practical, despite their high reactivity towards the analyte (see e.g. the A–M pairs of Hg–Se or Hg–Au or Se–O–C.

3. Both chemical and physical interactions between the analyte and modifier are responsible for chemical modification action. Although one of these mechanisms may prevail, depending on the particular A–M–O–C system, it would be counterproductive to argue about chemical or physical modifiers. Even the noble metals, which are relatively inert chemically, are stabilizing numerous analytes by both chemical and physical mechanisms. Ultimately, a purely chemical mechanism would mean that the analyte and modifier are strongly interacting with each other and are forming a stable and more refractory specie such as a stoichiometric compound or intermetallic alloy. Such compounds or phases have been observed experimentally (Appendix 4) but they do need further stabilization by an excess of modifier. A more physical mechanism would be an entrapping of a volatile analyte into a bulk of refractory modifier. Here again the analytes that interact stronger with the bulk modifier are stabilized better (cf. Mn and Cr in solid carbon residues wherein chromium is stabilized better due to carbide formation). Thus both extremes of only strong chemical interaction or only a bulk modifier effect have proved inefficient.

4. Graphite cannot be considered as an inert substrate; it may be penetrated by modifiers, analytes, oxygen, halides, and solvents. Modifiers, oxygen, and solvents may both create new and bound the existing active sites.

5. Modifiers are nonhomogeneously distributed over the surface and in-depth of graphite. Higher T_{pyr} promotes the jumpwise migration of analyte and modifier over the atomization surface due to processes of multiple release and adsorption, as well as an in-depth penetration.

6. Many elemental modifiers of the "oxide" and "carbide" type interact with analytes via oxygen, which actually forms strong chemical bonds with the analyte—e.g. –P–O–Cd– or –W–O–Se–. In this respect, the elemental modifier (P or W or Mg) may be considered as a high-temperature stabilizer of oxygen, until losses of oxygen and analyte start at higher T_{pyr} because of the formation of lower oxides or carbides. Thus oxygen may persist in the GA to temperatures around 900–1000 °C or higher. Even palladium, which thermodynamically should be in a metallic form already at room temperature, has been found to persist as an oxide and to stabilize certain analytes as [Pd,As,O] and [Pd,Se,O] compounds or mixed solutions (Styris et al., 1991a,b).

7. The composition of A–M–O or A–M species is changing with depth as well as in the course of pyrolysis and the onset of atomization. Intermetallic phases or mixed oxides are thus becoming enriched in the less-volatile component (modifier)—e.g. in the order $PdIn_3$–Pd_2In_3–PdIn–Pd_2In (Oishi et al., 1991) or Pd_3Sn_2–Pd_2Sn–Pd_3Sn (Yasuda et al., 1994).

8. Modifiers affect composition of the gas phase.

9. Clustering chemical modifiers and analytes into groups with similar behavior is useful for better understanding of their possible interactions and effects as well as for more rational designing of compositions of mixed and composite modifiers. Useful concepts for such classifications are the isomorphism between pairs of A–A, A–M, and M–M, as a general measure of chemical similarity/analogy and possibility of forming continuous solid solutions (Tsalev et al., 1989, 1990a,c); fundamental physicochemical parameters; the guiding and predicting power of the Periodic Law and Periodic Table of elements (Tsalev et al., 1990b; Tsalev and Slaveykova, 1992a); and phase diagrams of binary alloys (Hirokawa et al., 1992; Hirano et al., 1995).

10. Kinetics plays an important role in modifier transformations, A–M interactions, analyte loss, and atomization. The apparent activation energies (E_a) are significantly higher in the presence of efficient thermal stabilizers. Different methods are available for extracting energetic data from ETAAS measurements (Bass and Holcombe, 1988; Slaveykova and Tsalev, 1991, 1992; Rojas and Olivares, 1992; Yan et al., 1993b; Fonseca et al., 1994a), with their advantages and limitations, which have been compared experimentally by Fonseca et al. (1994a) and critically discussed by Bass and Holcombe (1988). There are still methodological problems with the simplifying assumptions for the order of release, mass-dependent E_a values, and interpretation of kinetic and thermodynamic data.

VI. FROM PRACTICE TO THEORY AND VICE VERSA (CONCLUSIONS)

Having started more than two decades ago as an empirical approach for performing in situ treatment of the analyte, matrix, or both, chemical modification has attained broad practical recognition and remarkable fundamental development as documented extensively in over 1400 relevant texts. After all and first of all, however, ETAAS is a routine tool for quantitative trace analysis, which is now being seriously rivaled by the powerful, multielement plasma spectrometric techniques. The future fate of chemical modification would be expected to closely parallel the forthcoming advances in ETAAS instrumentation and methodology. Future research and development should be directed in such a way that the main limitations and drawbacks of the chemical modification approach and of the ETAAS method as a whole are treated in a more rational and effective manner, as dictated by the following vital challenges of analytical practice:

- would it be possible to increase the sample throughput rates to more than 60 per hour by using fast programs compatible with chemical modification(?);
- reliable combination of chemical modifiers with fast sample pretreatment techniques such as slurry sampling, leachates and acid extracts, bomb-decomposed samples, and analysis of intact or simply diluted aqueous and solid microsamples;
- rational coupling of chemical modification ETAAS with (automated) enrichment and speciation techniques, down to pg/mL levels;
- exploiting the full potential of permanent modification;
- yet more reliable control of interferences and better understanding the role of matrix in impairing modifier effectiveness;
- routine performance of simultaneous multielement determinations;
- facilitating calibration;
- improving the lifetime of atomizer and long-term stability of measurements;
- would it be possible to achieve a reasonable degree of unification and standardization by using a limited number of more universal modifiers and/or establishing devoted, optimized modifiers with validated performance for certain groups of similar analytical tasks?—the large diversity of chemical modifier compositions would seem already to be a drawback of the current ETAAS methodology and hopefully, future research will give positive answers to most of all these demands.

ACKNOWLEDGMENTS

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APPENDIXES

Appendix 1. Examples of Non-ETAAS Applications of Chemical Modification

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Ag	NaCl solutions	NaCl	ETV-ICP-MS; LOD 0.23 pg	Lamoureux et al. (1994)
Al	Gelatin, liver	$Mg(NO_3)_2$	Resonance ionization spectrometry study	Zilliacus and Likonen (1992)
Al	Serum, urine	PTFE slurry	ETV-ICP-AES; LOD 0.5 µg/L	Hu et al. (1994a)
As	Aq. solutions	400 µg/g Ni $(NO_3)_2$-1% aq. NH_3	ETV-ICP-AES	Carey et al. (1991)
As	Aq. solutions	15 µg Pd-10 µg $Mg(NO_3)_2$	ETV-ICP-MS	Ulrich et al. (1992)
B	Aq. solutions	$Ni(NO_3)_2$	Atomization mechanism studied by ETV-ICP-MS	Byrne et al. (1994a)
B	Plant	6% PTFE	Slurry sampling ETV-ICP-AES; T_{pyr} 360 °C; T_{at} 2560 °C; LOD 2.4 µg/L	Hu et al. (1991b)
B	Plant leaves	6% PTFE	ETV-ICP-AES; sample carbonized at 250 °C, then slurried; LOD 2.4 µg/L	Hu et al. (1991b)
Br	Wheat flour	10 µL of 10 mM $Ba(OH)_2$	ETV-laser excited molecular fluorescence of AlBr; T_{pyr} 600 °C	Anwar et al. (1991)
Ca	Ga	HNO_3, HCl, NH_4Cl, Al	ETV-FAAS and ETAAS study of Ca and Ga volatization; LOD 0.06 µg/g	Kantor et al. (1994)
Cr	Liver, serum	PTFE slurry	Fluorination assisted ETV-ICP-AES; LOD 1.4 µg/L	Hu et al. (1991c)
F	Aq. solutions	20 µg $Ba(NO_3)_2$	ETV-laser excited molecular fluorescence of MgF	Yuzefovsky and Michel (1994)
F	Beverages, food, milk, plant, tea, urine, vinegar, wine, etc.	10 mM Al(III)-10 mM Sr(II)-0.3 M NH_4NO_3	MAS of AlF measured; T_{pyr} 700 °C	Gomez et al. (1990)
F	Seawater	10 mM Al(III)-10 mM Sr(II)-0.3 M NH_4NO_3	MAS of AlF; LOD 8-10 ng F^-	Palacios-Corvillo et al. (1990)

(*continued*)

Appendix 1. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
F	Urine, water	$Ba(NO_3)_2$ preferred to $Sr(NO_3)_2$	ETV-LEMOFS with GF atomizer; AlF measured; T_{pyr} 800 °C; LOD 0.3 pg	Butcher et al. (1991)
Hg	Aq. solutions	Pd	LEAFS; T_{pyr} 110 °C; LOD 9 ng/L	Resto et al. (1993)
Li	Liver, oyster, plant	50 ng La (as nitrate)	ETAES with W tube atomizer; T_{pyr} 300 °C; LOD 0.04 pg	Ohta et al. (1991a)
Mn	NaCl containing aq. solutions	Ascorbic acid	Elimination of Cl^- interference at T_{pyr} 450–1100 °C studied by ETV-ICP-MS	Byrne et al. (1993b)
Mo	Flour, food, garlic, liver, milk, pollen, spinach	6% PTFE	Slurry sampling ETV-ICP-AES; LOD 0.7 µg/L	He et al. (1991)
Mo	Plasma, serum	Pd-$Mg(NO_3)_2$	ETV-ICP-MS; T_{pyr} 700 and 1500 °C; STPF; LOD 0.01 µg/L	Schrammel and Wendler (1995)
P	Aq. solutions	2–3 µg La(III)	FANES and MONES; PO and HPO bands measured by MONES with LODs of 700 and 3400 pg, resp.	Dittrich and Fuchs (1990)
P	Liver, milk, Ni alloys, plant leaves	1–20 µg Ni	ETV-LEAFS: T_{pyr} 300 °C, T_{at} 2100 °C, LOD 8 pg; ETV-LEMOFS (PO measured): T_{pyr} 300 °C, T_{at} 2100 °C, LOD 80 pg	Liang et al. (1992)
P	Polymers	10 µg Ni	Solid sampling ETV-LEAFS; T_{pyr} 800 °C, T_{at} 2600 °C; LOD 8 pg	Lonardo et al. (1996)
Pb	Aq. solutions	10 µg PO_4^{3-}; O_2 treated platform	RBS study of reactions	Eloi et al. (1995b)
S	Steel	10 µg KOH	ETV-ICP-MS; KOH addition only partly eliminated interferences; LOD 0.05 µg/g	Naka and Gregoire (1996)
Se	Aq. solutions	Pd	RBS study of mechanisms	Majidi and Robertson (1991)
Tl	Leaves, liver	0.5% HNO_3	GF-LEAFS; Cl^- interference reduced	Anzano et al. (1991)

U	Aq. solutions	0.3% CHF_3 (Freon 23)-Ar	ETV-ICP-MS; Freon prevents intercalation and carbide formation	Goltz et al. (1995a)
W	Aq. solutions	0.2 µg of NaCl or NaF	ETV-ICP-MS; CMs are ineffective in preventing the formation of WC	Byrne et al. (1994b)
Ag, Cd	Aq. solutions	PO_4^{3-}	Mechanisms studied by SIMS	Hassell et al. (1991)
Br, Cl	Aq. solutions	$Pb(NO_3)_2$	ETV-MIP-AES; LODs 300 and 120 pg, resp.	Wu and Carnahan (1990)
Cl, F	Rain water (Cl^-), oyster tissue (F^-), dental rinse (F^-)	Co-Sr (for AlCl), Ba (for AlF)	MAS of AlCl or AlF measured	Fender and Butcher (1995)
Co, Pb	Coal fly ash, plant, sediment	Pd	Zeeman GF-LEAFS	Irvin et al. (1992)
Ti, V	Coal	6% PTFE	Slurry in 1% Triton X-100; ETV-ICP-AES	Hu et al. (1993a)
B, La, U	Aq. solutions	NH_4F, NH_4Cl, NH_4Br, NaCl, NaF, NH_4HSO_4, $(NH_4)_2HPO_4$; gaseous CMs: CHF_3, CCl_2F_2, HCl	ETV-ICP-MS T_{pyr} 1400–1500 °C; T_{at} 2650 °C; LODs 2–6 pg (B) and 10 fg (La, U)	Wanner et al. (1996)
Br, Cl, F	$CH_2ClCOOH$, milk and mouth wash (for Cl^-); dental rinse, CF_3COOH and tetraflouro-propan-1-ol (for F^-)	55 µg Ba (as nitrate)	MAS-ETAAS or MAS-FAAS; AlF, AlCl, AlBr, InBr absorbance measured; T_{pyr} 700 °C	Butcher(1993)
Ag, Pb, Sn	Aq. solutions	5 ng Pd-5 ng $Mg(NO_3)_2$	ETV-ICP-MS; T_{dry} 100 °C, T_{at} 2100 °C; sensitivity improved 5 ×	Gregoire et al. (1992)
Cd, Cu, Pb	Sediment	2% HNO_3-0.1% Triton X-100; Pd	Slurry sampling ETV-ID-ICP-MS; Pd not recommended, and T_{pyr} kept 200 °C for Cd	Liaw and Jiang (1996)

(*continued*)

Appendix 1. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cu, Mn, Ni	Milk, total diet	1 μg Pd; O_2 ashing	Slurry sampling ETV-ICP-MS vs. wet digestion; T_{pyr} 750 °C (in O_2)	Fonseca and Miller-Ihli (1996)
Al, Fe, Ti, V	SiC	$PdCl_2$	Solid sampling ETV-ICP-AES; stepwise pyrolysis up to 2200 °C; LODs 0.3–4.4 μg/g	Golloch et al. (1995)
As, Cd, Pb, Zn	Sediment, soil	$Na_2Se_2O_3$-graphite powder; toluene vapor added to Ar	Solid sampling-ETV-ICP-AES; improved transport efficiency	Zaray and Kantor (1995)
B, Cr, Mo, Ti	Plant	PTFE powder	In situ fluorination ETV-ICP-AES	Qin et al. (1995)
Nb, Ta, U, Zr	Aq. solutions	PTFE	Fluorination-ETV-ICP-AES	Hu et al. (1993c)
Ca, Cr, Mg, Si, Ti	Aq. solutions	Ascorbic acid, $Mg(NO_3)_2$, NaCl, $Ni(NO_3)_2$, $Pd(NO_3)_2$	ETV-ICP-MS study of the formation of background polyatomic ions resulting from CMs	Gregoire and Sturgeon (1993)
Cd, P, Pb, Te, Zn	Aq. solutions	Pd, Rh	Formation of molecular species reduced as demonstrated by FAPES	Sturgeon and Willie (1992)
Co, Cu, Mn, Ni, V	Seawater	5% HNO_3	ETV-ICP-MS; T_{pyr} 1150 °C, T_{at} 2400 °C	Chapple and Byrne (1996)
Cu, Mn, Ni, Pb, V	Coal, lobster, ouster, total diet	Pd	ETV-ICP-MS; slurry in 0.8 M HNO_3-0.005% Triton X-100; O_2 added during pyrolysis	Fonseca and Miller-Ihli (1995)
Ra, Tc, Th, U radioisotopes	Environmental waters	CHF_3 carrier gas; Ta-coated GT	ETV-ICP-MS of long-lived radioisotopes; stepwise pyrolysis; LODs improved down to 5, 0.9, 2, 1.4, 0.6, and 1.5 fg for ^{238}U, ^{236}U, ^{232}Th, ^{230}Th, ^{226}Ra, and ^{99}Tc, resp.	Alvarado and Erickson (1996)
Ag, Bi, Co, Cs, Cu, Pb, U	Aq. solutions, seawater	Acids (HCl, HNO_3, H_2SO_4, H_3PO_4), seawater matrix	ETV-ICP-MS study of vaporization; seawater matrix used as a physical carrier	Gregoire et al. (1994)
Al, B, Cu, Fe, Mo, Si, V	SiC ceramics	CoF_2-$Ba(NO_3)_2$	DC arc AES study; solid sampling	Florian et al. (1993)
Al, Cr, Cu, Fe, Mn, V, Zn	Ceramic powders, SiC	BaO-CoF_2	Solid sampling ETV-ICP-AES	Nickel and Zadgorska (1995)

Al, Cu, Fe, Na, Ni, Pb, Zn	Semiconductor process control reagents: HF, HF-NH_4F etch	1 μg KI	ETV-ICP-MS; T_{pyr} 500 °C, T_{at} 2500 °C	Hub and Amphlett (1994)
As, Be, Cd, Cr, Cu, Rh, Sb	Lake sediment, water	Various CMs compared: $Mg(NO_3)_2$, $Pd(NO_3)_2$, Pd-$Mg(NO_3)_2$, $Mg(NO_3)_2$-NaCl, $Ni(NO_3)_2$, KI, $NH_4H_2PO_4$	GF-ETV-ICP-MS; T_{pyr} 300 °C; sensitivity enhancement by 10–130-fold vs. nebulization mode	Berryman and Probst (1996)
As, Cd, Hg, Pb, Sb, Se, Zn	Alkaline and alkaline earth matrices	$Na_2S_2O_3$, or CCl_4 as volatilizers	GF-ETV-ICP-AES study in the presence of dilute HNO_3	Kantor (1996)
La, Mo, Ti, V, Y, Yb	Aq. solutions, slurries	PTFE	Fluorination-ETV-ICP-AES	Hu et al. (1993b)
Ag, As, Cd, Mn, Pb, Se, Sn, Tl	Aq. solutions (NaCl added)	0.5 μg Pd	FAPES study under STPF conditions	Sturgeon et al. (1991)
Al, Cr, Cu, Fe, Mn, Mo, V, Ti	SiC	BaO-CoF_2; also studied: KF, $(C_2F_4)_n$, $Na_2B_4O_7$, $BaCO_3$, $Ba(NO_3)_2$, BaO, AgCl, CoF_2, $Pb(BO_2)_2$	ETV-ICP-AES; BaO-CoF_2 recommended	Nickel et al. (1993)
Ag, Bi, Cd, Cs, Ga, Pb, Rb, Tl	Seawater	Seawater matrix	ETV-ICP-MS; matrix acts as a muticomponent physical carrier	Hughes et al. (1995)
Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, V, Zn	Water (rain, river)	Pd-$Mg(NO_3)_2$	ETV-ICP-MS; LODs 0.04–3.8 pg	Santosa et al. (1995)
Al, B, Cr, Er, Eu, La, Lu, Mo, Nb, Sc, Si, Ta, Ti, U, V, Zr, Y, Yb	Aqueous slurries	PTFE powder	Slurry sampling ETV-ICP-AES; LOD tabulated and mechanism of fluorination discussed	Hu et al. (1996)
Ag, Al, As, Cd, Co, Cr, Cu, Ba, Bi, Fe, Ga, Hg, In, Mn, Ni, Pb, Se, U, V, Zn	Aq. solutions	0.01–1 μg Pd (as nitrate); NaCl; $Mg(NO_3)_2$; 1 μg Fe (as nitrate); 0.1 μg citric acid	ETV-ICP-MS; CMs as physical carriers reviewed and experimentally evaluated	Ediger and Beres (1992)

(*continued*)

Appendix 1. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Sc, Y and lanthanoids	Aq. solutions; La_2O_3 (Y determined)	PTFE slurry	Fluorinating vaporization in GF-ETV-ICP-AES	Huang et al. (1991)
	Aq. solutions	40 μg HNO_3, 10 μg $Mg(NO_3)_2$-40 μg HNO_3; 10 μg Pd-40 μg HNO_3;	Spatial distribution of molecular species studied (C_2, CN, Ag_2, AgH, Ga_2O etc.)	Frech and Baxter (1996)

Appendix 2. Applications of Instrumental Techniques and Theoretical Approaches to Studying Mechanisms of Chemical Modification

Technique	*Modifier*	*Observations and Comments*	*Reference*
CCD-Digital imaging	B	A gas-phase thermal dissociation of boron oxide species, resulting in the formation of $BO_{(g)}$ at temperatures < T_{at} is suggested; preatomization loss of B as molecular species; desorption of B atoms from the decomposition of solid boron carbide	Goltz et al. (1995b)
Diode array UV spectrophotometry	Pd-Mg	Vapor phase behavior of atomic and molecular species resulting from slurries of CRMs	Tittarelli and Biffi (1992)
Diode array UV spectrophotometry	—	$SiO_{(g)}$ and $GeO_{(g)}$ evolved during atomization; $SiS_{(g)}$ and $GeS_{(g)}$ observed in the presence of $CaSO_4$ or FeS_2; bituminous coal slurry matrix	Tittarelli et al. (1994)
Dual cavity platform	Pd	Mechanisms of action of Pd to reduce Cl^- interferences in determinations of Pb, Sb, and Tl	Qiao et al. (1993)
Dual cavity platform	$CoCl_2$	Zinc volatization losses due to $ZnCl_2$ formation	Doner and Akman (1994)
Dual cavity platform	$Mg(NO_3)_2$; Pd, etc.	Cl^- interferences on Zn and Co studied	Akman and Doner (1994)
Dual cavity platform	$NiCl_2$	Interference mechanism of $NiCl_2$ in determination of Co and Zn	Akman and Doner (1995)
ETV-ICP-MS	Ascorbic acid	$MgCl_2$ interference on Mn studied; Mn losses via molecular species formation; ascorbic acid retards hydrolysis of the $MgCl_2$ matrix	Byrne et al. (1992)
ETV-ICP-MS	B	Majority of boron vaporized in molecular form [$HBO_{2(g)}$, $BO_{(g)}$, $B_4C_{(s)}$] and removed from the furnace at temperatures < T_{app} for B atoms; Ni addition increases $BO_{(g)}$ formation	Byrne et al. (1994a)
ETV-ICP-MS	W	Tungsten oxides volatilized at 850 °C, carbides above 2500 °C	Byrne et al. (1994b)
ETV-ICP-MS	U	Uranium atoms formed at temperature above 2400 °C, oxide above 1100 °C; U carbides formed at 2000 °C, volatilized at 2600 °C; addition of 0.3% CHF_3 to Ar prevents both intercalation of U in graphite and carbide formation at 2700 °C	Goltz et al. (1995a)
ETV-ICP-MS	Y and REE	Volatization of oxides at temperatures < 2500 °C: $Ln_2O_{3(s)} \rightarrow xLnO_{(g)} + (2 - x)Ln_{(g)} + (3-x)O_{(g)}$ and $Ln_2O_{3(s)} \rightarrow 2LnO_{(g)} + 0.5O_{2(g)}$; at temperatures > 2500 °C: $LnO_{(l)} + C_{(s)} \rightarrow LnC_{x(l)} + Ln_{(l)} + CO_{(g)}$, $Ln_{(l)} + C_{(s)} \rightarrow LnC_{x(l)}$, and $LnC_{x(l)} \rightarrow InC_{(g)} + Ln_{(g)} + C_{(g)}$	Goltz et al. (1995c)

(*continued*)

Appendix 2. Continued

Technique	*Modifier*	*Observations and Comments*	*Reference*
FANES; MONES	2–3 μg La(III)	Phosphorus as analyte; $LaPO_4$ formation during pyrolysis; $LaPO_4$ then reduced by solid C to LaP; stable PO and HPO molecules observed at 1000–2000 °C in the gas phase and analytically utilized	Dittrich and Fuchs (1990)
FAPES	Pd; Rh	Molecular species measured by FAPES (CdCl, PbCl, PbO, PO, TlCl, ZnCl); reduced Pd modifier effective in their elimination	Sturgeon and Willie (1992)
FTIR	Ni, Pd	Ga and Pb as analytes; $PdCl_2$ decreases the temperature of reduction of PbO and Ga_2O_3 by graphite; Ni catalyses early reduction of Ga_2O_3	Volynsky et al. (1991b)
HR-TEM	Pd	Analyte (Sn) atoms, tightly caught in the top surface of the intermetallic compound (ca. 10 atomic layers), were either strongly vibrating or swaying at the melting temperature for a while and then evaporated all at once	Yasuda et al. (1993)
HR-TEM	Pd	Intermetallic compounds formation (SnPd, Sn_2Pd_3, $SnPd_2$, and $SnPd_3$; Pd and Sn atoms evaporated simultaneously; analyte activity coefficients estimated	Yasuda et al. (1994)
HR-TEM	Pd	Pd clusters with approx. diameter of 10 nm at 840 °C; In-Pd intermetallic compounds formed; Pd-In intermetallic compounds which remained after the evaporation of In shifted into other phases with higher atomic % of Pd, and eventually reached almost 100% Pd phase	Yasuda et al. (1995)
IC	300 μg NH_4NO_3	85–90% of chloride (100 μg NACl) removed from the platform at 200 °C; complete removal of Cl^- at 1000 °C; Na evaporation started at 800 °C and almost completed at 1100 °C	Chaudhry and Littlejohn (1992)
IC	5 μg Pd-0.5 μg Mg	Elimination of interferences by NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgSO_4$, and $CaSO_4$ studied; amount of salt residue left on the platform measured by IC	Cabon and LeBihan (1996a)
MAS	$Al(NO_3)_3$; $Cu(NO_3)_2$; $Pb(NO_3)_2$	Simultaneous measurements of molecular and atomic absorption; Ta-lined and unlined GT; $CuO_{(g)}$ appears immediately after the AA signal for Cu has disappeared; $PbO_{(g)}$ appears prior Pb atoms appearance; $Pb_{2(g)}$ appears coincident with Pb atoms	Ratliff and Majidi (1992)
MAS	40 μg HNO_3; 10 μg $Mg(NO_3)_2$-40 μg HNO_3; 10 μg Pd-40 μg HNO_3	In situ measurements of C_2, CN, Ag_2, AgH, and various oxides performed; nonuniform distribution over the tube cross section and light scattering due to particles formed by condensation of supersaturated matrix vapors observed	Frech and Baxter (1996)

MAS	W- or Zr-coated GT	Influence of bases and acids, T_{pyr} and CO alternate gas on GeO and Ge absorbance; reduction of GeO_2 to volatile GeO can be suppressed by addition of oxidizing agents ($HClO_4$ or HNO_3), alkali, or by use of W- or Zr-treated tubes	Zheng and Zhang (1992)
MAS	Nitrates of Be, Mg, Ca, Sr, and Ba; Ta-lined GT	Vaporization and atomization mechanisms of the Group IIA metal nitrates are similar from graphite and Ta-lined surfaces; temporally resolved MAS measurements; hydroxides and oxides but not carbides confirmed; accelerated degradation of GT observed	Ratliff (1996)
Microscopic studies	Pd-plated GT	Electrodeposited Pd layer is stable up to about 60 atomization cycles	Bulska and Jedral (1995)
MS	Pd	Atmospheric pressure and vacuum measurements; $As_xPd_yO_z$ system studied; stoichiometric compound formation; $PdO_{(s)}$ reactions with condensed phases of As and AsO; $Pd_{(s)}$ reaction with condensed-phase As_2O_3	Styris et al. (1991a)
MS	Pd	Atmospheric pressure and vacuum measurements; compound formation through $PdO_{(s)}$ interactions with condensed phases of Se and SeO_2; $Se_{(g)}$ from decomposition of $Se_xPd_yO_z$ readsorbs at sites associated with the presence of adsorbed Pd	Styris et al. (1991b)
MS	Ba, Be, Ca, Mg, Sr (as nitrates)	Atmospheric pressure and vacuum measurements; oxides and hydroxides observed for all elements except Be at low temperatures; gas-phase carbides at high temperatures	Prell et al. (1991)
MS	Y	YO and $Y_2O_{3(g)}$ above 2380 K; $Y(OH)_{3(g)}$ above 2450 K; YC_2 above 2760 K; Y detected above 2700 K	Prell and Styris (1991)
MS	Oxygen	Gas-phase reactions between the free Pb and O_2	Byrne et al. (1993b)
MS	Co, Cu, Mg, Ni, and Pb (as nitrates)	Quadrupole MS with cross-beam rather than axial sampling of gas from the furnace; thermal decomposition of nitrates to solid oxides and gaseous NO_2; no gaseous metal oxides detected over a range of heating rates from slow drying to rapid atomization	McAllister (1994)
Radiotracers	$NH_4H_2PO_4$; BN-coating; WC-coating	Review on the use of radiotracers in AAS; examples given for Cr(III), Cr(VI), Pb(II), Se(IV), and Se(VI) thermal stabilization and atomization	Krivan (1992)
Radiotracers	Ir; Pd; Pt; Rh	Comparison of modifiers in chloride and pre-pyrolyzed forms at 1500 × molar excess over ^{75}Se; chloride forms less effective; dissolution of elemental Se in the noble metals at relatively low T_{pyr} diminishes losses of Se in the pyrolysis stage; dips in pyrolysis curves at 600 °C (Pd < Pt < Rh < Ir); Pd superior	Volynsky et al. (1996)
Radiotracers	0.025% of each Pd-Pt-Rh-Ru + 1% ascorbic acid	^{125}Sb study reveals no volatization losses of Sb in blood and urine matrices in the presence of this mixed modifier; addition of H_2 alternate gas during pyrolysis also beneficial	Dahl et al. (1994)

(*continued*)

Appendix 2. Continued

Technique	*Modifier*	*Observations and Comments*	*Reference*
Radiotracers	W-treated GT vs. Zr, Ir, Ir-Mg, Ir-Pd	^{210}Pb evaluation of lead hydride generation (95%) and trapping efficiency (71%) on W-coated GT; tube coating lifetime ca. 400 cycles; adsorptive carry-over effect on the injection tip of the quartz capillary at $T_{coll} > 450$ °C	Haug (1996)
Radiotracers	Zr-treated tubes for in situ hydride collection	Hydride generation yield > 95% for both ^{207}Bi and ^{125}Sb; trapping efficiency 56% for BiH_3 and 91% for SbH_3 on the Zr-coated tube; other coatings also studied (Ir, Ir-Mg, Ir-Pd, Nb, Ta, and W)	Haug and Liao (1996)
Raman	—	The state of the Pb analyte in sulfur matrix in a GA in an air stream was a mixture of PbS and PbO_2 at 300 °C; then changed into a mixture of α-PbO_2, β-PbO and $PbSO_4$ at 500 °C and β-PbO at 750 °C	Koshino and Narukawa (1994)
RBS	1.25 μg Pd	Modifier digs channels through the graphite substrate, and adsorbs on the sites throughout the channels; $Se_xPd_yO_z$ formation	Majidi et al. (1991)
RBS	200 μg PO_4^{3-} as $NH_4H_2PO_4$	Ag, Cd and Pb as analytes (1 μg); formation of $xMO.P_2O_5$ glasses; no interaction between 2 μg Ag(I) and 200 μg PO_4^{3-}	Eloi et al. (1993)
RBS	$NH_4H_2PO_4$	1 μg Pb + 10 μg PO_4^{3-} formed lead oxyphosphorus compounds; surface bound Pb-O formation	Eloi et al. (1995b)
SEM	Ascorbic acid	Less porous and more smooth surface observed	Imai and Hayashi (1991)
SEM	Mg, Pd	Co, Cu, Fe, Mn, and Ni in silica glasses; particle size distribution and behavior of slurries examined	Bendicho and de Loos-Vollebregt (1990b)
SEM	Pd	Effects of the physical character of the pyrolyzed modifier residues; well separated particles with approx. diameter 0.1 μm observed at 300 ng Pd levels; significant agglomeration seen at 100 μg Pd levels; Se analyte	Docekalova et al. (1991)
SEM	Ir	Nonuniform distribution of modifier when deposited as solution; homogeneous distribution of the sputtered iridium (700 μg)	Rademeyer et al. (1995)
SEM	Pd	Colloid particles of Pd with diameters 2–10 nm	Volynsky and Krivan (1996)
SEM	WC coating	WC sputtered on new and exhausted pyrolytic platforms (similar morfology of the surface observed); fracturing and agglomeration at 1000 °C; softening and uniformation of the coating layer at 2800 °C	Benzo et al. (1992)

SEM; visual examination	Cu; Ni	Se as analyte; mixtures of NiO and Ni observed at 600, 900, and 1200 °C; the relative proportion of Ni increases with temperature; metallic Cu above 1200 °C; agglomeration of particles; stabilization due to selenides entrapped in the large excess of modifier; kinetically controlled release of the analyte from the molten droplets of modifier during atomization	Mahmood et al. (1995)
SIMS	Ag; Cu	Dispersed Cu species at lower concentrations while surface aggregates or microdroplets observed at higher concentration levels; silver exists as aggregates for the range of concentrations studied	Jackson et al. (1994)
SIMS	Ag, Au, Cu, Pd	Alloy formation between the analyte (In) and modifiers	Hirano et al. (1995)
TPS-SIMS	PO_4^{3-}	Cd-oxyphosphorus reactions initiated on the surface at drying stage temperatures, with further stabilizing reactions at pyrolysis temperatures; no surface reactions observed for Ag(I) and PO_4^{3-}, thus no change in appearance temperature and reduced sensitivity for Ag entailed	Hassel et al. (1991)
SSDI with CCD camera	20 µg Au; 50 µg $MgCl_2$; 200 µg $(NH_4)_2HPO_4$; 50 µg $La(NO_3)_3$; 15 µg Pd-10 µg $Mg(NO_3)_2$	Review and own experimental data; condensation of chemical modifiers and salt matrix vapors examined by imaging their spatial and temporal distributions and light scattering by microparticles; the effects of heating rate, mass, temperature, gas flow rate and orientation of sample injection hole addressed; very little light scattering observed with the 15 µg Pd-10 µg $Mg(NO_3)_2$ modifier	Hughes et al. (1996b)
TD model	Ascorbic acid; H_2, CO or CO_2 in Ar	ETAAS measurements in agreement with the gas-phase TD equilibrium model; absorbance pulse shifts in the presence of ascorbic acid are due to the production of H_2 and CO by pyrolysis of modifier; H_2 and CO are both effective in eliminating the HCl interference on Pb, likewise CO on As and Se; gaseous modifiers considered more practical than ascorbic acid	Gilchrist et al. (1990)
TD model	W	The effect of W concentration on T_{vap}, shape of absorption peaks, and analyte loss kinetics found to be in acceptable agreement with the thermodynamic model based on the regular solid solution theory	Mandjukov et al. (1992)
TD model	$(NH_4)_2Ce(NO_3)_6$	Experimental study on kinetics of Cd and Pb vaporization in the presence of Ce(IV) modifier found to be in acceptable agreement with the regular solution model; thermal stabilization may be considered as kinetic effect of slowing down analyte evaporation	Mandjukov et al. (1995)
XPS	Pd	InH_3 trapping on a Pd-treated graphite surface; oxygen associated with both In and Pd; no evidence for Pd-In bond formation	Liao and Li (1993)

(*continued*)

Appendix 2. Continued

Technique	*Modifier*	*Observations and Comments*	*Reference*
XRD	Ascorbic acid; Pd; Pd-ascorbic acid; Pd-serum	Sn as analyte; existence of Pd_3Sn_2 during ashing of Pd + blood serum; this alloy was not found when only Pd was used as modifier	Gong et al. (1993)
XRD	Eu	Atomization mechanism of Yb in the resence of Eu modifier studied	Zhang and Guo (1995)
DTG; TGA	Organic additives	Thermal decomposition of ascorbic acid, fructose and glucose studied; wetting properties of melts and changes in the composition of the gas phase discussed	Volynsky et al. (1993)
TEM; XRD	Pd	Reduction of In_2O_3 to In and formation of Pd-In intermetallic compounds during pyrolysis stage; $PdIn_3$ observed and related to the Pd-In phase diagram and crystal-lattice structures	Yasuda et al. (1996)
SEM; EDXRF	$Pd(NH_3)_4Cl_2$-$(NH_4)_2C_2O_4$	Differences in the structure of Pd deposits on the platform and inhomogeneous distribution of particles observed	Sachsenberg et al. (1993)
SEM; XRD	Pd; $ZrOCl_2$; W	Ammonium paratungstate decomposes at 250–400 °C to WO_3; WC formation up to 800 °C; only ZrC identified above 900 °C; more narrow droplet size distribution in the mixed Pd-W-citric acid modifier	Havezov et al. (1995)
ETV-ICP-MS; SEM; XRD	$PdCl_2(CH_3CN)_2$ in tributylphosphate	Organotins stabilized and sensitivity greatly increased; reaction products identified at the end of pyrolysis: $Sn_2P_2O_7$, SnP_2O_7, Pd_9P_2, PdSn, Pd_3Sn, Pd_2Sn, Pd_3Sn_2, and $PdSn_3$	Li et al. (1996a)
MAS; XPS; XRD	Mg; Pd, Pd-Mg	Ge-Pd and Ge-Mg bonds; Ge atom formation from Ge_9Pd_{23} and $GePd_2$; $MgGeO_3$ dissociation to GeO_2 and GeO	Xuan (1992b)
SEM; XPS; XRD	Pd	Stabilization of analytes (As, Pb, and Zn) due to the formation of solid solutions	Yang et al. (1992)
DTG; IR; TGA; XRD	Pd	$Pd(NH_3)_2Cl_2$ and $Pd(NH_3)_2(NO_2)_2$ decomposed to metallic Pd at temperatures above 365 and 222 °C, resp.; trace amounts of PdO also detected	Popova and Bratinova (1990)
MAS; TD	$Mg(NO_3)_2$; $(NH_4)_2HPO_4$	The use of $Mg(NO_3)_2$ and $(NH_4)_2HPO_4$ as modifiers caused reduction of the pCN and thus aided analytically by minimizing the formation of analyte carbides and increasing efficiency of analyte atomization	Ohlsson and Frech (1991)
Auger; SEM; XPS; XRD	La	La_2O_3, $La(OH)_3$ and probably La carbide identified; blisters (shells) formation on the surface of Ta probe, probably caused by lattice defects on Ta probe or $La(OH)_3$ formation owing to La_2O_3 absorbing water vapors	Deng and Gao (1994)

Auger; SEM; XPS; XRD	500 μg of Sm or La; Ta probe	$La(NO_3)_3$ first decomposed into La_2O_3; then La carbides formed at ≥ 2300 K; $Sm(NO_3)_3$ decomposed into Sm_2O_3; Sm carbides formed above 2000 K; $SmTaO_4$ formed on Ta probe	Gao and Deng (1996)
ETV-ICP-MS; Raman	Ascorbic acid	Pyrolysis of ascorbic acid studied; formation of hydrocarbons, CO and CO_2 at temperatures < 580 K; formation and release of active carbon species at 600–1100 K; formation of thermally stable amorphous carbon residues at 1000–1200 K; active carbon species produced at 1200–2400 K; alteration of the thermally stable amorphous carbon species into less well oriented pyrographite above 2500 K	Imai et al. (1995a)
ESCA; SEM; XRD	V	Solid phase reactions of V on uncoated GT; stable carbides formed during charring; free V atoms and C observed at temperatures > 2570 K	Wang and Deng (1992b)
EDXRF; radiotracers; SEM	ZrO_2; ZrO_2-Y_2O_3	Slurry vs. liquid sampling and GT lifetime studies	Schneider and Krivan (1995)
EDXRF; SEM	W-treated tubes	100 ng Ba as analyte; carbide formation; nodular deposits; exfoliation and delamellation of the pyrolytic layer; bad performance of W-treated tubes for Ba determination; W coverage is discontinuous and melting of the tungsten phase decreases the coverage and leads to destruction of the pyrocoating	Monteiro and Curtius (1995)
DSC; TGA; LD-TOF-MS	$AgNO_3$, $Cd(NO_3)_2$	Decomposition temperature for $Cd(NO_3)_2$ or $AgNO_3$ is < 130 °C; room temperature diffusion of analytes into graphite substrate; non-graphite surfaces also studied	Majidi et al. (1996)
RBS; SEM	O_2- or H_2-treated graphite surface	Pb migration into the bulk increased and decreased with O_2 and H_2 pretreatment, resp.	Eloi et al. (1995a)
MS; TD	Ascorbic acid; oxalic acid	1% m/v of organic modifier; evolution of CO and H_2 during pyrolysis; residual char from ascorbic acid at temperature > 540 K but no carbonaceous residue from oxalic acid	Byrne et al. (1993a)
IC, radiotracers	—	The decomposition and elimination of NaCl, $MgCl_2$, and $NiCl_2$ (50–200 μg) studied	Chaudhry et al. (1992)

Abbreviations

Auger: Auger Spectroscopy Secondary Ion Mass Spectrometry
CCD: Charge Coupled Device
DSC: Differential Scanning Calorimetry
DIT: Digital Imaging Technique
DTG: Differential Thermogravimetry
EDXRF: Energy Dispersive X-ray Fluorescence
ESCA: Electron Spectroscopy for Chemical Analysis

(continued)

FANES: Furnace Atomic Non-thermal Excitation Spectrometry
FAPES: Furnace Atomization Plasma Emission Spectrometry
FTIR: Fourier Transform Infrared Spectrophotometry
HR-TEM: High Resolution Transmission Electron Microscopy
IC: Ion Chromatography
IR: Infrared Spectrophotometry
LD-TOF-MS: Laser Desorption Time-of-Flight Mass Spectrometry
MAS: Molecular Absorption Spectrometry
MONES: Molecular Non-thermal Excitation Spectrometry
MS: Mass Spectrometry
Raman: Raman Spectroscopy
RBS: Rutherford Backscattering Spectroscopy
REE: Rare Earth Elements
SEM: Scanning Electron Microscopy
SIMS: Secondary Ion Mass Spectrometry
SSDI: Spectral Shadow Digital Imaging
TD: Thermodynamic Calculations and Models
TGA: Thermogravimetric Analysis
TPS-SIMS: Temperature Programmed Secondary Ion Mass Spectrometry
XPS: X-ray Photoelectron Spectroscopy
XRD: X-ray Diffraction

Appendix 3. Recent Studies And Applications Of Chemical Modification[a]

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Ag	Acidic digests	4% $(NH_4)_2HPO_4$-2% thiourea	HNO_3-HF-$HClO_4$ digests	Yang (1992b)
Ag	Aq. solutions	Ascorbic acid, Cu, Triton X-100	Mechanisms studied; E_a evaluated; kinetic orders of release discussed	Rojas (1995)
Ag	Blood, tissues, urine	4% NH_4NO_3-0.05% Triton X-100	T_{pyr} 700 °C; LOD 0.4 µg/L	Wan et al. (1991)
Ag	Coal fly ash, rock	0.62 µg Pd	T_{pyr} 700 °C; LOD 1.9 pg	Bhattacharyya (1994)
Ag	Liver, milk, plant leaves	5 µg NH_4SCN	Mo tube atomizer; T_{pyr} 500 °C; m_p 5.4 fg	Ohta et al. (1992c)
Ag	*Ostrea rivularis*	0.4% $(NH_4)_2HPO_4$-0.2% thiourea	Digests in 2% HNO_3	Li and Zhang (1993)
Ag	Seawater	$Mg(NO_3)_2$, $NH_4H_2PO_4$, $Pd(NO_3)_2$, etc.	$Mg(NO_3)_2$ preferred; T_{pyr} 800, 900, and 1100 °C; LOD 0.5–1.1 µg/L; STPF	Bermejo-Barrera et al. (1996b)
Al	Aq. solutions (acids and Cl^- added)	$Ca(NO_3)_2$, $Mg(NO_3)_2$, $Pd(NO_3)_2$, $NH_4H_2PO_4$	Multiple peaks with $Mg(NO_3)_2$ modifier, especially with aged tubes; T_{pyr} > 1700 °C; Zeeman STPF	Tang et al. (1995)
Al	Beer	$K_2Cr_2O_7$ vs. $Mg(NO_3)_2$	$K_2Cr_2O_7$ recommended	Wagner and McGarrity (1991b)
Al	Beer	$Mg(NO_3)_2$-Triton X-100	LOD 6.4 µg/L	Wagner and McGarrity (1992)
Al	Biological fluids, serum	$Mg(NO_3)_2$-Triton X-100-dil. HNO_3	1 + 5 dilution with CM solution	Winnefeld et al. (1993)
Al	Biol. RMs: cellulose, corn, egg, flour, gluten, meat, milk, starch	$Mg(NO_3)_2$	T_{pyr} 1400 °C; STPF	Motkosky and Kratochvil (1993)
Al	Bone, tissues	$NH_4H_2PO_4$	T_{pyr} 1200 °C; Zeeman STPF	Radunovic et al. (1993)
Al	Bone, soft tissues	$Ca(NO_3)_2$	HNO_3 digests; T_{pyr} 1450 °C; Zeeman STPF	Liang et al. (1991)
Al	Bone	0.1% $Ca(NO_3)_2$-1% HNO_3	Modifier added only to standard solutions; T_{pyr} 1400 °C; STPF	Tang et al. (1996)
Al	Bone, hair, tissues	$Mg(NO_3)_2$	Ca interference tolerated	Wieteska and Drzewinska (1995)
Al	Brain tissue, mussel, oyster, plant leaves	1 g/L $K_2Cr_2O_7$	T_{pyr} 1400 °C; dichromate minimizes phosphate interference	Xu et al. (1992)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Al	Cerebrospinal fluid, serum, urine	$Mg(NO_3)_2$	T_{pyr} 1400 °C	Johnson and Treble (1992)
Al	Chewing gum	0.2% $Mg(NO_3)_2$-4% H_2O_2-1% HNO_3-8% C_2H_5OH	Carbonized samples slurried in CM solution; T_{dry} 200 °C; fast program	Vinas et al. (1995c)
Al	Food and beverages: beans, bread, coffee, meat, milk, tea, etc.	$Mg(NO_3)_2$	STPF	Mueller et al. (1995)
Al	Food: egg, fish, fruit, meat, plant, vegetables, tea, etc.	50 µg $Mg(NO_3)_2$-0.3% HNO_3	HNO_3-$HClO_4$ digestion; T_{pyr} 1000 °C; LOD 0.24 ng; STPF	Wang et al. (1991)
Al	Liver, mussel, serum	6% m/v PTFE slurry	T_{pyr} 1200 °C; LOD 6 µg/L	He et al. (1994)
Al	Milk dessert	Pd-$Mg(NO_3)_2$	Slurry sampling; FI-ETAAS; T_{pyr} 800 and 1700 °C	Arruda et al. (1995a)
Al	Milk, milk shake	$Mg(NO_3)_2$, Pd, HF, H_3PO_4 compared	T_{pyr} 1500 °C; $Mg(NO_3)_2$ preferred	Arruda et al. (1994b)
Al	$NaNO_3$, $Mg(NO_3)_2$, K_2SO_4, $(NH_4)_2HPO_4$	Same as matrix	Reagents purified by Spheron-Oxine chelating resin from Al traces; T_{vap} 1200 °C	Bulska and Pyrzynska (1996)
Al	Plasma, serum	HNO_3-Triton X-100; $Mg(NO_3)_2$	Both diluents satisfactory; T_{pyr} 1400 or 1700 °C, resp.; STPF	Hewitt et al. (1990)
Al	Shellfish	10 mM $Mg(NO_3)_2$	FI microwave decomposition with 3 M HNO_3; T_{pyr} 800 and 1700 °C	Arruda et al. (1995b)
Al	Si	$Mg(NO_3)_2$	HF interference better controlled	Sako et al. (1994)
Al	Tissues	0.2% $Mg(NO_3)_2$-2% HNO_3-0.2% Triton X-100	Solid sampling; working range 0.2–100 µg/g	Nordahl et al. (1990)
Al	Water	Pd-$Mg(NO_3)_2$	T_{pyr} 1100 °C; STPF	Bermejo-Barrera et al. (1992)
As	Aq. solutions	$Pd(NO_3)_2$	Stabilization mechanisms studied by MS and ETAAS	Styris et al. (1991a)
As	Aq. solutions	15 µg Pd-10 µg $Mg(NO_3)_2$	Organarsenic species studied with fast and conventional programs; STPF	Larsen (1991)

As	Aq. solutions, urine	Various CMs compared: Co, Cu, Ni, Pd, Ni, Ni-H_2O_2, Ni-$K_2S_2O_8$, Ni-$KMnO_4$, Pd-H_2O_2, Pd-$K_2S_2O_8$, Pd-$KMnO_4$	"Effective" atomic vapor temperatures evaluated	Hirano et al. (1994a)
As	Beer	100 μg Ni-400 μg ascorbic acid	Slurry of sample ash; T_{pyr} 800 and 1400 °C; Zeeman STPF	Cervera et al. (1991)
As	Edible vegetable oils	$PdCl_2$	Sample solubilized in ethanolic 3 M KOH; T_{pyr} 1400 °C	Tao and Peng (1993)
As	FE(III) oxide pigments	25 μg Ni-0.1% Triton X-100	Slurry sampling; T_{pyr} 1400 °C; LOD 0.05 μg/g; STPF	Lopez Garcia and Hernandez Cordoba (1990)
As	Fish	50 μg Ni	HNO_3-H_2O_2 digests	Ji et al. (1992)
As	Hair	Pd-$Mg(NO_3)_2$	Solid sampling of 5-mm segments to distinguish between chronic and acute exposure to As	Koons et al. (1994)
As	H_3PO_4 (food grade)	Pd, Ni	Pd preferred; standard additions calibration	Bradshaw (1991)
As	HPLC effluents	5 mM Ni (as sulfate) present in the (phosphate) mobile phase	As(III), As(V), MMA and DMA stabilized	Gailer and Irgolic (1994)
As	HPLC effluents in CH_3OH	Pd, W and Pd-W compared	6 μg Pd-20 μg W optimal for org. As species; T_{vap} 1400–1500 °C	Slaveykova et al. (1996a)
As	Lead shotgun pellets	100 μg/mL Ni	T_{pyr} 1000 °C	Suzuki and Marumo (1993)
As	Marine tissues: fish, mussel, oyster, etc.	50 μg Ni or 15 μg Pd-10 μg $Mg(NO_3)_2$	Interlaboratory study; both modifiers acceptable; T_{pyr} 1100–1300 °C	Julshamn et al. (1996)
As	Mussel	Graphite cloth ribbon	T_{pyr} 700 °C	Iwamoto et al. (1992a)
As	Mussel	Pd-$Mg(NO_3)_2$	Slurry in 0.015% Triton X-100; T_{pyr} 480 °C (air) and 1200 °C (Ar)	Bermejo-Barrera et al. (1994b)
As	Ni-base alloys	KI vs. citric acid-hydrazine hydrate	KI (+ Ni matrix) preferred; T_{pyr} 1300 °C; STPF	Tsai and Bae (1993)
As	Oyster	Pd-citric acid	Simplex optimization study; arsenobetaine, arsenocholine and $(CH_3)_3As^+$ recovered	Pergantis et al. (1994)
As	Pb and Pb-base alloys	100 μg Ni	T_{pyr} 1100 °C; Zeeman STPF, spectral interferences study	Epstein et al. (1994)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
As	Seawater	Various CMs compared: $Pd(NO_3)_2$, Pd-$Mg(NO_3)_2$, Pd-reductant, $LaCl_3$, $ZrOCl_2$, $AgNO_3$	0.8 μg Pd-4 μg ascorbic acid preferred; T_{pyr} 1200 °C; STPF; hot injection	Bermejo-Barrera et al. (1996f)
As	Urine	25 μg Rh as $(NH_4)_3RhCl_6 \cdot 1.5\ H_2O$-1.2 mg citric acid preferred to Pd or Ni	1 + 4 dilution; T_{pyr} 1600 °C; phosphate interference better tolerated with Rh-citric acid; LOD 25 pg; LOD 6.3 ng/mL; Zeeman	Ni et al. (1996)
As	Water	Ni, Pd-$Mg(NO_3)_2$, H_2-Ar	Zeeman STPF	Eaton (1994)
Au	Ag	Ag matrix	Matrix effect studied by two-dimensional laser imaging and ETAAS	Masera et al. (1995)
Au	Aq. solutions	Ascorbic acid	T_{pyr} 700 °C; mechanisms studied	Imai and Hayashi (1992)
Au	Aq. solutions	Several components at μg levels: Au, $MgCl_2$, NaCl, $(NH_4)_2HPO_4$, $La(NO_3)_3$, Pd-$Mg(NO_3)_2$	Vapor condensation in GFAAS studied by the shadow spectral imaging technique	Hughes et al. (1996a)
Au	Aq. solutions	V	T_{pyr} 600–900 °C Zeeman STPF	Aller (1993)
Au	Aq. solutions and organic solvents	Ascorbic acid, glucose, sucrose	Mechanisms studied	Imai et al. (1995b)
Au	Aq. solutions, ores	0.1% V	T_{pyr} 600 °C; stabilization mechanisms studied	Aller (1994)
Au	Geol. RMs: minerals, rocks, ores, etc.	$Cu(NO_3)_2$	T_{pyr} 700 °C	Zeng et al. (1991)
Au	Geological samples	5 μg Pd	T_{pyr} 900 °C; STPF	Yang and Ni (1996)
Au	Milk, liver, plant leaves	10 mg/mL thiourea	Mo tube atomizer; T_{pyr} 720 °C; m_p 1.8 pg; LOD 130 ng/L	Ohta et al. (1995)
Au	Ore, silicate	0.1% V	T_{pyr} 450, 600 and 900 °C; m_o 1 pg; LOD 0.1 μg/g	Garcia-Olalla and Aller (1991)
Au	Serum, urine	Cu, Ni, Pd, Pt, Re, Rh, Ru, Re-Rh, with or without 20 μg ascorbic acid or NH_4SCN	T_{pyr} 700–1000 °C; best sensitivity with Re-Rh, Pd-ascorbic acid and Rh-ascorbic acid	Thomaidis et al. (1995a)

B	Alloys (Ni, Cu-Ni), mild steel	10 mM $Sr(NO_3)_2$-10 mM $Ni(NO_3)_2$-0.8% ascorbic acid	T_{pyr} 1400 °C; GT pretreatment with Ti-W	Matsusaki et al. (1996)
B	Aq. solutions	Ag, Pd-Mg, La, $(NH_4)_2HPO_4$, $MgCl_2$, NaCl	Review on digital imaging; thermal stabilization of B, atomization mechanisms of Al and Au, and vaporization of CMs discussed	Hughes et al. (1996b)
B	Aq. solutions	Ca-Mg, Ti-ascorbic acid, La- or W-treated GT	Best sensitivity with Ca-Mg (m_p 0.8 ng); mechanisms studied	Wiltshire et al. (1994)
B	Cobalt-base alloys	60 µg Ni-20 µg Zr	Final digests in 0.2% HNO_3 neutralized with aq. NH_3; T_{pyr} 1200 °C; Zr-treated GT	Gong et al. (1995b)
B	Drinking water	Ca, Ca-Mg, Sr-Mg	—	Yao and Jiang (1991a)
B	Fe-, Ni-, and Fe-Ni-based alloys, cast iron	Ni-Zr on Zr-treated GT	m_p 500 pg	Liu et al. (1994)
B	Plant	Ni vs. $Mg(NO_3)_2$ or $La(NO_3)_3$	Slurry sampling; totally pyrolytic GTs; Ni recommended	Barnett et al. (1991)
B	Plant leaves	Ca, La, Mg, Ni, Y; Ta- or W-treated tubes; Ta-foil	10 µg Ca (as $CaCl_2$) recommended; T_{pyr} 1350 °C; m_o 450 pg	Botelho et al. (1994)
B	Water	0.5 mg/L Ca(II)	T_{pyr} 1000 °C	Usenko and Prorok (1992)
B	Water (river, waste)	Ni, Pd, ascorbic acid, NaF; Ta-V- and Zr-treated GTs	20 µg Ni on Zr coating gives best m_p (88 pg); T_{pyr}, 900 °C	Luguera et al. (1991)
Ba	Citrus leaves	W-treated GT and N_2 alternative gas studied	Modification not recommended; wall atomization in a pyrocoated tube in Ar gives best performance	Monteiro and Curtius (1995)
Ba	Seawater, sediment porewater	Si-V	T_{pyr} 1150–1200 °C; m_o 5.6 pg; Zeeman	Bishop (1990)
Ba	Solid Ba compounds	Molybdate, molybdovanadate, vanadate	Interference by PO_4^{3-} and SiO_3^{2-} controlled	Kelemen et al. (1990)
Ba	Water	EDTA and H_2-Ar	W coil atomizer; EDTA minimizes Ca interference; LOD 2 pg; m_o, 3.6 pg	Silva et al. (1994)
Be	Biological materials, liver, water	1 mM $Mg(NO_3)_2$	Acid digests; T_{pyr} 1250 °C	Nakagawa et al. (1994)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Be	Coal fly ash, sediment, silicate, soil, urine	Pd	Digests in 0.1 M HNO_3; standardless analysis possible; T_{vap} 1100 °C; m_o 0.41 pg; STPF	Yang and Ni (1994)
Be	Sediment	$Al(NO_3)_3$	HNO_3-HF digestion; T_{pyr} 1500 °C	Luo et al. (1990)
Be	Water (drinking, waste)	$Al(NO_3)_3$	WETA tungsten atomizer; T_{pyr} 1400 °C; LOD 0.16 pg	Cernohorsky and Kotrly (1995)
Bi	Aq. solutions	12 modifiers compared: Ag, Au, Cd, Co, Fe, Mo, Pb, Pd, Pt, La, Zn	Cd and Pb enhancers; Pd depresant; Co, Mo, and Zn give rise to double peaks	Brazdes and Fazakas (1991)
Bi	Blood, serum	800 µg/mL $Rh(NO_3)_3$-0.01% Triton X-100-0.1 M HNO_3	1 + 9 dilution; T_{pyr} 750 °C; Zeeman; wall atomization	Oster (1991)
Bi	Serum, urine	$PdCl_2$-NH_4NO_3	Serum deproteinized with HNO_3; T_{dry} 95, 110 and 200 °C; T_{pyr} 1030 °C; Zeeman STPF	Dean et al. (1992)
Cd	Al_2O_3 (high purity)	$Al(NO_3)_3$ matrix; $PdCl_2$; NH_4NO_3	Sample fused with $Na_2B_4O_7$-Na_2CO_3; NH_4NO_3 recommended; T_{pyr} 1100 °C; wall atomization	Popova et al. (1993)
Cd	Aq. solutions	$(NH_4)_2HPO_4$	Fractional factorial design optimization	Araujo et al. (1995)
Cd	Aq. solutions	$(NH_4)_2SO_4$-TRIS	—	Saho et al. (1993)
Cd	Aq. solutions	1% S in CS_2	Mo tube atomizer	Ohta et al. (1990b)
Cd	Biol. RMs: oyster, plant leaves	Air alternate gas (during pyrolysis)	Pt tube atomizer; T_{pyr} 1450 °C	Ohta et al. (1991b)
Cd	Blood	HNO_3, $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, etc.	Collaborative study; deproteinization with 1 M HCl and dilution with 1 M HNO_3 recommended; T_{pyr} 300 °C	Herber et al. (1990a)
Cd	Blood	$Mg(NO_3)_2$-$(NH_4)_2HPO_4$	CM added to standards only; T_{pyr} 450 °C; platform; A_p measurements	de Benzo et al. (1990)
Cd	Blood, milk, urine	6 µg/mL Pd-500 µg/mL NH_4NO_3	T_{pyr} 700 °C; LOD 0.5 µg/L; Zeeman STPF	Smeyers-Verbeke et al. (1990)
Cd	Blood, saliva	2% HNO_3-0.1% Triton X-100 vs. 0.2% $(NH_4)_2HPO_4$-2% HNO_3	1 + 1 dilution with the former CM; T_{pyr} 350 °C STPF;	White et al. (1992)

Cd	Blood, urine	20 µg Pd, 30 µg Pd-20 µg $Mg(NO_3)_2$, 50 µg Pd-500 µg NH_4NO_3	Pd-Mg preferred; T_{pyr} 700 °C; in situ decontamination of modifier by pretreatment at 1200 °C	Moreira et al. (1995)
Cd	Cabbage, flour, fly ash, liver, rock, sediment, soil, tea	Pd, NaH_2PO_4, ascorbic acid	Ta-foil platform in a GT; T_{pyr} 1200 °C	Ma et al. (1992b)
Cd	Cabbage, flour, fly ash, liver, rock, sediment, soil	Pd-tartaric acid, Pd, ascorbic acid	Mixed modifier and W-foil platform in a GT preferred	Ma et al. (1994)
Cd	Cocoa, plant	$Pd(NO_3)_2$	Multivariate optimization	Araujo et al. (1994)
Cd	Diet, food: dairy products, fish, liver, oil, wine, water, etc.	0.2% $(NH_4)_2HPO_4$	T_{pyr} 600 °C	Lopez-Artiguez et al. (1993)
Cd	Edible oils and fats	$PdCl_2$ preferred to lecithin, Nb, org. Pd compounds, Pd-$Mg(NO_3)_2$ and Nb coating	T_{pyr} 750 °C; m_o 0.9 pg; LOD 0.4 ng/g; STPF	van Dalen (1996)
Cd	Feed, crops, food, fruit, plant, vegetables	Mo-treated platform	HNO_3-V_2O_5 digestion; T_{pyr} 450 °C; STPF	Cabrera et al. (1992)
Cd	Flour	5 µg Pd	Slurry in 0. 1% Triton X-100; T_{pyr} 500 °C (O_2) and 700 °C (Ar); LOD 0.28 ng/g	Shiowatana and Siripinyanond (1996)
Cd	Food: fish, liver, milk, plant	800 µg/mL Pd, $MH_4H_2PO_4$ Pd-$Mg(NO_3)_2$, $NH_4H_2PO_4$-$Mg(NO_3)_2$	Slurry sampling; Pd preferred; T_{pyr} 750 °C; Zeeman STPF; LOD 10 ng/g	Lynch and Littlejohn (1990)
Cd	Hair, milk, mussel, plant	Pd, $(NH_4)_2HPO_4$	Slurry in 1 M HNO_3; T_{pyr} 550 °C	Stupar and Dolinsek (1996)
Cd	Hair, sargasso	Triethyl phosphite, triethyl phosphate, trimethyl phosphite; $NH_4H_2PO_4$	T_{vap} 950 °C, 700 °C; the first gaseous modifier preferred due to lower blanks	Ebdon et al. (1992)
Cd	H_3PO_4	H_3PO_4 matrix (1 + 4 dilution)	T_{pyr} 350 °C; LOD 3 pg or 1 µg/L	Wifladt et al. (1992)
Cd	Kidney, mussel, sewage sludge	Various CMs compared: $(NH_4)_2HPO_4$, Pd, Ni, thiourea, Triton X-100	5–250 µg Ni preferred; T_{pyr} 600 °C	Chakraborty et al. (1996)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cd	Liver, oyster, plant	Sulfur	Slurry sampling; Mo tube atomizer	Ohta et al. (1990a)
Cd	Marine sediments, silicate rocks	5 μg Pd	Total contents and extracted fractions; STPF	Mazzucotelli et al. (1991)
Cd	Plant	0.2% $(NH_4)_2HPO_4$-0.02% $Mg(NO_3)_2$	Bomb microwave digestion; T_{pyr} 650 °C	Jackson and Alloway (1990)
Cd	Plant	50 μg $NH_4H_2PO_4$-1 μg $Mg(NO_3)_2$-2 μg $AlCl_3$-5% butanol	Final digests in 0.2 M HNO_3; T_{pyr} 950 °C; butanol improves platform wetting	Temminghoff (1990)
Cd	Seawater	$(NH_4)_2HPO_4$	Zeeman STPF; multiple injections	Chuang and Huang (1994)
Cd	Seawater	800 μg NaOH	T_{pyr} 1400 °C; LOD 15 ng/L	Lan (1993)
Cd	Seawater	Oxalic, citric, lactic, ascorbic acids, EDTA, H_3PO_4, HNO_3, etc.	Oxalic acid recommended; low-temperature atomization promoted; m_o 23 pg; LOD 3 ng/L with multiple injections; Zeeman; wall atomization	Cabon and Le Bihan (1992)
Cd	Sediments	40 μg Pd (as $PdCl_2$)	T_{pyr} 800 °C	Millward and Kluckner (1991)
Cd	Serum	15 μg Pd-10 μg $Mg(NO_3)_2$	Cd removed from preinjected CM at 1100 °C; T_{pyr} 550 °C (air), then 800 °C (Ar)	Bulska et al. (1990)
Cd	Soil	50 μg $NH_4H_2PO_4$	Slurry sampling; T_{pyr} 800 °C	Deng and Li (1992)
Cd	Soil	Various CMs compared: 0.6% HNO_3, 5 μg $NH_4H_2PO_4$, 30 μg $Mg(NO_3)_2$, 200 μg $NH_4H_2PO_4$-10 μg $Mg(NO_3)_2$	5 μg $NH_4H_2PO_4$ preferred (T_{pyr} 750 °C); STPF	Carlosena et al. (1996)
Cd	Soil	$(NH_4)_2SO_4$	HNO_3-HCl-$HClO_4$ digests	Shou and Shao (1990)
Cd	Urine	30 mM HNO_3	Preferred to other inorganic and organic additives	Komarek et al. (1991a)
Cd	Urine	$(NH_4)_2HPO_4$	1% HNO_3 medium	Hao et al. (1991)
Cd	Urine	2% HNO_3, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, NH_4NO_3, etc.	Collaborative study; 2% v/v HNO_3 recommended; T_{pyr} 450 °C	Herber et al. (1990b)

Co	Aq. solutions	10 μg $Mg(NO_3)_2$, 5 μg Pd-15 μg $Mg(NO_3)_2$, 200 μg $NH_4H_2PO_4$-10 μg $Mg(NO_3)_2$	Transverse heated graphite atomizer with end-capped tubes studied	Frech and L'vov (1993)
Co	Blood	50 μg $Mg(NO_3)_2$	Fl-on-line microwave digestion; T_{pyr}, 1400 °C; T_{vap} 1450 °C	Burguera et al. (1995b)
Co	Blood	Pd	ETAAS vs. ICP-MS and voltammetry; ICP-MS preferred	Godlewska et al. (1994)
Co	Liver	$Mg(NO_3)_2$, $Pd(NO_3)_2$	$HClO_4$ digests; modifiers not recommended due to overcompensation errors with deuterium background correction; STPF	Campos and Moraes (1993)
Co	Plant, forage	50 μg NH_4VO_3-100 μg NH_4NO_3-50% C_2H_5OH	T_{pyr} 1300 °C; solid sampling	Ma and Wang (1992)
Co	Serum	10 μg $Pd(NO_3)_2$	T_{pyr} 1300 °C; LOD 0.7 μg/L; STPF	Perez Parajon and Sanz-Medel (1993)
Co	Serum	$Pd(NO_3)_2$, $MgHPO_4$, $Ca(NO_3)_2$, $Mg(NO_3)_2$	Pd preferred	Bulska et al. (1991)
Cr	Aq. solutions (mineral acids present)	W- or Zr-treated GTs	T_{pyr} 900 °C; LODs 0.45 and 0.48 μg/L, resp.	Pyrzynska (1995a)
Cr	Biological materials, food	$Mg(NO_3)_2$	Dry ashed samples; STPF	Miller-Ihli and Greene (1992)
Cr	Cocaine, heroin	$Mg(NO_3)_2$ vs. HNO_3, Pd, Pd-$Mg(NO_3)_2$	Samples in dil. HNO_3; $Mg(NO_3)_2$ provides lower LODs (5.77 ng/g); T_{pyr} 1600 °C; STPF	Bermejo-Barrera et al. (1996c)
Cr	Geological RMs, sediment	EDTA (NH_4^+-salt)	—	Zheng and Su (1993)
Cr	Infant formula, milk	0.5% $Mg(NO_3)_2$-0.2% Triton X-100-0.2% HNO_3	1 + 1 dilution with CM solution	Cocho et al. (1992)
Cr	Milk	0.5 M EDTA (NH_4^+-salt)	La-treated GT	Tan and Liu (1991)
Cr	Plant, sediment	$NaVO_3$, $Mg(NO_3)_2$ and $Pd(NO_3)_2$ compared	$NaVO_3$ preferred	Chakraborty et al. (1995)
Cr	Rain water, serum	20 μg $Mg(NO_3)_2$, 1 μg Rh, 1 μg Pt, etc.	T_{pyr} 1100–1400 °C; many other modifiers tested; m_o 2.8–3.2 pg	Thomaidis et al. (1996)
Cr	Seawater	Ascorbic acid, $(NH_4)_3$ citrate	—	Yang et al. (1991)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cr	Seawater, serum, urine	5 mg/mL $Ca(NO_3)_2$-$Mg(NO_3)_2$	T_{vap} 1550 °C	Gong and Liu (1990)
Cr	Serum, urine, water	$Mg(NO_3)_2$-$Ca(NO_3)_2$	Wall, platform and probe atomization compared; T_{pyr} 1400 °C	Alvarez-Cabal Cimadevilla et al. (1994)
Cr	Serum, water	20 µg V; 20 µg V-20 µg Mo	Improved lifetime of atomizer	Manzoori and Saleemi (1994)
Cr	Urine	2% HNO_3-0.001% Triton X-100	T_{pyr} 800 °C; LOD 0.5 µg/L	Paschal and Bailey (1991)
Cr	Water (coastal, estuarine, sea)	100 µg $Mg(NO_3)_2$; 2.5 µg Na_2WO_4	Better LODs with $Mg(NO_3)_2$	Apte et al. (1991)
Cu	Aq. solutions	Mo, Pd, W; Mo- and W-treated platforms	Kinetics of atomization studied; T_{pyr} 1300, 1400, 1300, 1400, and 1300 °C, resp.; STPF	Alvarez et al. (1996)
Cu	Cataractous human lenses	$NH_4H_2PO_4$	HNO_3 digests	Giordano et al. (1992a)
Cu	Cocaine, heroin	Pd-$Mg(NO_3)_2$	Dilute HNO3 medium	Bermejo-Barrera et al. (1995d)
Cu	Glass	0.5 mg NH_4F	Slurry (30 mg per 5 mL of 10% glycerol); T_{pyr} 700 °C	Morita et al. (1993)
Cu	Liver biopsies	Pd-$Mg(NO_3)_2$-0.2% Triton X-100	Solid sampling; "cup-in-tube"	Aadland et al. (1990)
Cu	Plant, sediment, soil	NH_4NO_3-10% HNO_3 (for plant)	Solid sampling; T_{pyr} 1100 °C	Ma et al. (1992a)
Cu	Plasma, serum	1% $NH_4H_2PO_4$-0.6% $Mg(NO_3)_2$-0.4% Triton X-100 vs. Pd-$Mg(NO_3)_2$	50-fold dilution with CM solution; PO_4^{3-} modifier preferred; T_{pyr} 900 °C; Zeeman STPF	Lapointe and LeBlanc (1996)
Cu	Seawater	700 µg NH_4NO_3	T_{pyr} 1500 °C; LOD 0.07 µg/L; 5 × 20 µL multiple injections; Zeeman STPF	Huang and Shih (1993)
Cu	Skim milk	15 µg Pd-10 µg Mg (as nitrates)	T_{pyr} 1000 °C; LOD 0.47 µg/L; Zeeman STPF	de la Fuente et al. (1995)
Dy	Serum	CMs tested: Eu, Gd, Ho, La, Lu, Pd, Rh, Th, Tm, W, Yb; Ta-foil; W-foil; CHF_3 (Freon 23)	10 µg Gd recommended; LOD 11 pg or 1.1 µg/L; m_o 18 pg	Knutsen et al. (1995)

Eu	Aluminate type luminophors	La	m_p 19 vs. 41 pg in the presence of La with W atomizer (WETA); T_{pyr} 1200 °C; T_{at} 2600 °C; no effect of La in pyrocoated GT but similar enhancement with Ta-coil lined GT	Komarek and Ganoczy (1991)
Eu	Aq. solutions	HNO_3	Background decreased	Lin et al. (1993c)
Fe	Fish, liver, SeS	20 μg Ni, 50 μg $Mg(NO_3)_2$	Ni recommended; T_{pyr} 1450 °C	Peramaki (1991)
Ga	Al_2O_3 (corundum)	Al_2O_3 matrix	Solid sampling; wall vs. platform atomization; T_{pyr} 800 °C	Marecek and Synek (1990)
Ga	Aq. solutions	Ascorbic acid	T_{pyr} 600 °C; STPF; non-resonance lines examined	Botha and Fazakas (1993)
Ga	Aq. solutions	Ascorbic acid, O_2, sucrose	Atomization mechanisms studied; T_{pyr} 900 °C	Imai et al. (1994)
Ga	Aq. solutions	Nitrates of Al, Ca, Co, Cu, K, Mg, Na, Ni; EDTA	50 mM $(NH_4)_4$EDTA-20 mM $Ni(NO_3)_2$-l mM $Al(NO_3)_3$	Matsusaki and Izuchi (1991)
Ga	Aqueous and $CHCl_3$ solutions	Ascorbic acid, citric acid, glycerol, oxalic acid, polyethylene glycol, various monosaccharides	Ascorbic acid and fructose most effective	Volynsky et al. (1992)
Ga	Coal, coal fly ash	Al, Co, Mg, and Ni (as nitrates), $PdCl_2$, $(NH_4)_4Mo_7O_{24}$	Slurry in 20% C_2H_5OH; Ni recommended; T_{vap} 1200 °C	Shan et al. (1992b)
Ga	Complex samples	$Ni(NO_3)_2$	STPF with uncoated platform	Zhou et al. (1993)
Ga	Environmental samples	Cu-V	Ta-foil lined GT	Yao et al. (1991)
Ge	Aq. solutions	Pd, $Mg(NO_3)_2$	T_{pyr} 1000 °C (Mg), 1400 °C (Pd)	Xuan (1992b)
Ge	Aq. solutions	Aq. HNO_3, $HClO_4$, KOH, NaOH; W- or Zr-treated GTs; 20% CO-N_2	Premature volatization of GeO prevented; T_{pyr} 900 °C	Zheng and Zhang (1992)
Ge	Aq. solutions	Pd, 1% HNO_3, 1% H_2SO_4, NaOH	Analyte loss/atomization mechanisms studied by ETAAS, MS and thermodynamic calculations	Doidge and McAllister (1993)
Ge	Biological fluids (plasma)	0.5% Ca-0.25% Triton X-100-1% HNO_3	1 + 3 dilution with CM solution; T_{pyr} 1000 °C; LOD 1.7 ng	Guo et al. (1993)
Ge	Chloride and sulfate matrices	Nitrates of Al, Co, Cu, Mg, Na, Ni; EDTA, CH_3COONH_4, ascorbic acid, etc.	10 mM $Co(NO_3)_2$-20 mM $Al(NO_3)_3$-0.2 M HNO_3 recommended; T_{pyr} 870 °C; 0.2 M CH_3COONH_4 added for Cl^- matrixes; 0.1 M ascorbic acid added for SO_4^{2-} matrices	Matsusaki et al. (1994)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Ge	Coal fly ash, org. Ge compounds	$Ca(NO_3)_2$	—	Yao and Jiang (1990)
Ge	Food	Pd	—	Liang and Huang (1992)
Ge	Garlic, ginseng	30 µg $Pd(NO_3)_2$-10 µg $Mg(NO_3)_2$	T_{pyr} 1200 °C	Schleich and Henze (1990)
Ge	Herbal medicine, ginseng, jiaogulan, tea	$Ni(NO_3)_2$	HNO_3-HF digests	Lin et al. (1991)
Ge	NaCl, Zn plant slag	Various CMs compared: NH_4NO_3, $Ni(ClO_4)_2$, $Ni(NO_3)_2$, $Zn(ClO_4)_2$, $Zn(NO_3)_2$ at 0.25 µmol levels	T_{vap} 1000 °C; up to 300 µg NaCl tolerated; uncoated tubes	Anwari et al. (1996)
Ge	Serum	Ca, La, Mg, Mg-Pd, Ni, Pd, Pt, org. acids, EDTA, thiourea, HNO_3, H_3PO_4 tested	1 + 4 dilution with 0.1 M La(III) recommended; T_{pyr} 1200 °C; LOD 133 pg	Xu et al. (1995)
Hg	Aquatic plant, coal fly ash, fish, sediment	15 µg Pd	T_{vap} 400 °C; T_{at} 1000 °C; m_o 0.1 ng	Welz et al. (1992b)
Hg	Cabbage, fish, pine needles, sediment, spinach	Thioacetamide, $PdCl_2$, $(NH_4)_2Ce(NO_3)_6$	HNO_3 digests vs. slurry sampling; T_{vap} up to 400 °C; T_{pyr} 220–240 °C	Karadjova et al. (1995)
Hg	Drinking water	TeO_2-HCl	—	Ferng et al. (1991)
Hg	Marine sediment	15 µg/mL Pd	Slurry sampling; T_{pyr} 200 °C	Bermejo-Barrera et al. (1994d)
Hg	Phosphors from fluorescent lamp cullet	1 µg Pd as $Pd(NO_3)_2$	Slurry in 0.05% HNO_3; T_{dry} 105 °C, T_{pyr} 200 °C; LOD 24 ng/g	Dobrowolski and Mierzwa (1996)
Hg	Soil	Au, Ir, Pd, Rh, Au-Rh, electroplated Pd or Rh	Pd or Au-Rh can serve as permanent modifiers; m_o 80–220 pg; Zeeman STPF	Bulska et al. (1996)
Hg	Soil	Pd	Zeeman STPF vs. CVAAS	Bulska et al. (1995)

Hg	Urine	Pd-dil. HNO_3	Zeeman	Zhou and She (1992)
In	Aq. solutions (Cl^- added)	50 mM $(NH_4)_2EDTA$-4 mM $Ni(NO_3)_2$-0.3 M NH_3-1 mM $Al(NO_3)_3$	Sensitivity (20 ×) and tolerance to Cl^- (400–1000 ×) improved	Matsusaki (1990)
In	Geol. samples, rock, sediment	Pd-$(NH_4)_2EDTA$	V-shaped boat preferred to wall or platform atomization	Zheng and Su (1994)
In	Urine	20 µg Pd as $PdCl_2$	T_{pyr} 1200 °C; uncoated GT; Zeeman	Bertram and Mueller (1991)
In	Aq. solutions	Ascorbic acid, sucrose	T_{pyr} 800 °C	Imai et al. (1996b)
In	Aq. solutions	Pd	Stabilization mechanisms studied	Yasuda et al. (1995)
In	Aq. solutions	Pd-ascorbic acid-Triton X-100	Stabilization mechanisms studied	Yasuda et al. (1996)
In	Aq. solutions	2 µg Pd; Zr-treated GT	Kinetics of atomization studied; Pd pretreated at 900 °C	Yan et al. (1993a)
In	Aq. solutions	Pd-$(NH_4)_4EDTA$	Atomization efficiency improved	Zheng (1994)
In	Aq. solutions	Zr-treated or W-treated GT; O_2 or CO additives	Atomization mechanism study; E_a evaluated	Imai et al. (1996a)
K	Biol. RMs: mollusc, plant, tissue	Thiourea	HNO_3-H_2O_2 digestion; Mo-tube atomizer; LOD 0.12 ng in a 1 µL aliquot	Ohta et al. (1993)
Li	Erythrocytes	0.2 M K_2HPO_4-1 % Triton X-100	LOD 50 pg; wall atomization	Yang et al. (1995)
Li	Renal tubular fluid, plasma	Ta-foil platform	Matrix-matched standards; T_{pyr} 400 and 800 °C; LOD 45 nmol/L	Boer et al. (1993)
Mn	Aq. solutions	800 µg/mL Ca^{2+}-0.5 M H_3PO_4-0.5 M HNO_3	T_{pyr} 1100 °C; STPF vs. wall atomization	Hulanicki et al. (1990)
Mn	Aq. solutions (Cl^- added)	HNO_3	Interferences by chlorides of Ba, Ca, Mg, Sr eliminated	Zu and Li (1993)
Mn	Aq. solutions ($MgCl_2$ added)	Ascorbic acid	$MgCl_2$ interference studied by ETAAS and ETV-ICP-MS. Ascorbic acid prevents the loss of Mn at T_{pyr} > 700 °C	Byrne et al. (1992)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Mn	Liver, milk, plant	10 μg thiourea; H_2-Ar purge gas	Mo-tube atomizer; T_{vap} 1000 °C	Ohta et al. (1992b)
Mn	Milk powder	Pd-$Mg(NO_3)_2$	Digests in 0.8 M HNO_3; T_{pyr} 1200 °C; Zeeman STPF	Koops and Westerbeek (1993)
Mn	Seawater	NaOH	T_{pyr} 1400 °C	Lan and Alfassi (1994)
Mn	Serum	0.2% $Mg(NO_3)_2$	1 + 1 dilution with modifier solution	Ronchi et al. (1991a)
Mn	Silicate rock	40 μg Ni vs. 19 μg Mg and 18 μg Pd	Na_2CO_3-H_3BO_3 fusion; Ni recommended; T_{pyr} 1000 °C; Zeeman STPF	Koshino and Narukawa (1993a)
Mn	Total diet, total parenteral nutrition	5% ascorbic acid	Bomb decomposition; T_{pyr} 1000 °C; LOD 0.04 μg/L	Stobbaerts et al. (1992)
Mn	Urine	0.2% $Mg(NO_3)_2$	1 + 1 dilution with modifier solution	Ronchi et al. (1991b)
Mo	Hair, serum	CaF_2	—	Gao and Li (1995)
Mo	Infant formula, milk	0.005% BaF_2-octanol	LOD 0.89 μg/L	Bermejo-Barrera et al. (1990c)
Mo	Liver	BaF_2 on a La-treated platform	T_{pyr} 1800 °C	Zeng (1993)
Mo	Milk	0.3% HNO_3; 0.005% BaF_2	T_{pyr} 600 and 1700 °C; LOD 0.89 μg/L with BaF_2	Bermejo-Barrera et al. (1990b)
Mo	Rice	$CaCl_2$ on a La-treated GT	SO_4^{2-} interference eliminated	Yang (1992a)
Mo	Serum	$Mg(NO_3)_2$, BaF_2, HNO_3, Pd-$Mg(NO_3)_2$ and Pd-NH_2OH·HCl	T_{pyr} 600 and 1700 °C; m_o 18, 22, 17, 12 and 13 pg, resp.	Bermejo-Barrera et al. (1991)
Mo	Serum	0.005% $Mg(NO_3)_2$-0.05% Triton X-100	T_{pyr} 600 and 1900 °C	Pita-Calvo et al. (1992)

Mo	Urine	BaF_2, Pd-$Mg(NO_3)_2$, Pd-NH_2OH·HCl, HNO_3 and $Mg(NO_3)_2$ compared	Pd-$Mg(NO_3)_2$ selected	Pita-Calvo et al. (1995)
Mo	Water	Pd-$Mg(NO_3)_2$, Pd-NH_2OH·HCl	T_{pyr} 600 and 1800 °C	Beceiro-Gonzalez et al. (1992)
Ni	Cocaine, heroin	$Mg(NO_3)_2$, HNO_3, Pd, Pd-$Mg(NO_3)_2$	$Mg(NO_3)_2$ preferred; T_{pyr} 1600 °C	Bermejo-Barrera et al. (1995e)
Ni	Serum	NH_4VO_3 on Mo-coated GT, La	Samples from cancer patients	Sun et al. (1994)
P	Aq. solutions	Zr	Mechanisms studied	Kubota et al. (1992)
P	Aqueous and organic solutions	Pd	Mechanisms studied	Kutseva et al. (1993a)
P	Liver, plant	HF, NaF, NH_4F, Pd, KF, CsF	NaF recommended; T_{pyr} 1350 °C	Alvarado et al. (1995)
P	Mussel, tea leaves	Pd-Ca	T_{pyr} 1600 °C	Yao and Ji (1992)
P	Mussel, tea leaves	1.5 mg/mL Pd-0.2 mg/mL Ca	Digests in 0.2% HNO_3	Yao and Yang (1992)
P	Water	Mo	Review on ETAAS methods for P determination	Kutseva et al. (1993b)
Pb	Air filters	200 µg $NH_4H_2PO_4$-70 µg $Mg(NO_3)_2·6H_2O$-1% HNO_3	HNO_3-$HClO_4$ digestion; final solutions in 1% HNO_3; T_{pyr} 900 °C; LOD 0.03 µg/m^3	Kalaidjieva (1995)
Pb	Air particulate matter	1.5 µg $NH_4H_2PO_4$	Bomb HNO_3 digestion; T_{pyr} 700 °C; STPF	Chernyakhovskiy et al. (1994)
Pb	Aq. solutions	200 µg ascorbic acid	T_{pyr} 700 °C; mechanisms studied	Imai and Hayashi (1991)
Pb	Aq. solutions	Ascorbic acid, oxalic acid, 1% HNO_3	Gas-phase reaction mechanism proposed	Byrne et al. (1993a)
Pb	Aq. solutions	H_2-Ar purge gas	Mechanisms studied; H_2 reduces Cl^- interference	Gilchrist et al. (1993)
Pb	Aq. solutions	K, Mg, Ni, Pd, Pt, Ti, Y	"Effective vapor temperature" increased in the presence of CMs	Terui et al. (1991b)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Pb	Aq. solutions	$Mg(NO_3)_2$, $MgCl_2$, $Cr(NO_3)_3$, $CrCl_3$, $(NH_4)_2CrO_4$, $K_2Cr_2O_7$	Mechanisms studied; E_a evaluated; T_{app} up to 1400 K	Imai et al. (1991b)
Pb	Aq. solutions	O_2-treated pyrolytic platform	Effect of O_2 and H_2 studied	Eloi et al. (1995a)
Pb	Aq. solutions (Cl^- added)	Pd	Effect of cations and acids studied	Pszonicki and Essed (1993a)
Pb	Aq. solutions	Pd	"Overstabilization" effects on Pb observed	Dabeka (1992)
Pb	Aq. solutions	300 µg/L Pd $(NO_3)_2$ vs. 0.1% $Mg(NO_3)_2$, $NH_4H_2PO_4$, and HNO_3	Three different atomizers compared for absolute analysis; Pd on graphite surface recommended; Ta platform also useful	Fagioli et al. (1991)
Pb	Aq. solutions	Pd-$Mg(NO_3)_2$	T_{vap} 1100 °C	Pszonicki and Essed (1993b)
Pb	Aq. solutions	W	Modifier mass varied within broad interval	Mandjukov et al. (1992)
Pb	Beer	$NH_4H_2PO_4$	Zeeman STPF; LOD 0.87 µg/L	Wagner (1995)
Pb	Beverages	$NH_4H_2PO_4$	LOD 0.82 µg/L	Yuan and Yang (1990)
Pb	Blood	10 mM $Mg(NO_3)_2$-150 mM $NH_4H_2PO_4$-20 mM HNO_3	T_{pyr} 700 °C; composite diluent containing also $Mg(NO_3)_2$, oxalic acid, Triton X-100, and antifoam agent; STPF	Iikov (1996)
Pb	Blood	$(NH_4)_2HPO_4$	Zeeman STPF	Schumacher et al. (1993)
Pb	Blood	$(NH_4)_2HPO_4$-$PdCl_2$	—	Yoo and Kwon (1992)
Pb	Blood	0.2% $NH_4H_2PO_4$-0.1% Triton X-100	1 + 9 dilution; T_{pyr} 700 °C; STPF	Bosnak et al. (1993)
Pb	Blood	$NH_4H_2PO_4$-$Mg(NO_3)_2$	1 + 9 dilution with 0.1% Triton X-100	Heron (1991)

Pb	Blood	5 μL of 70 mM $NH_4H_2PO_4$-0.16 M HNO_3	Triton X-100 and antifoam agent added	Jacobson et al. (1991)
Pb	Blood	1.25% $(NH_4)_2HPO_4$-0.5% Triton X-100; 10 μg/mL Pd-0.1% HNO_3-0.1% Triton X-100	Dried blood spot (on filter paper) extracted with CM solution; T_{pyr} 800 °C; Zeeman STPF	Wang and Demshar (1992)
Pb	Blood	0.2% $NH_4H_2PO_4$-0.5% Triton X-100-0.2% HNO_3	T_{pyr} 700 °C; hot injection; Zeeman STPF	Parsons and Slavin (1993)
Pb	Blood	0.2% $NH_4H_2PO_4$-0.5% Triton X-100-0.2% HNO_3	Low-cost W filament atomizer; 1 + 9 dilution with CM solution	Parsons et al. (1995)
Pb	Blood	1% $Ni(NO_3)_2$-0.5 M HNO_3	After protein precipitation	Sato and Nomoto (1990)
Pb	Blood	20 ng Pd-200 μg citric acid-10 mM HNO_3	T_{pyr} 800 °C (O_2) and 1100 °C (Ar); m_o 15 pg	Granadillo et al. (1991a)
Pb	Blood	Various	Review	Mi (1990)
Pb	Blood, chlorella, sargasso, sediment, serum, tea leaves, vehicle exhaust particulates	0.5 μg/mL Pd-2% citric acid; 0.3% $NH_4H_2PO_4$-0.3% $Mg(NO_3)_2$-8% citric acid	T_{pyr} 600 and 800 °C, resp.; LOD 0.1 μg/L; m_o 10 pg; STPF	Granadillo and Romero (1993a)
Pb	Blood, saliva, sweat, urine	0.1% Triton X-100-0.11% $NH_4H_2PO_4$	Blood diluted 1 + 9 with CM solution; T_{pyr} 650 °C; standard additions for other biological fluids	Omokhodion and Crockford (1991)
Pb	Blood, serum	$Cr(NO_3)_3$ vs. $Pd(NO_3)_2$ or $NH_4H_2PO_4$	Advantages of Cr: lower LODs, RSD and background; better sensitivity	Imai et al. (1990)
Pb	Bone	$NH_4H_2PO_4$	Overcompensation problems (due to PO) with the longitudinal Zeeman STPF	Zong et al. (1994)
Pb	Bone	20 μg $NH_4H_2PO_4$-2 μg Ca (as nitrate); 20 μg $NH_4H_2PO_4$-2 μg Mg (as nitrate)	Bomb HNO_3 digestion; T_{pyr} 900 °C; T_{at} 1600 °C; LOD 0.6 μg/g; Zeeman STPF	Zong et al. (1996)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Pb	Cheese, milk	$NH_4H_2PO_4$-$Mg(NO_3)_2$	Dry ashing at 460 °C, then HNO_3 treatment	Zurera-Cosano et al. (1994)
Pb	Cola beverages	La(III)-1% HNO_3	T_{pyr} 400 °C; LOD 9.8 μ/L; wall atomization	Barbera et al. (1992)
Pb	Copper alloy	Cu matrix	Multiple peaks at reduced pressure (0.1 torr) in solid sampling-ETAAS attributed to spatial distribution of Pb	Wang and Holcombe (1994)
Pb	Egg	0.1% $Mg(NO_3)_2$-2% $NH_4H_2PO_4$	Digests in 0.1 M HNO_3 diluted 1 + 1 with CM solution; T_{pyr} 900 °C; Zeeman STPF	Hong (1991)
Pb	Fish	$Bi(NO_3)_3$ vs. $Pd(NO_3)_2$ and $Mg(NO_3)_2$-$NH_4H_2PO_4$	Bi preferred	Chakraborty et al. (1993a)
Pb	Flour (rice, wheat)	$NH_4H_2PO_4$	Slurry sampling	Zhou et al. (1992)
Pb	Food: flour, milk, plant, meat, etc.	0.1% Pd vs. PO_4^{3-}	Pd preferred; m_p 3–8 pg	Tahvonen and Kumpulainen (1994b)
Pb	Fructose, sucrose, sugar syrups	60 μg $Mg(NO_3)_2$	Ashing in air at 750 °C; LOD 0.9 ng/g; STPF	Miller-Ihli and Greene (1993)
Pb	GaAs	NH_4Cl-$CrCl_3$	Samples dissolved in HCl-Br_2;T_{pyr} 600 °C; LOD 5 ng/g	Beinrohr et al. (1991)
Pb	Grapes, plant leaves, lees, musts, rapes, soil	10 μL of 6% H_3PO_4	Microwave vs. dry ashing; T_{pyr} 900 °C	Teissedre et al. (1993)
Pb	Hair	0.4 μg Pd-0.5 μg $Mg(NO_3)_2$	Slurry in 0.4% glycerol; T_{vap} 1100 and 1300 °C for hair slurry and aq. standards, resp.; STPF	Bermejo-Barrera et al. (1996e)
Pb	Illicit drugs	Pd preferred to Pd-$Mg(NO_3)_2$	T_{pyr} 1000 °C	Bermejo-Barrera et al. (1995c)

Pb	Liver, oyster	$NH_4H_2PO_4$	Solid (microboat) sampling; T_{pyr} 950 °C	Liu et al. (1990)
Pb	Marine sediments	Pd-$Mg(NO_3)_2$	Slurry sampling; T_{pyr} 480 and 900 °C	Bermejo-Barrera et al. (1994a)
Pb	Milk	0.02% $Mg(NO_3)_2 \cdot 6H_2O$	Probe atomization	Watling and Haines (1990)
Pb	Mussel	Pd-$Mg(NO_3)_2$	Slurry sampling	Bermejo-Barrera et al. (1993a)
Pb	Ni alloys, steel	6% $NH_4H_2PO_4$-1% Ni(II)	Samples dissolved in HF-HNO_3-H_2O (1 + 1 + 1 or 3 + 1 + 1); T_{pyr} 950 °C; LOD 0.1 µg/g Zeeman STPF	Mile et al. (1992)
Pb	Paprika	0.1% $NH_4H_2PO_4$-0.1% Triton X-100	Carbonization at 350 °C; powdered residue slurried; T_{pyr} 1000 °C; LOD 0.2 µg/g; STPF	Hernandez-Cordoba and Lopez Garcia (1991)
Pb	Pb binding protein in erythrocytes	2% $NH_4H_2PO_4$-1% HNO_3	Pb haem saturation method	Vasikaran et al. (1992)
Pb	Plants (aquatic and terrestrial)	15–30 µg $NH_4H_2PO_4$	Slurry sampling; Viscalex, antifoam and aq. NH_3 added; T_{pyr} 400 °C; LOD 0.4 µg/g	Yu et al. (1990)
Pb	Rice	20 µg $Mg(NO_3)_2$-400 µg $NH_4H_2PO_4$	Zeeman STPF; T_{pyr} 900 °C	Ji and Ren (1995)
Pb	River water	$Co(NO_3)_2$-$NH_4H_2PO_4$	—	Shirasaki et al. (1994)
Pb	Sulfur	Sulfur matrix; air alternate gas during pyrolysis	Solid sampling; T_{pyr} 850 °C (stepwise heating); Zeeman STPF	Koshino and Narukawa (1994)
Pb	Salt matrices: NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgSO_4$, $CaSO_4$	5 µg Pd-0.5 µg Mg	Matrix effects studied by IC and ETAAS (STPF)	Cabon and Le Bihan (1996a)
Pb	Seawater	0.07 M oxalic acid; Pd-$Mg(NO_3)_2$-0.1 M HNO_3	Low-temperature atomization and thermal stabilization of Pb with the first and the second modifier, resp.; LODs 0.3–0.5 µg/L; Zeeman STPF	Cabon and Le Bihan (1996b)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Pb	Seawater	Pd-Sr$(NO_3)_2$; Pd-Mg$(NO_3)_2$; Pd; La$(NO_3)_3$	SO_4^{2-} interference better tolerated with Pd-Sr; T_{pyr} 1100 °C	He and Ni (1996)
Pb	Sediment, soil	4 μg Pd-20 μg W	HNO_3-HF or HNO_3-$HClO_4$ digests	Slaveykova et al. (1992)
Pb	Serum	0.2% Cr-0.1 M HNO_3-1% Triton X-100	1 + 1 dilution with modifier solution; T_{pyr} 530 °C	Imai et al. (1991c)
Pb	Soil	Pd-Mg$(NO_3)_2$	Slurry sampling; T_{pyr} 900 °C	Hinds and Jackson (1990)
Pb	Soil	Pd-Mg$(NO_3)_2$, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$	Slurry sampling; determination without CM recommended; fast program; STPF	Hinds et al. (1991)
Pb	Sugar	Mg$(NO_3)_2$	Ashing in air; STPF	Miller-Ihli (1995)
Pb	Sugar, syrups	Mg$(NO_3)_2$	HNO_3-H_2O_2 digestion; ashing in air; LOD 10 pg or 3.3 ng/g; STPF	Miller-Ihli (1994)
Pb	Urine	Pd-Mg$(NO_3)_2$	Probe atomization; no modifier required	Marchante-Gayon et al. (1993)
Pb	Water (lake, tap)	Ni-NH_4-tartrate vs. NH_4NO_3, $NH_4H_2PO_4$, ascorbic acid, Ni, Pd, citric acid, oxalic acid, etc.	W ribbon atomizer; the first CM recommended; T_{pyr} 700 °C; LOD 0.1 μg/L with multiple injections	Sekerka and Lechner (1991)
Pb	Wine	75 mM HNO_3-0.037% Triton X-100	T_{pyr} 650 °C; STPF	Jorhem and Sundstrom (1995)
Pb	Wine	Dilute H_3PO_4-aqueous NH_3	Zeeman STPF	Probst-Hensch et al. (1991)
Pb	Wine	$NH_4H_2PO_4$	STPF	Sun (1996)

Pb	Wine	0.25% $NH_4H_2PO_4$-0.0125% $Mg(NO_3)_2$-0.25% HNO_3	1 + 3 dilution with CM solution; T_{pyr} 700 °C; Zeeman STPF; LOD 6.2 µg/L	Matthews and Parsons (1993)
Pb	Wine	4 µg Pd-20 µg W	T_{pyr} 800 °C; LOD 3 µg/L	Slaveykova et al. (1996b)
Pb	Wine (red/white)	50 µg $NH_4H_2PO_4$-3 µg $Mg(NO_3)_2$	T_{pyr} 500 °C (air), then 850 °C (Ar); STPF	Ruhnke and Ristow (1993)
Pd	$Pd(NH_2)_2Cl_2$, $Pd(NH_2)_2(NO_2)_2$	Pd-ascorbic acid	Aq. NH_3 solutions; T_{vap} 1300 °C	Popova and Bratinova (1990)
Rb	Water	Ascorbic acid	LOD 0.27 µg/L; Zeeman	Dai et al. (1994)
Sb	Air particulate matter	$Ni(NO_3)_2$	Graphite probe used as collector and atomizer	Zhang (1993)
Sb	Aq. solutions	0.1 M $(NH_4)_4EDTA$-10 mM $Ni(NO_3)_2$-20 mM $Al(NO_3)_3$; also + $Mg(NO_3)_2$	Tolerance to SO_4^{2-} and Cl^- improved in the presence of 80 mM $Mg(NO_3)_2$	Matsusaki and Harada (1992)
Sb	Blood, urine, NaCl	0.025% each of Pd-Pt-Rh-Ru + ascorbic acid	T_{pyr} 1200 °C	Dahl et al. (1994)
Sb	Urine	20 µg Ni	T_{pyr} 1200 °C; STPF	Chen et al. (1992)
Sc	Ilmenite	La	—	He (1994)
Se	Air particulate matter	7.5 µg Pd-5 µg $Mg(NO_3)_2$ or 1.25 µg ascorbic acid	Probe atomization; the same graphite probe used for sample collection; no pyrolysis step; CM eliminates double peaks	Chakrabarti et al. (1996)
Se	Aq. solutions	Al, Ca, Eu, La, Mg, Ni, Pd (as nitrates	Se(IV), Se(VI), selenomethionine and $(CH_3)_3Se^+$ studied at different molar ratios of modifier-to-Se	Docekalova et al. (1991)
Se	Aq. solutions	Ca, Eu, La, Mg (as nitrates)	Spectral interference due to NO at high modifier mass and low T_{pyr} (< 600 °C)	Docekal et al. (1991)
Se	Aq. solutions	Cu, Ni; H_2	Mechanisms studied	Mahmood et al. (1995)
Se	Aq. solutions	$HgCl_2$	Atomization mechanisms studied	Garcia-Olalla and Aller (1992a)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Se	Aq. solutions	Ir, Pd, Pt and Rh at 1500-fold molar excess	Mechanisms, advantages and disadvantages of high-melting CMs studied and discussed	Volynsky et al. (1996)
Se	Aq. solutions	Ni	T_{vap} 1200 °C; injection preferred to aerosol deposition	Howell and Koirtyohann (1992)
Se	Aq. solutions (Cl^- added)	Pd	T_{pyr} 1000 °C	Mazzucotelli and Grotti (1995)
Se	Aq. solutions	$Pd(NO_3)_2$; Pd (thermally pre-reduced at 1300 K)	Mechanisms studied by MS and ETAAS	Styris et al. (1991b)
Se	Aq. solutions	Pt-ascorbic acid; Pd-ascorbic acid	T_{pyr} 1100 °C; Fe interference eliminated with impregnated platforms	Kumar and Gangadharan (1993)
Se	Aq. solutions	Various CMs compared: Ag, Cu, Cu, Hg, Mg, Ni, Pd, Hg-Pd, etc.	Best sensitivity with Hg-Pd; E_a evaluated	Garcia-Olalla et al. (1991b)
Se	Aq. solutions (Cl^- added)	$CdCl_2$, $HgCl_2$, $PdCl_2$, $HgCl_2$-$PdCl_2$, $CdCl_2$-$PdCl_2$	Interferences by chlorides and nitrates of Ca^{2+}, Mg^{2+} and Al^{3+} studied	Aller and Garcia-Olalla (1992)
Se	Aq. solutions (Cl^- added)	$(NH_4)_2[Pd(C_2O_4)_2]\cdot 2H_2O$, $Pd(NO_3)_2$, colloidal Pd, etc.	Best stabilization with prereduced (at 1000 °C) Pd	Volynsky and Krivan (1996)
Se	Blood	Ir-$Mg(NO_3)_2$	T_{pyr} 800 °C (O_2) and 1300 °C (Ar); m_o 35 pg, m_p 12 pg; Zeeman STPF	Hoenig (1991)
Se	Blood	Pd	T_{pyr} 600 and 1200 °C; LOD 5 µg/L	Pohl and Schneider (1990)
Se	Blood	Pd-aq. NH_3	Zeeman	Shimmura et al. (1990)
Se	Blood	Pd-$Mg(NO_3)_2$-Triton X-100	10-fold dilution	Van Cauwenbergh et al. (1990)
Se	Blood, occular tissues and fluids, plasma	5 µg Pd	T_{pyr} 350 and 1100 °C; Zeeman STPF	McGahan and Grimes (1991)

Se	Blood, serum	10 µL of 0.186% $Cu(NO_3)_2$-0.173% $Mg(NO_3)_2 \cdot 6H_2O$ solution	T_{pyr} 600 °C; STPF	McMaster et al. (1990)
Se	Blood plasma/serum	4 µg Pd-0.1% Triton X-100	T_{pyr} 1200 °C; phosphate added to standards; LOD 6 µg/L; Zeeman STPF	Gardiner et al. (1995)
Se	Blood, urine	Pd, Ni	Thermal stabilization of Se and P studied	Radziuk and Thomassen (1992)
Se	Coal fly ash	$CdCl_2$-$PdCl_2$, $PdCl_2$, $CdCl_2$-$HgCl_2$, $CdCl_2$-$CuCl_2$	$CdCl_2$-$PdCl_2$ recommended; T_{pyr} 500–1500 °C	Garcia-Olalla et al. (1991a)
Se	Coal fly ash	$HgCl_2$-$PdCl_2$, $HgCl_2$, $PdCl_2$, $CaCl_2$, $TiCl_3$	$HgCl_2$-$PdCl_2$ recommended; T_{pyr} 500–1300 °C; wall atomization; LOD 7.45 µg/L	Garcia-Olalla and Aller (1992b)
Se	Drinking water	Ni, Pd-Ni	—	Ferng et al. (1992)
Se	Fish, liver, muscle	Cu-Pd-Triton X-100; Cu; Pd; Ni, etc.	Mixed CM preferred; solid sampling; "cup-in-tube"; T_{pyr} 1100 °C	Oilunkaniemi et al. (1994)
Se	Flour	Pd	Slurry in 25% triethanolamine; T_{pyr} 1200 °C; STPF	Qian and Yang (1990)
Se	Food, total diet, flour, milk, muscle, plant	0.75% Pt(IV)-0.25% $Mg(NO_3)_2$; Cu-$Mg(NO_3)_2$	Pt-Mg recommended; T_{pyr} 1100 °C	Kumpulainen and Saarela (1992)
Se	Fruit juices	Pd, Mg and Ni (as nitrates) compared	Slurry sampling; T_{pyr} 900 °C; Pd recommended	Arruda et al. (1994a)
Se	Hair, nail	5 µg Pd	HNO_3-H_2O_2 digests; T_{pyr} 1200 °C; m_o 66 pg STPF	Harrison et al. (1995)
Se	Heart tissue	Pd-Cu	Zeeman STPF	Tummalapalli et al. (1994)
Se	HPLC effluents; also from urine (speciation)	100 µg Cu	Various org. Se species studied; T_{pyr} 1200 °C; STPF	Marchante-Gayon et al. (1996)
Se	Marine food: fish, lobster, mussel, oyster	50 µg Ni	T_{pyr} 1250 °C; STPF	Maage et al. (1991)
Se	Marine tissues	Pd, Ni, Cu, Pd-$Mg(NO_3)_2$, Cu-$Mg(NO_3)_2$	Stabilization of inorg. and organoselenium species	Deaker and Maher (1995)
Se	Meat, tissues	40 µg Pd	HNO_3 digests	Medeiros et al. (1993)
Se	Millet	$Ni(NO_3)_2$	T_{pyr} 600 °C	Zeng (1991b)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Se	Mineral water	Pd-Mg-Ba (as nitrates)	SO_4^{2-} interference better tolerated with Ba(II) additions	Welz et al. (1992a)
Se	Mineral water	Ba, La, Pd, Sr, Pd-Ba, Pd-Sr, Pd-Mg-Sr, Pd-Mg-Ba	SO_4^{2-} interference best tolerated in the presence of Pd-Sr or Pd-Ba CMs; T_{pyr} 800 °C; wall atomization	Ni et al. (1994)
Se	Ni-base alloy	Pd	Bomb decomposition with aqua regia	Yao et al. (1993)
Se	Pharmaceuticals	Ni	HNO_3 digestion	Lin et al. (1993a)
Se	Tissue	10 µg Pd	Stepwise pyrolysis at 300, 500, 1000, and 1150 °C; STPF	Burguera et al. (1995a)
Se	Tissues	Pd-$Mg(NO_3)_2$	Zeeman STPF	Chen and Chen (1990)
Se	Total diet	100 µg Ni	HNO_3-H_2O_2 digestion; T_{pyr} 1000 °C; Zeeman STPF	Ari et al. (1991)
Se	Sediment, soil	1% $Ni(NO_3)_2$-40% m/v HF	Slurry sampling; fast program; no drying stage; T_{pyr} 400 °C; LOD 0.03 µg/g; Zeeman STPF	Lopez-Garcia et al. (1996b)
Se	Serum	15 µg Pd (as $PdCl_2$ in 0.5 M HCl)	T_{vap} 1150 °C; m_o 28 pg; no species-dependent effect for Se(IV), Se(VI), selenomethionine, and selenocystine; Zeeman STPF	Roesick et al. (1991)
Se	Serum	Pd-ascorbic acid	Diluent: Triton X-100	Burrini et al. (1993)
Se	Serum	Pd-CH_3COONH_4	Porous carbon plate furnace	Itai et al. (1995)
Se	Serum	15 µg Pd-10 µg $Mg(NO_3)_2$	1 + 9 dilution; T_{pyr} 1200 °C; LOD 6.5 µg/L; Zeeman STPF	Van Dael et al. (1995)
Se	Serum	0.01% $Pd(NO_3)_2$-0.1% Triton X-100	Zeeman; LOD 8 µg/L	Zhu et al. (1993)
Se	Serum	5.64 mM $PdCl_2$-24 mM HCl-25% aq. NH_3	1 + 1 or 1 + 2 dilution with modifier solution; STPF	Forrer et al. (1991)
Se	Serum	10 µg Rh-5 µg Mg (as nitrates)	T_{pyr} 1100 °C; Zeeman STPF	Haldimann et al. (1996)
Se	Serum	0.1% $Rh(NO_3)_3$-0.25% Triton X-100	1 + 4 dilution with CM solution	Kimura et al. (1990)
Se	Serum, urine	7.5 µg Pd-5 µg $Mg(NO_3)_2$ vs. Ni, Cu, Pd, $Mg(NO_3)_2$, Cu-$Mg(NO_3)_2$	Selenite, selenate, selenomethionine and $(CH_3)_3Se^+$ studied; Pd-Mg recommended; T_{pyr} 1100 °C	Johannessen et al. (1993)

Se	Serum, urine	0.3 μg Pd-30 μg Ni-80 μg NH_4NO_3-0.04% Triton X-100-0.2% HNO_3 (for serum); 0.6 μg Pd-25 μg Ni-80 μg NH_4NO_3-0.2% HNO_3 (for urine)	T_{pyr} 400, 1000, and 1300 °C; LODs 2.36 and 4.9 μg/L, resp.; Zeeman	Kao et al. (1993)
Se	Shellfish	10 mM $Pd(NO_3)_2$; Pd-$Mg(NO_3)_2$; thiourea; butylamine; thiourea-butylamine	Fl-microwave digestion; Pd preferred; T_{pyr} 1100 °C	Arruda et al. (1996)
Se	Urine	100 μg Cu-200 μg $Mg(NO_3)_2$	T_{pyr} 1100 °C; $(CH_3)_3Se^+$ incompletely recovered in the presence of phosphates (78 ± 21%); Zeeman STPF	LeBlanc (1996)
Se	Urine	Ni, Pd	SeO_3^{2-} and $(CH_3)_3Se^+$ studied; T_{pyr} 900 °C (Ni, recommended) and 1200–1300 °C (Pd)	Laborda et al. (1993b)
Se	Urine	Ni-Sr (as nitrates)	T_{pyr} 1400 and 900 °C for aq. solutions and 1 + 2 diluted urine, resp.; Zeeman STPF	Liang et al. (1996)
Se	Urine	$Pd(NO_3)_2$, $Mg(NO_3)_2$, $Ba(NO_3)_2$	Single component and mixed modifiers evaluated	Drake and Hain (1994)
Se	Urine	Pd, Rh	Thermal stabilization mechanisms studied	Hirano et al. (1994b)
Se	Water	6 μg Pd-13 μg Ni-16.2 μg $Mg(NO_3)_2$	T_{pyr} 1100 °C; LOD 5.4 pg	Yang et al. (1990)
Se	Water (river)	200 μg Pt-1 mg ascorbic acid	T_{pyr} 1200 °C; STPF	Tian et al. (1991)
Se	Wheat flour	Pd-$Mg(NO_3)_2$	Slurries in 0.005% Triton X-100	Bendicho and Sancho (1993)
Se	Wild fruit juice (*Viccinum uliginosam*)	Five CMs compared: Cu-Ni, Pd-Mg, Pt-Mg, Pt-Ni and Pt-Cu	10 μg Pd-200 μg Ni preferred; T_{pyr} 1200 °C	Liu et al. (1996)
Si	Albumin, plasma protein solutions	490 mg/L $Ca(NO_3)_2$	T_{pyr} 600 and 1600 °C	Holden et al. (1992)
Si	Au	Au matrix	Solid sampling vs. decomposition; T_{pyr} 1200–1400 °C; LOD 3 μg/g	Hinds and Kogan (1994)
Si	Au	Au matrix	Solid sampling; T_{pyr} 1400 °C	Hinds et al. (1994)
Si	Bone, tissues	Ca-La-$NH_4H_2PO_4$ (for tissue); tartaric acid (Na_2-salt) for bone	HNO_3 digests; m_o 37 pg	Huang (1994)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Si	Electrolyte solutions (1 M LiOD in D_2O)	5 μg Pt	T_{pyr} 700 °C; matrix-matched calibration	Fukushima et al. (1995)
Si	Photoresist	Ca^{2+} in 20 mM HCl	T_{pyr} 850 and 1200 °C	Motoyama and Yoshida (1995)
Si	Plasma, urine	0.02% K_2EDTA-0.27% KH_2PO_4-20 μg/mL Ca(II)-0.088% NaCl in 50% v/v C_2H_5OH; pH 6.0–6.5	10–20-fold dilution with CM solution; T_{pyr} 750 and 1450 °C; Zeeman STPF	Gitelman and Alderman (1990)
Si	Polyimides (for microelectronics)	30 μg Pd-20 μg $Mg(NO_3)_2$	Solutions in dioxane; T_{pyr} 1200 °C; LOD 25 ng/g	Krivan and Koch (1995)
Si	Process chemicals for semiconductor production: HCl, HNO_3, $HClO_4$, H_2O_2, HCOOH, H_3PO_4, etc.	1–2.5 μg Pd	5-fold sensitivity improvement; organic solvents and H_2SO_4 evaporated with NaOH before analysis	Fuchs-Pohl et al. (1992)
Si	Serum, urine	$CaCl_2$-$La(NO_3)_3$-$NH_4H_2PO_4$-Na_4EDTA-0.1% HNO_3	T_{pyr} 1400 °C; other modifier components also tested	Huang (1995)
Si	Serum, urine	1 μg $Ca(NO_3)_2$; 29 μg KF; Ta-Mo-, W-, and Zr-coated GTs	W-treated GTs recommended; T_{pyr} 1200 °C; LOD 3.5 μg/L	Perez Parajon and Sanz-Medel (1994)
Si	TiO_2, ZrO_2	80 μg $Ca(NO_3)_2$ vs. 80 μg $Mg(NO_3)_2$	Slurry sampling; Ca recommended; T_{pyr} 1000 °C; Zeeman STPF; LODs 7 and 2 μg/g in TiO_2 and ZrO_2, resp.	Hauptkorn et al. (1993)
Si	Steel	10 μg Pd	Improved sensitivity; T_{pyr} 400 and 1300 °C	Zhuang et al. (1993)
Si	Urine	$NiCl_2$ preferred to Ca and Pd	T_{vap} 2200, 2000, and 1600 °C with Ni, Ca, and Pd, resp.	Kobayashi et al. (1995)
Sn	Aq. solutions	Ag, Au, Mo, Pd, W, Zr	T_{app} increased from 1600 °C up to 2200 °C (Pd, Zr)	Sahayam et al. (1993b)
Sn	Aq. solutions	Ag, Au, Mo, Pd, W, Zr	Shorter atomization times in the presence of carbide-forming CMs	Sahayam and Gangadharan (1994)
Sn	Aq. solutions	La-treated GT; La(III)	Interferences from S-containing amino acids removed	Takeo et al. (1995)

Sn	Aq. solutions	O_2-treated GT; Zr-treated GT	T_{vap} 1300 K on ZrC; reaction mechanisms studied	Mueller-Vogt et al. (1996)
Sn	Aq. solutions	Pd	Stabilization mechanisms studied	Yasuda et al. (1993)
Sn	Aq. solutions	Pd-treated GT; Zr-treated GT	Kinetic studies; sensitivity improvement and peak shifts observed	Quan et al. (1994)
Sn	Aq. solutions (Cl^-, SO_4^{2-} added	1% H_3BO_3	Better tolerance to Cl^- and SO_4^{2-}	He (1990)
Sn	Blood	KNO_3	Organic emulsifier added	Lin et al. (1993b)
Sn	Blood	120 µg/mL Ni-0.1% H_3PO_4-10% ascorbic acid	LOD 20 µg/L	Chiba et al. (1994)
Sn	Blood serum	CMs compared: Pd, Pd-ascorbic acid, ascorbic acid	Pd preferred; T_{pyr} 1200 °C	Gong et al. (1993)
Sn	Blood, tissue	7.5% ascorbic acid	Wet digestion; final solutions in 2 M HCl; T_{pyr} 800 °C; LOD 20 pg	Itami et al. (1991)
Sn	Canned mushrooms	200 µg/mL Cu(II)	HNO_3-HCl digests; Ta-foil lined GT in 5% H_2-Ar; T_{pyr} 1000 °C	Wu et al. (1990)
Sn	Fe, steel	Citric acid	—	Xuan and Cai (1992)
Sn	Fish	100 µg Na_2WO_4; W-treated vs. Zr-, Ta-, and Pd-treated GTs	W-treated GTs preferred for better sensitivity and interference control	Iwamoto et al. (1992b)
Sn	Ga	Mo	HNO_3 decomposition at 60–70 °C for 6–7 h	Yudelevich et al. (1993)
Sn	Ga (high purity)	10 mM $AgNO_3$-1000 µg/mL Mo (as NH_4^+ salt)	T_{pyr} 1100 °C	Sahayam and Gangadharan (1993)
Sn	Gelatine, milk, polymers	Pd-$Mg(NO_3)_2$	T_{pyr} 1200 °C; Zeeman	Seltner et al. (1991)
Sn	H_3BO_3	Ascorbic acid; $PdCl_2$ (1 µg Pd)	T_{pyr} 400 °C; STPF	Volynsky et al. (1991a)
Sn	InP	H_3PO_4-$Mg(NO_3)_2$	LOD 5 µg/g; STPF	Taddia et al. (1993)
Sn	Ni alloys, steel	Pd-$Mg(NO_3)_2$	W-treated GT; T_{pyr} 800 °C	Osojnik and Drglin (1993)
Sn	Polyvinylchloride (PVC)	200 µg $NH_4H_2PO_4$	Four sample preparation techniques compared; T_{pyr} 800 °C; LOD 0.4 µg/g	Sipos and Adamis (1991)
Sn	Seawater	50 µL 10 mM Pd in W-treated GT	T_{vap} 1700 °C; LOD 0.08 ng	Iwamoto et al. (1993)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Sn	Sediments	200 μg Ni vs. Pd	Digests in 6% HNO_3; organotins 100% recovered; LOD 54 pg or 0.27 μg/g; STPF	Ide et al. (1995)
Sn	Tap water	300 mg/L Mg-0.4% HNO_3; 150 mg/L Pd-100 mg/L Mg	T_{pyr} 1200 °C; m_o 25 and 27 pg, resp.; STPF	Bermejo-Barrera et al. (1993b)
Sn	TiO_2	Ascorbic acid and TaC-coated GT	Slurry in 0.1% Na hexametaphosphate	Oimatsu et al. (1993)
Sn	Tributylphosphate solutions	10 μg/mL Pd as $PdCl_2(CH_3CN)_2$ in tributylphosphate	Thermal stabilization of butyltins studied by GFAAS and ETV-ICP-MS; complete isoformation not obtained	Li et al. (1996a)
Sn	Water	Pd-Ni-$MgCl_2$	T_{pyr} 850 °C	Yang and Dai (1990)
Sn	Water (mineral, tap)	Pd-Mg$(NO_3)_2$, Zr-treated platform	T_{vap} 1600 and 1400 °C, resp.; Pd-Mg preferred for better control of Cl^- and SO_4^{2-} interferences	Bermejo-Barrera et al. (1995f)
Sn	Water, seawater	$Pd(CH_3CN)_2Cl_2$ in org. solvents: tributylphosphate (best), toluene, ethylacetate	Various organotins studied; complete isoformation not achieved	Li et al. (1993a)
Sr	Sediment	10 μg EDTA (NH_4^+-salt)	T_{pyr} 1400 °C	Zheng and Zhou (1992)
Te	Chloride matrices (Ca, K, Mg, Na)	Ni- or Pd-coated platform; Ta platform	Experimental design study of interferences. Modifier eliminates double peaks; STPF	Grotti et al. (1996)
Te	Cu, Cu alloy	20 mM Ni$(NO_3)_2$-10 mM Al$(NO_3)_3$-20 mM $(NH_4)_4$EDTA	Cl^- and SO_4^{2-} interferences eliminated	Matsusaki et al. (1993)
Te	Ge, $GeCl_4$, GeO_2	Ni	T_{pyr} 900 °C; Zeeman STPF; many other elements determined without CM	Sentimenti et al. (1993)
Te	Urine	Pt, Mg$(NO_3)_2$	Zeeman STPF vs. ID-GC-MS; Mg$(NO_3)_2$ preferred to Pt; T_{pyr} 900 and 1150 °C, resp.	Aggarwal et al. (1994)
Te	Waste water (industrial)	5 μg Pd-0.25% Triton X-100	Samples pretreated with alkaline EDTA solution; T_{vap} 1250 °C	Klinkenberg et al. (1993)
Ti	Sediment, coal fly ash	40 μg $Pd(CH_3COO)_2$; $PtCl_4$; $IrCl_4$	Pd preferred; T_{pyr} 1000 °C	Bhattacharyya et al. (1993)
Tl	Aq. solutions (mineral acids added)	Ni, Ta, Zr, W; Ta-, W-, and Zr-treated GTs	T_{pyr} 1000 °C (W)	Hamid et al. (1991)

Tl	Aq. solutions (Cl^- added)	$(NH_4)_4EDTA$-$Ni(NO_3)_2$	$(NH_4)_4EDTA$ improves tolerance to Cl^-	Matsusaki et al. (1991b)
Tl	Aq. solutions	O_2-treated GTs	Atomization peaks shifted to higher temperatures	Hahn et al. (1993)
Tl	Aq. solutions (Cl^- added)	Pd	Pre-pyrolysis of modifier at 900 °C; tolerance to 200 µg NaCl at T_{pyr} 900 °C	Qiao et al. (1993)
Tl	Bi_2Te_3	$Mg(NO_3)_2$-tartaric acid-ascorbic acid	LOD 12 pg or 0.6 µg/L	Sramkova et al. (1995)
Tl	Blood, urine	6 µg Pd-100 µg NH_4NO_3	Better elimination of Cl^- interference than in the presence of H_2SO_4 modifier	Yang and Smeyers-Verbeke (1991)
Tl	Environmental materials	Pd-ascorbic acid; H_2SO_4; Triton X-100	5 different types of GTs and platforms compared; Zeeman STPF	Wegener et al. (1992)
Tl	Fly ash, pine needles	Pd-ascorbic acid	Digestion with HNO_3-H_2O_2 (plant) or HNO_3-HF-H_2SO_4 (fly ash)	Pohl (1993)
Tl	Geol. materials, rock, sediment	10 µg Pd-2% $(NH_4)_4$ EDTA	V-shaped boat preferred	Zheng and Wang (1994)
Tl	Ni-base alloys	Ascorbic acid	H_2SO_4-HNO_3-HF or H_2SO_4-HF-H_2O_2 pretreatment; T_{pyr} 500–550 °C; LOD 0.1 µg/L; STPF	Saraswati et al. (1994)
Tl	Seawater	20 µg Pd	Flashlamp continuum ETAAS; T_{pyr} 900 °C; m_0 28 pg; LOD 20 µg/L	Becker-Ross et al. (1995)
Tl	Sediment	5 µg Pd-3 µg $Mg(NO_3)_2$	Slurry sampling; pyrolysis in 5% H_2-Ar at 700 °C; STPF	Schlemmer (1996)
Tl	Sediment	Pd-$Mg(NO_3)_2$ and H_2-Ar	T_{pyr} 250 and 700 °C (H_2-Ar), then 700 °C (Ar); Zeeman STPF	Schlemmer et al. (1996)
Tl	Water	10 µg/L $PdCl_2$	T_{pyr} 600 °C; STPF	Li et al. (1993b)
V	Alkaline sludge	$Cr(NO_3)_3$	LOD 0.56 ng	Chakraborty and Das (1994)
V	Blood, erythrocytes, plasma, serum	100 µg/L Pd-2% citric acid-0.1% Triton X-100-10 mM HNO_3	1 + 1 dilution with CM solution	Navarro et al. (1991)
V	Fuel oil	La(III)	Dry ashed samples	Chen (1990)
V	Oil, water	Various CMs compared: ascorbic acid, NH_4SCN, $Mg(NO_3)_2$, Pt, Rh	1 µg Pt recommended; T_{pyr} 1400 °C	Thomaidis and Piperaki (1996)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
V	Seaweed, sediment, serum, urine, vehicle exhaust particulates	100 µg/L Pd-2% citric acid-0.1 M HNO_3-0.1% Triton X-100; Pd; CO; citric acid	Mixed modifier recommended; T_{pyr} 800 °C (air), then 800, 1100, and 1700 °C (Ar); m_o 44 pg	Granadillo and Romero (1993c)
V	Sediment, steel	0.25% $(NH_4)_4EDTA$-15% aq. NH_3	Total pyrolytic graphite graphite tubes preferred	Zheng and Xiang (1990)
V	Urine	40 µg $(NH_4)_4Pd(NO_3)_2 \cdot 2H_2O$-10 µg $Mg(NO_3)_2$-40 µg NaF in 1 mM NH_3/NH_4^+ buffer	T_{pyr} 1500 °C	Fleischer et al. (1991)
V	Water (mineral)	2.5 mg/mL $Mg(NO_3)_2$	T_{pyr} 1500 °C; hot injection; multiple injections	Bermejo-Barrera et al. (1990a)
Yb	Rare earth oxides mixture, crude yttria	Eu, Sm	Eu preferred; m_p 1.3 pg; LOD 0.25 pg	Zhang and Guo (1995)
Zn	Adipose tissue	Pd-$Mg(NO_3)_2$-Triton X-100	Fl-on-line microwave digestion	Burguera et al. (1995a)
Zn	Aq. solutions	$CoCl_2$	Interference effects studied by dual-cavity platform	Doner and Akman (1994)
Zn	Beer, wort	$NH_4H_2PO_4$	HNO_3 pretreatment for wort; beer analyzed undiluted	Wagner et al. (1991a)
Zn	Milk	0.1% Triton X-100-0.1–0.3 M HNO_3	Direct dilution with Triton X-100 vs. dry or wet ashing compared; T_{pyr} 650 °C	Arnaud et al. (1991)
Zn	Seawater	0.7 M oxalic acid	Various nitrate salts and org. acids compared	Cabon and Le Bihan (1994)
Zn	Seawater	5 µg V (as NH_4VO_3); 70 µg citric acid	T_{pyr} 400 °C; LOD 0.11 and 0.024 µg/L without and with V, resp.; Zeeman STPF	Huang and Shih (1995)
Zn	Soil extracts	1% H_3PO4	50 mM $CaCl_2$ extracts	Bogacz (1992)
Ag, Bi	Ni-base superalloys, steel	Ni-$NH_4H_2PO_4$ (for Ag); Ni-HF-tartaric acid (for Bi)	T_{pyr} 1100 and 850 °C, resp.; LODs 0.06 and 1 µg/L, resp.; Zeeman STPF	Mile et al. (1995)
Ag, Cd	Aq. solutions (PO_4^{3-} added)	PO_4^{3-}	Stabilization mechanisms studied	Hassel et al. (1991)
Ag, Cd	Geological materials	$NH_4H_2PO_4$	Standardless analysis	Zheng and Su (1993)

Ag, Co	Wine	15 μg $NH_4H_2PO_4$ (for Ag); 2 μg $Mg(NO_3)_2$ (for Co)	T_{pyr} 700 and 1400 °C, resp.; LODs 0.2 and 1.6 μg/L, resp.; STPF	Soares et al. (1995a)
Ag, Cu	Aq. solutions	Pd, Mg, Pd-Mg	Thermal and temporal effects of CMs studied	Rayson and Fresquez (1993)
Ag, Mn	Cocaine, heroin	Pd, $Mg(NO_3)_2$, Pd-$Mg(NO_3)_2$, HNO_3	Pd recommended; T_{pyr} 1000 and 1300 °C resp.	Bermejo-Barrera et al. (1996d)
Al, As	Si	$Ni(NO_3)_2$-$Mg(NO_3)_2$	HNO_3-HF-H_2O_2 decomposition	Lajunen et al. (1990)
Al, Cr	Serum	0.1% Triton X-100, 0.1 M HNO_3, 200 μg/mL Mg as $Mg(NO_3)_2$, etc.	$Mg(NO_3)_2$-1 M HNO_3 preferred; T_{pyr} 1450 °C	Bulska et al. (1992)
Al, Cr	Vegetables	4% v/v H_2O_2-1% HNO_3	0.1% m/v slurries; fast program	Vinas et al. (1995b)
Al, Pb	Wine	30 μg Pd-20 μg $Mg(NO_3)_2$	Modifier needed for Pb (T_{pyr} 1200 °C); STPF	Almeida et al. (1992)
Al, Sn	Infant formula, milk (evaporated)	1 μ Pd	Samples reconstituted in aq. citric acid-HNO_3	Dabeka and McKenzie (1992)
Al, Zn	Suspended matter in estuarine and sea water	2000 μg/mL Pd-300 μg/mL Si-10 μg/mL each of Ca-Fe-Na-K-Mg-P	Slurry sampling; 1600 and 1000 °C, resp.	Hoenig et al. (1991b)
As, Ga	Si	10 μg Ni; 1–10 μg Pd (for As); 7.5 μg Pd-5 μg Mg or 1 μg Pd-5 μg ascorbic acid (for Ga)	Glassy carbon platform; T_{pyr} 1000–1200 °C; ascorbic acid also added in the presence of HCl	Beisel et al. (1991)
As, Pb	Catalysts	1.2 μg Pd vs. Ni or Ga	Final digests in 5% HF-0.4% H_3BO_3; T_{pyr} 600 °C; Pd recommended	Grey (1990)
As, Pb	Sediment, urine	Pd-$Mg(NO_3)_2$	T_{pyr} 1000 and 850 °C, resp.; fast program possible	Zhang et al. (1993a)
As, Pb	Wine	5 μg Pd (for As); 10 μg Pd-15 μg $Mg(NO_3)_2$ (for Pb)	PTFE bomb decomposition with HNO_3 for As; 1 + 4 dilution with 0.2% HNO_3 for Pb	Bruno et al. (1994)
As, Sb	Rye grass	10 μg Pd (pretreated at 1200 °C)	T_{pyr} 400 and 900 °C, resp.; LODs 25 and 36 pg, resp.	Walcerz et al. (1994)
As, Sb	Wine (red/white)	Pd vs. $Ni(NO_3)_2$ or $NiSO_4$ (20–100 μg)	T_{pyr} 1200 or 1400 °C for intact and decomposed samples, resp.	Kildahl and Lund (1996)
As, Se	Cabbage and serum (for Se)	Pd-ascorbic acid	T_{pyr} 1100 and 1200 °C, resp.	Pohl et al. (1992)
As, Tl	Te	30 μg Pd-20 μg Mg	HNO_3 digests	Beisel et al. (1992)
Bi, Pb	KBr, KI, NaCl	Pt	Samples in 0.5% HCl	Chen and Xu (1991)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Bi, Sn	Serum (Bi), urine (Sn)	Pd	Dilution only	Pohl and Lange (1994)
Bi, Tl	Sulfate matrices	20 mM $(NH_4)_4EDTA$-10 mM $Ni(NO_3)_2$-10 mM $Cu(NO_3)_2$ (for Bi); 50 mM $(NH_4)_2EDTA$-20 mM $Ni(NO_3)_2$ (for Tl)	T_{vap} 750 °C (Bi); 800 °C (Tl); sulfate interference eliminated	Matsusaki and Oishi (1993)
Cd, Pb	Liver	50 µg $NH_4H_2PO_4$-3% HNO_3	Solid sampling	Luecker (1992)
Cd, Pb	Blood, serum	$NH_4H_2PO_4$	LODs 0.36 and 0.026 µg/L, resp.	Imai et al. (1991a)
Cd, Pb	Coastal sediment	0.2% $NH_4H_2PO_4$-0.02% $Mg(NO_3)_2$ (for Cd)	Final digests containing HCl-HNO_3-HF-H_3BO_3; 10 × higher concentration of modifier needed for Pb	Giordano et al. (1992b)
Cd, Pb	Food	200 µg $NH_4H_2PO_4$-20 µg $Mg(NO_3)_2 \cdot 6H_2O$	T_{pyr} 800–900 °C for Cd and 850 °C for Pb; Zeeman STPF	Ellen and Van Loon (1990)
Cd, Pb	Milk, milk serum	H_3PO_4	Casein and fat separated for 48 h at pH < 4.6	Jeng et al. (1994)
Cd, Pb	Blood	$NH_4H_2PO_4$	T_{pyr} 600 °C; simultaneous determination	Deval and Sneddon (1995)
Cd, Pb	Tissue	1% $NH_4H_2PO_4$	Levels in renal cancer studied; Zeeman STPF	Ala-Opas and Tahvonen (1995)
Cd,Pb	Cabbage, leaves, liver	Pd-$Mg(NO_3)_2$ vs. $(NH_4)_2HPO_4$	"Cup-in-tube" solid sampling vs. constant-temperature two-step atomizer	Baxter and Frech (1990)
Cd, Pb	Fly ash, plant leaves, sediment, soil	125 µg $(NH_4)_2HPO_4$-0.04% Triton X-100	Solid and slurry sampling; T_{pyr} 600–900 and 1000 °C, resp.	Dolinsek et al. (1991)
Cd, Pb	Plant, vegetables	0.1% $NH_4H_2PO_4$	Slurry in 20% ethanol	Vinas et al. (1994a)
Cd, Pb	Algae, pine needles, tobacco leaves	80 µg $NH_4H_2PO_4$	Various acid extraction methods tested; T_{pyr} 700 and 850 °C, resp.; STPF	Wieteska et al. (1996)
Cd, Pb	Ginseng	Pd-La	—	Yao et al. (1990b)
Cd, Pb	Marine tissues	Ascorbic acid	SO_4^{2-} interference on Pb in acid digests eliminated	Tinggi et al. (1992)
Cd, Pb	Air particulate matter, plant, sediment	4 µL of 3 M $(NH_4)_2HPO_4$	T_{pyr} 550 and 1100 °C, resp.	Okamoto et al. (1993)

Cd, Pb	Milk	H_3BO_3-$NH_4H_2PO_4$-$Mg(NO_3)_2$ or Pd-NH_4NO_3 in H_2-Ar	T_{pyr} 550 °C (H_3BO_3) or 1000 °C (Pd)	Martin et al. (1991)
Cd, Pb	Aq. solutions	$(NH_4)_2Ce(NO_3)_6$	Experimental results agreed with the regular solutions model	Mandjukov et al. (1995)
Cd, Pb	Seawater	0.25 µg Pd	Pd electrodeposited; then analyte preconcentrated by electrolysis and the residual matrix solution removed (pipetted off); m_o 1 and 7 pg, resp.	Matousek and Powell (1995)
Cd, Pb	Sediment, tea leaves	$NH_4H_2PO_4$	Composite modified simplex optimization detailed; T_{pyr} 400 and 500 °C, resp.	Stalikas et al. (1996)
Cd, Pb	Flour	Pd	Slurry in 25% triethanolamine; STPF	Qian and Yang (1991)
Cd, Pb	Ginseng	Pd-La	Platform atomization	Yao et al. (1990)
Cd, Pb	Ginseng	Pd-La	Final solutions in 0.64 M HNO_3; m_o 0.88 and 17 pg, resp.	Yao et al. (1990a)
Cd, Pb	Sediment	9 µg Pd	Slurry sampling; T_{pyr} 550 and 900 °C, resp.; STPF	Sandoval et al. (1992)
Cd, Pb	Biomonitors (hay, humus, moss, rye grass)	$NH_4H_2PO_4$	T_{pyr} 700 °C	Lippo and Sarkela (1995)
Cd, Pb	Liver, meat, poultry	$NH_4H_2PO_4$	HNO_3 digests; Zeeman STPF	Tahvonen and Kumpulainen (1994a)
Cd, Pb	Biscuits, bread, cereal-based food	PO_4^{3-} (for Pb); Pd or Cu in aq. NH_3 (for Cd)	Slurry in 20% C_2H_5OH; LODs 0.5 and 8 ng/g; STPF	Vinas et al. (1994c)
Cd, Sb	Aq. solutions	Ca, K, Mg, Na, Ni, La, Pd, Pt (as nitrates)	Thermal stabilization studied and mechanisms discussed	Morishige et al. (1994)
Cd, Zn	Aq. solutions	10 µg Pd-100 µg citric acid	T_{vap} 900 and 1000 °C, resp.	Zhuang et al. (1991)
Cr, Pb	Aq. solutions	Pd (for Cr); Pd-$Mg(NO_3)_2$-$NH_4H_2PO_4$ (for Pb)	T_{pyr} 1100 and 1000 °C, resp; STPF for Pb; effect of "cool-down" studied	Hoenig et al. (1990)
Co, Fe	ZrF_4-H_2O	$Pd(NO_3)_2$-dil. HNO_3	Samples in dil. HF; 1 and 4 M HNO_3 for Co and Fe, resp.; LODs 4.1 and 3.8 ng/g, resp.	Jaganathan et al. (1991)
Co, Zn	Aq. solutions	$Mg(NO_3)_2$	Interference and stabilization mechanisms studied	Akman and Doner (1994)
Co, Zn	Aq. solutions	Ni	$NiCl_2$ interferent; mechanisms studied	Akman and Doner (1995)

(continued)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cu, Ni	ZrF_4	4.5 μg Pd-1 M HNO_3	Background reduced; T_{pyr} 1400 °C; Zeeman STPF	Jaganathan et al. (1990)
Cu, Pb	Kerosene	1 μg $(C_4H_9)_4H_2PO_4$ (for Pb); no CM for Cu	Kerosene-water-propan-1-ol solution analyzed; T_{pyr} 1000 and 600 °C, resp.; Zeeman STPF	Silva et al. (1993)
Cu, Pb	SiC, Si_3N_4	Mg, Ni, Pd, Rh (as nitrates); graphite powder	Slurry sampling; 1 + 2.5 dilution with graphite powder recommended	Nakamura et al. (1995)
Co, Ni	Plant leaves, seafood, vegetables	10% H_2O_2-1% HNO_3-0.025% Triton X-100	Slurry sampling; T_{pyr} 250 °C; LODs 36 and 42 ng/g, resp.; $Mg(NO_3)_2$, PO_4^{3-} or Pd produced no significant advantage	Vinas et al. (1995a)
Fe, Ni	Edible oils and fats	Nb-treated platform (for Fe)	T_{pyr} 600 and 1110 °C; fast program; Zeeman STPF	van Dalen and de Galan (1994)
Ga, In	Aq. solutions (SO_4^{2-} added)	0.1 M EDTA (NH_4^+ salt)-0.1 M $Ni(NO_3)_2$-1 mM $Al(NO_3)_3$	Tolerance up to 20 mM Na^+ and SO_4^{2-}	Matsusaki and Sata (1994)
Ga, Pb	Aq. solutions	Ni, Pd	Stabilization mechanisms studied	Volynsky et al. (1991b)
Ge, Sr	Serum	20 μg Pd	1 + 4 dilution with 10 mM HNO_3-0.1% Triton X-100	Shi et al. (1993)
Hg, Se	Dolphin liver	7.5 μg of Pd as acetylacetonate (acetone-ethanol extracts)	Org. Hg (T_{pyr} 350 °C), org. Se (T_{pyr} 1400 °C) in ethanol (for Hg), 8 μg Pd as $PdCl_2(C_6H_5CN)_2$ in ethanol (for Se)	Li et al. (1996b)
Hg, Se	Hair	$PdCl_2$	Zeeman STPF	Bortoli et al. (1991)
In, Pb	Aq. solutions	Ag, Au, Cu, Pb	Formation of alloys and intermetallic compounds studied by SIMS	Hirano et al. (1995)
In, Pb	Aq. solutions	Pd	Atomic vapor temperature increased in the presence of Pd	Hirano et al. (1994c)
K, Na	Renal tubular fluid	$(NH_4)_2HPO_4$	Graphite boat and alternative wavelength employed	Boer et al. (1994)
Mg, Si	Graphite powder	3 μg Pd (for Mg); 5 μg Pd-3 μg $Mg(NO_3)_2$ (for Si)	Slurry in 0.1 M HNO_3-0.008% Triton X-100; T_{pyr} 1000 and 1200 °C, resp.; nine analytes determined without CM; Zeeman STPF	Schaeffer and Krivan (1996)
Mo, V	Soil	1 mg/mL Pd (for V only)	Aqua regia digests; T_{pyr} 1700 and 1400 °C, resp.; LODs 75 and 250 pg, resp.	Lechotycki (1990)

Mo, Se	Plant (rice, sesame)	$Ni(NO_3)_2$	T_{pyr} 1600 and 1300 °C, resp.	Ji (1993)
Pb, V	Blood, plant, sediment, serum, tea, urine	Pd-citric acid-Triton X-100	T_{pyr} 600 and 1700 °C, resp.; m_o 12 and 44 pg, resp.	Granadillo et al. (1991b)
Pb, Ni	Coal fly ash, milk, plant leaves, sediment, sewage sludge, soil	10 µg Pd-8 µg Mg	Slurry sampling; vapor-phase molecular spectra studied; T_{pyr} 700 and 1300 °C, resp.	Tittarelli and Biffi (1992)
Pb, Sn	Aq. solutions (for Sn); blood and NaCl (for Pb)	10–20 µg Pd (as nitrate)	T_{pyr} 1000 °C (Pb), 1300 °C (Sn)	Fuchs-Pohl and Solinska (1990)
Pb, Sn	Aq. solutions	Ag, Au, Cd, Cu, Mg, Pd, Pt, Sb	Mechanisms studied	Ouishi et al. (1994)
Pb, Pd	Aq. solutions	Pd (for Pb); Ni (for Pd)	"Effective vapor temperature" measured in the absence and presence of CM	Terui et al. (1991c)
Se, Te	Ni- and Ni-Fe-base alloys	3 g/L Ni-100 mg/L Pd	m_o 19 pg (Se), 19 pg (Te)	Gong et al. (1995a)
Sb, Se	Seawater (spiked)	2% glucose	T_{vap} 1300 °C	Perez-Corona et al. (1995)
Ag, Cd, Pb	Aq. solutions	$NH_4H_2PO_4$	Mechanisms studied; Zeeman STPF	Eloi et al. (1993)
Ag, Cd, Pb	Minerals, ores, rocks	0.3% $(NH_4)_2HPO_4$	5% HNO_3 medium; STPF	Chen (1990)
Ag, In, Tl	Geol. materials, rock, sediment	Pd-$(NH_4)_4$EDTA	V-shaped boat	Zheng and Wang (1995)
Al, As, Sb	HF, NH_4F and other F^- containing etching media	10 µg Pd (for As and Sb); H_2-Ar (for Al)	Glassy carbon platforms; T_{pyr} 1300 °C; STPF	Heinrich and Emrich (1991)
Al, Cr, Cu	SiC	200 µg $Mg(NO_3)_2 \cdot 6H_2O$	Slurry sampling; T_{pyr} 1700, 1500, and 1200 °C, resp.; many other elements determined without CM; Zeeman STPF	Docekal and Krivan (1992)
Al, Pb, V	Erythrocytes, plasma	Pd-citric acid-0.1% Triton X-100	0.01–0.1 M HNO_3 media; no modifier for Al	Granadillo and Romero (1993b)
As, Cd, Pb	Aq. solutions (Cl^- added)	Pd-$Mg(NO_3)_2$	Standard additions and successive dilution method applied	Pszonicki et al. (1995)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
As, Cd, Pb	Kidney	Pd-$Mg(NO_3)_2$	Bomb decomposition; STPF	Soares et al. (1995b)
As, Cd, Pb	Plant	5 μg Pd-50 μg $Mg(NO_3)_2 \cdot 6H_2O$	Solid or slurry sampling; T_{pyr} 700/900 (As), 600/400 (Cd) and 700/500 °C (Pb) in solid/slurried samples, resp.	Mohl et al. (1993)
As, Cd, Pb	Seawater	10 μg Pd (+ NH_4NO_3 for Cu)	T_{pyr} 1200–1400 °C (As), 900 (Cd), and 700–1200 °C (Pb); probe, wall and platform atomization compared	Alvarez-Cabal Cimadevilla et al. (1995)
As, Cr, Pb	Sediment, soil	$Mg(NO_3)_2$ (for Cr); Pd-$Mg(NO_3)_2$ (for As and Pb)	Slurry sampling STPF; T_{pyr} 700, 900, and 1100 °C, resp.	Klemm and Bombach (1995)
As, Pb, Se	Aq. solutions	Cu, Ni, Pd, Pd-$Mg(NO_3)_2$	Effect of large CM masses and tube aging studied; STPF vs. side-heated GT	Frech et al. (1992)
As, Pb, Zn	Aq. solutions	Pd	Stabilization mechanisms studied	Yang et al. (1992)
As, Se, Si	Aq. solutions	Pd; Rh (as permanent modifiers)	Electroplating of CMs detailed; T_{vap} 1300, 1200, and 1200 °C on Pd and 1450, 1400, and 1600 °C on Rh for As, Se, and Si, resp.	Bulska and Jedral (1995)
As, Te, Tl	Cd	30 μg Pd-20 μg Mg	HNO_3 digests	Beisel et al. (1992)
Bi, Ge, Pb	Aq. solutions	2 μg Pd-3 μg Mg for Bi and Pb; 10 μg Pd-8-10 μg Mg for Ge	—	Xuan (1992a)
Bi, Pb, Tl	Aq. solutions	O_2 pretreated GTs/platforms	O_2 conditioning results in thermal stabilization due to intercalation	Mueller-Vogt et al. (1995)
Bi, Sb, Sn	WO_3	$Pd(NO_3)_2$	Solid or slurry sampling vs. direct ETAAS of dissolved samples and extraction-ETAAS; STPF	Havezov et al. (1991)
Cd, Co, V	Aq. solutions	$NH_4H_2PO_4$; La (for V only); Pd	W tube atomizer; T_{pyr} 400–600, 900–1200, and 1400 °C, resp.; A_p measurements recommended	Krakovska and Pulis (1996)
Cd, Cr, Pb	Blood	$(NH_4)_2SO_4$ (for Cd); NH_4NO_3 (for Cr); $(NH_4)_3PO_4$ (for Pb)	Samples digested with HNO_3-$HClO_4$	Zeng (1991a)

Cd, Cr, Pb	Sewage sludge	Pd, Pt	Pt preferred; three digestion methods compared	Thomaidis et al. (1995b)
Cd, Cu, Pb	Animal and marine tissues	$NH_4H_2PO_4$ (for Cd); NH_4NO_3 (for Cu); $Pd(NO_3)_2$ (for Pb)	Slurry in 0.25% TMAH-10% ethanol; T_{pyr} 600, 900, and 950 °C, resp.	Tan et al. (1996b)
Cd, Cu, Pb	Mussel	$NH_4H_2PO_4$ (for Cd and Pb)	Slurry sampling; STPF	Hu (1991)
Cd, Mn, Pb	$ZnSO_4$	0.5 M H_3PO_4	Solutions in 10 mM HNO_3	Hulanicki et al. (1992a)
Cd, Mn, Zn	Coal fly ash, geol. materials, rock	0.1–3% HF; also 0.1% $NH_4H_2PO_4$ for Cd and Zn	Slurry sampling; fast program; T_{pyr} 400, 200, and 400 °C, resp.	Lopez Garcia et al. (1993b)
Cd, Mo, Se	Aq. solutions	$NH_4H_2PO_4$-$Mg(NO_3)_2$	Overcompensation error for Cd due to Zeeman splitting	Heitmann et al. (1996)
Cd, Ni, Pb	$Al(NO_3)_3$	Al matrix	Zeeman ETAAS study of $Al(NO_3)_3$ effects	Elci and Dogan (1991)
Cd, Pb, Mn	Seawater	H_2-Ar (for Cd); 4 µL of 0.2% Pd-0.1% $Mg(NO_3)_2$-0.1% $NH_4H_2PO_4$ (for Pb); 3 µL of 0.05% Pt (for Mn)	Pyrolysis in H_2-Ar for Cd and Pb; Zeeman STPF	Hoenig et al. (1991a)
Cd, Pb, Mn	Seawater	$(NH_4)_2C_2O_4$ (for Cd); Pd-$(NH_4)_2C_2O_4$ (for Pb and Mn)	—	Sachsenberg et al. (1993)
Cd, Pb, Tl	Plant, vegetal food, soil	Pd, H_3BO_3, Pd-H_3BO_3-citric acid	T_{pyr} 500–550 °C (H_3BO_3); T_{pyr} 1000 °C (Pd)	Martin (1993)
Cd, Pb, Tl	Sediment, soil	5–30% v/v HF	Slurry sampling; fast program; T_{pyr} 400 °C; STPF	Lopez-Garcia et al. (1996a)
Cd, Pb, Zn	Aq. solutions	Ascorbic acid, $Mg(NO_3)_2$, oxalic acid	$MgCl_2$ interference mechanisms studied by ETAAS and ETV-AES	Kantor (1995)
Cr, Cu, Mn	Seawater	0.15 M HNO_3 or 0.1 M oxalic acid	T_{pyr} 1150 °C; LODs 42, 75, and 26 ng/L; Zeeman STPF	Cabon and Le Bihan (1995)
Cu, Fe, Mn	Na	20 µL of 1% $Ni(NO_3)_2 \cdot 6H_2O$ vs. $Mg(NO_3)_2$	Sample transformed into NaOH; then neutralized with HNO_3; T_{pyr} 1100, 1300, and 1100 °C; Zeeman STPF	Koshino and Narukawa (1993b)

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Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cr, Mn, Mo	Seawater	Ascorbic acid, Pd, $Mg(NO_3)_2$, Pd-$Mg(NO_3)_2$, Pd-NH_4NO_3, Pd-NH_2OH-HCl	Effect of CMs systematically studied; 1500, 1300, and 1800 °C, resp; STPF (for Cd and Mn)	Huang et al. (1995)
Cr, Mn, Pb	Sewage sludge, soil	10% H_2-Ar during pyrolysis	Slurry sampling; background reduced	Ebdon et al. (1993)
Cr, Pb, Se	Blood, serum, urine	Pd-$Mg(NO_3)_2$	Platform vs. wall atomization	Streck and Pawlik (1995)
Ga, Pb, Sn	Aq. solutions	Ascorbic acid, fructose, glucose, glycerol, manitol, oxalic acid, polyethylene glycol, sucrose, tartaric acid	Mechanisms studied; STPF conditions	Volynsky et al. (1993)
In, Pb, Sn	Aq. solutions	Mn, Ni, Pb	Stabilization mechanisms studied and discussed	Yasuda et al. (1994)
Fe, Si, Ti	Oxide powders	Carbon powder	5% suspension of carbon black	Yoshimura and Fujino (1991)
Ga, Ge, In	Aq. solutions	1.6 μg Ni (for Ga); 1.2 μg Ni or 0.15 M NaOH (for Ge); Pd-$(NH_4)_2$EDTA (for In)	Modifier significantly improves m_0 for In; effects of platform and V-shaped boat studied	Zheng et al. (1993c)
Pb, Se, Tl	Al_2O_3, sediment	8 μg Pd-6 μg Mg	Slurry sampling; mechanisms studied; during pyrolysis analytes migrated and interacted with the physically separated modifier T_{pyr} 600 °C; STPF	Chen and Jackson (1996)
Pb, Sn, Tl	Aq. solutions	O_2-treated GT	Thermal stabilization and higher t_{app}	Brennfleck et al. (1996)
Sb, Ni, V	Coal fly ash, air particulate matter	20 μg Pd-50 μg Mg (for Sb)	Digests in HNO_3-H_2SO_4-HF-H_3BO_3; T_{pyr} 1300, 1200, and 1400 °C, resp.	Carneiro et al. (1993)
Ag, Bi, Cd, Pb	Geol. RMs, rock, sediment, water	Pd-$Mg(NO_3)_2$	T_{pyr} 420 °C	Sen Gupta and Bouvier (1995)
Ag, Cd, Pb, Sb	Water (potable)	5 μg Pd-3 μg $Mg(NO_3)_2$	Simultaneous Zeeman STPF; T_{pyr} 400 °C	Latino et al. (1995)

Ag, Co, Mn, Tl	Aq. solutions	Pd	Atom release kinetic studies	Liang and Ni (1994)
Al, Cr, Fe, Si	KH_2PO_4	Ca-KH_2PO_4	—	Zolotovitskaya et al. (1995)
Al, Cu, Pb, Zn	Animal and plant tissues	$Mg(NO_3)_2$ (for Al and Zn), Pd-$Mg(NO_3)_2$ (for Cu); PO_4^{3-}-$Mg(NO_3)_2$ (for Pb)	T_{pyr} 1200, 700, 1200, and 850 °C, resp.; STPF	Zhou et al. (1996)
Al, Fe, Pb, V	Blood, bone, plasma	100 µg/L Pd-2% citric acid (for V); 0.6% $NH_4H_2PO_4$-0.15% $Mg(NO_3)_2$ (for Pb); Triton X-100 (for Al and Fe)	Bone digests in 10 mM HNO_3; blood diluted with 0.01–0.1 % Triton X-100; T_{pyr} 700 and 1500 °C (Al), 500 and 1300 °C (Fe), 800, 1100, and 1700 °C (V) and 800 °C (Pb)	Navarro et al. (1992)
As, Bi, Pb, Se	Aq. solutions	Ascorbic acid, Ni, Pd, Pt, Triton X-100	CMs compared and mechanisms discussed	Terui et al. (1991a)
As, Bi, Sb, Se	Ni alloys, steel	Pd-$Mg(NO_3)_2$	Digests in aqua regia; no modifier needed for Sb; T_{pyr} 1300, 900, 900, and 1100 °C, resp.; Zeeman STPF	Bettinelli et al. (1994)
As, Cd, Cu, Pb	Heavy oil samples	4 µg Ni (for As); 20 µg $(NH_4)_2HPO_4$ (for Cd, Cu and Pb)	HNO_3-H_2SO_4 digestion; T_{pyr} 1200, 800, 1000, and 1000 °C, resp.	Turunen et al. (1995)
As, Cd, Pb, Se	Aq. solutions	Pd-$Mg(NO_3)_2$	Simultaneous determination; T_{pyr} 350 °C; 600 °C for As, Se, and Pb; 900 °C for As and Se	Sneddon and Farah (1994)
As, Cd, Pb, Se	Highly mineralized waters	15 µg Pd-10 µg $Mg(NO_3)_2$ vs. Ni, Ni-$Mg(NO_3)_2$, and $NH_4H_2PO_4$-$Mg(NO_3)_2$	Pd-Mg recommended; T_{pyr} 1300, 800, 1100, and 1000 °C, resp.; Zeeman STPF	Bozsai et al. (1990)
Bi, Cd, Pb, Sb	Ta_2O_5 (high purity)	Ta_2O_5 matrix	Solid sampling	Belskii and Ocherty-anova (1993)
Cd, Cr, Pb, Ni	Urine	10 µg Pd	1 + 1 dilution; simultaneous determination; T_{pyr} 900 °C	Kobayashi and Imaizumi (1991)
Cd, Co, Ni, Pb	Cabbage, plant leaves, tobacco	Pd-Triton X-100	Slurry sampling; T_{pyr} 650, 1000, 1200, and 550 °C, resp.	Dobrowolski and Mierzwa (1993)

(continued)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cd, Cr, Ni, Pb	Urinary calculi	50 μg $Mg(NO_3)_2$ (for Cr); 15 μg Pd-10 μg $Mg(NO_3)_2$ (for Cd, Ni, and Pb)	Solid sampling (without modification) vs. bomb decomposition STPF; T_{pyr} 800, 1650, 1400, and 850 °C for Cd, Cr, Ni, and Pb in digests	Struebel et al. (1990)
Cd, Cu, Mn, Pb	Blood	10 μg Pd	Simultaneous determination; T_{pyr} 800 °C	Drews (1993)
Cd, Cu, Pb, Zn	Fish, meat	$Mg(NO_3)_2$, $NH_4H_2PO_4$	$HCl-HNO_3$ (1 + 1) digestion vs. dry ashing	Zachariadis et al. (1995)
Co, Cu, Fe, Ni	HfF_4	$NH_4H_2PO_4$, HNO_3, H_2SO_4	Modifiers decrease background but impair recoveries (85%); final solutions in dil. HF; Zeeman STPF	Jaganathan and Aggarwal (1993a)
Co, Cu, Fe, Ni	LaF_3	5 M HNO_3, $NH_4H_2PO_4$	5 M HNO_3 preferred; phosphate increased background; Zeeman STPF	Jaganathan and Aggarwal (1993b)
Co, Cu, Fe, Ni	Zr based glass	$ZrOCl_2$-4 M HNO_3	—	Jaganathan et al. (1992)
Cr, Cu, Fe, Mn	Silicon nitride	$NH_4H_2PO_4$-$Mg(NO_3)_2$	Slurry sampling	Friese and Krivan (1995)
Cr, Mn, Ni, Pb	Blood	Pd preferred to Mg or Ni	Simultaneous determination; T_{pyr} 500 °C; STPF	Hirano et al. (1992)
Cu, Fe, Pb, Ni	Milk, liver, urine	Pd-H_2	Modifier conditioned in H_2 at 300 °C; T_{pyr} 1000 °C (in Ar); hot injection; fast program (45 s)	Kunwar et al. (1990)
Ga, In, Te, Tl	Ni base alloy	0.05–0.1% $Rh(NO_3)_3$	T_{vap} 1100 °C	Funato and Takasaka (1991)
Al, Cu, Fe, Mn, Zn	Biological RMs	$NH_4H_2PO_4$	Microwave bomb decomposition; final digests in 1 M HNO_3	Isoyama et al. (1990)
Cd, Cr, Cu, Pb, V	Aq. solutions, serum	Pd-$Mg(NO_3)_2$	Simultaneous multielement determination; Zeeman STPF	Harnly and Radziuk (1995)

As, Cr, Pb, Se, Sn	Aq. solutions	Ascorbic acid, H_2, CO, CO_2	Mechanisms studied in pyrocoated and glassy carbon tubes	Gilchrist et al. (1990)
Cd, Cu, Ge, Pb, V	Aq. solutions	WC sputtered platform	T_{pyr} 700, 1400, 550, 1000, and 2500 °C, resp.; m_o for Ge improved 2-fold	Benzo et al. (1992)
Cd, Cr, Cu, Ni, Pb	Air filters	Pd (for Cd and Pb), 0.2% HNO_3 (for Cu, Cr and Ni)	Solid sampling; "cup-in-tube"; T_{pyr} 850, 1300, 1200, 1400, and 1200 °C, resp.	Almeida and Lima (1995)
As, Cd, Hg, Pb, Sn	Marine sediment	Pd-$Mg(NO_3)_2$-Triton X-100	Slurry sampling; T_{pyr} 1200, 700, 200, 900, and 1300 °C, resp.	Bermejo-Barrera et al. (1996a)
Cr, Cu, Fe, Mn, Ni	Fish, feed, food, oyster, plant, tissues	60 μg $Mg(NO_3)_2$ (for Cr); 50 μg NH_4NO_3 (for Cu); 25 μg Pd-125 μg citric acid (for Fe and Mn)	Slurry in 0.25% TMAH-10% ethanol; T_{pyr} 1450, 900, 1100, 800, and 1200 °C for Cr, Cu, Fe, Mn, and Ni, resp.; no CM for Ni; Zeeman	Tan et al (1996a)
Cu, Fe, Mn, Na, Zn	Ta powders (high purity)	Ta matrix	Solid sampling; T_{pyr} 1200, 1200, 1400, 1300, and 800 °C, resp.; LODs 1, 27, 1.5, 0.7, and 0.1 ng/g, resp; STPF	Friese et al. (1996)
Cd, Cu, Fe, Mn, Pb	Flour, kidney, liver, milk, mussel, plant, sediment, soil, urban particulate	$NH_4H_2PO_4$-$Mg(NO_3)_2$ (for Cd and Pb); Se (for Cu); $Mg(NO_3)_2$ (for Fe and Mn)	Microwave digestion; Zeeman STPF	Chakraborty et al. (1993b)
Bi, Cr, Ga, Mn, Pb	Aq. solutions	Pd	Atomization efficiencies estimated; STPF	Yang and Ni (1995)
Co, Cr, Fe, Mn, Ni	Reactor coolant water	2 μL of 50% HF	H_3BO_3 interference (up to 13 g/L) eliminated; LODs improved; STPF	Tompuri and Tumavuori (1996)
Al, Cd, Cu, Fe, Pb	Cork stoppers	$Mg(NO_3)_2$ (for Al and Fe); Pd-$Mg(NO_3)_2$ (for Pb); $NH_4H_2PO_4$ (for Cd)	HNO_3-HCl-HF digestion	Soares et al. (1993)
Bi, Pb, Se, Te, Tl	High-temperature alloys	Pd-$Mg(NO_3)_2$; Ni; PO_4^{3-}-$Mg(NO_3)_2$ (for Pb)	HNO_3-HF digests	Reichardt (1992)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Bi, Pb, Se, Te, Tl	Ni-base alloys	1 mg Ni (matrix); 20 μg Pd also tested	Solid sampling, "cup-in-tube"; Ni pretreated at 1000 °C in 5% H_2-Ar preferred; 20 μg Pd useful for Bi and Tl; Zeeman	Irwin et al. (1990)
Cd, Mn, Pb, Se, V	Aq. solutions	Ir (deposited by cathodic sputtering)	T_{vap} 800, 1200, and 1400 °C for Cd, Pb, and Se, resp.; permanent modification	Rademeyer et al. (1995)
Cd, Cu, Pb, Se, Zn	Blood (Pb), serum (Cd, Cu, Se, Zn)	0.1 M NH_4NO_3-0.1% $Mg(NO_3)_2$-0.2% Triton X-100 (for Cu, Pb, Zn); 0.2% Triton X-100 (for Cd); 0.5 g/L Fe-1.25 g/L Ca^{2+}-0.2% Triton X-100 (for Se)	2-21-fold dilution with CM solution; T_{pyr} 530, 800, 700, 1000, and 700 °C, resp.; Zeeman STPF	Zhao et al. (1990)
Cr, Cu, Fe, Pb, Zn	Chewing gum, sweets	0.1% $NH_4H_2PO_4$-4% v/v H_2O_2-8% C_2H_5OH	Slurry of calcinated samples	Vinas et al. (1994b)
Ag, Cd, Co, Cr, Pb, V	Aq. solutions	100–200 μg $NH_4H_2PO_4$ or 1–2.5 μg Pd; 1 μg La (for V)	WETA 90 tungsten tube atomizer; T_{pyr} 500–600 °C (Ag), 500–600 °C (Cd), 1200 °C (Co), 1100–1200 °C (Cr), 700–1000 °C (Pb), and 1400 °C (V)	Krakovska and Pulis (1993)
Cd, Cr, Cu, Fe, Mn, Pb	Aquatic moss, grass, plant, total diet	Pd-$Mg(NO_3)_2$	Simultaneous multielement determination with frequency-modulated ETAAS; T_{pyr} 850 °C (Cd)	Edel et al. (1995)
Co, Cr, Cu, Fe, Mn, Ni	Glass, quartz	Pd, $Mg(NO_3)_2$, Pd-$Mg(NO_3)_2$	No influence of CMs on performance in slurry sampling ETAAS	Bendicho and de Loos-Vollebregt (1990a)
Co, Cr, Cu, Fe, Mn, Ni	Glass, quartz	3% HF	Slurry sampling; Zeeman STPF	Bendicho et al. (1990b)
In, Ni, Pb, Pd, Se, Sn	Aq. solutions	Pd; Ni (for Pd)	Mechanisms studied; alloy formation discussed	Oishi et al. (1991)
Cd, Co, Mn, Pb, Se, Tl	Aq. solutions	8 μg Pd; 8 μg Pd-24.5 μg C; 8 μg Pd-60 μg ascorbic acid; 8 μg Pd-6 μg Mg; 8 μg Pd-6 μg Mo	Mechanisms studied, STPF	Qiao and Jackson (1991)

Al, Cu, Fe, Pb, V, Zn	Blood, bone, erythrocytes, plant, sediment, serum, urine, vehicle exhaust particulates	0.1–0.5 μg/mL Pd-2% citric acid (for Pb and V)	Samples/digests in 10 mM HNO_3-0.1% Triton X-100; LODs 0.5, 0.3, 0.5, 0.1, 0.4, and 0.1 μg/L, resp.	Tahan et al. (1994)
As, Cd, Pb, Sb, Se, Sn	Hair, nail	20 μg Pd (for As, Sb, Se and Sn); 50 μg $(NH_4)_2HPO_4$ (for Cd and Pb)	TAAH solubilized samples; 15 elements determined; T_{pyr} 600 (Cd), 750 (Pb), 1100 (Se), and 1200 °C (As, Sb and Sn)	Tsalev et al. (1993)
Cd, Cr, Cu, Ni, Pb, Zn	Sediment/soil extracts	Pd	CH_3COONH_4 extracts	Ure et al. (1993)
Al, Cd, Co, Cr, Pb, Mn	Serum	Pd, $Mg(NO_3)_2$	Overview; standard additions often lead to erroneous results	Hulanicki et al. (1992b)
Cd, Cr, Cu, Fe, Mn, Mo, Pb	Diet, liver, milk, oyster, plant, sludge, tissues, urine, vegetables, water	2 μg Pd; 2 μg Rh; H_2 during pyrolysis	Pd more useful with samples other than water; ETAAS, FANES, and continuum-source ETAAS for multielement determinations	Littlejohn et al. (1991)
Co, Cr, Cu, Fe, Mg, Mn, Ni	Molybdenum (metal, oxide, silicide)	H_2-Ar, CCl_4, CF_4 (volatilizers)	Atomization and cleaning stages assisted by reactive gases additions	Docekal and Krivan (1993a)
As, Bi, Cd, Pb, Sb, Se, Tl	Bone, fish, hair, kidney, mussel, plant, urine	Pd-W; Pd-W-NH_4NO_3; W-NH_4NO_3	HNO_3 digested tissues; TAAH solubilized hair; 5–10-fold diluted urine	Tsalev et al. (1996c)
Ag, As, Bi, Ga, In, Pb, Sb, Se	Aq. solutions	1–2 μg Pd; 1 μg Pd-1 mg ascorbic acid (for Ga)	WETA tungsten tube atomizer; T_{pyr} 850, 1200, 1100, 1200, 1200, 1100, 1300, and 1300 °C, resp.; interference study	Shan et al. (1992a)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Ag, As, Bi, Ga, In, Pb, Sb, Se	Aq. solutions	Pd; Pd-ascorbic acid (for Ga)	WETA tungsten tube atomizer; T_{vap} 850, 1200, 1100, 1200, 1200, 1100, 1300, and 1300 °C, resp.; m_o improved 3–10-fold vs. GFAAS	Shan et al. (1991)
Ag, Cd, Co, Cr, Mn, Mo, Pb, V	Aq. solutions	7.5 μg Pd	T_{pyr} 900 °C, T_{at} 2390 °C (multielement conditions); Zeeman STPF	Berglund et al. (1991)
Cd, Cu, Cr, Fe, Mn, Ni, Pb, Zn	Fish	$Mg(NO_3)_2$-$NH_4H_2PO_4$	HNO_3-$HClO_4$ digests; STPF	Currey et al. (1992)
Bi, Cu, Fe, Ni, Pb, Se, Te, Zn	Ag	Ag matrix	Fast program; STPF	Hinds (1992)
Al, Cd, Cr, Cu, Mn, Ni, Se, Zn	Blood, serum	Pd-Triton X-100	—	Nomura et al. (1995)
Al, Cr, Cu, Fe, K, Li, Mg, Mn, Na	Quartz (high purity)	W- or Zr-treated platform; $Mg(NO_3)_2$ (for Al)	Solution vs. slurry sampling; Zeeman STPF	Hauptkorn and Krivan (1996)
As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	Plant, seawater, sediment, soil	Pd (for Cd, Co, Cr, Cu, Ni and Zn); Ir-Mg (for As); Pt (for Mn); Pd-$Mg(NO_3)_2$-$NH_4H_2PO_4$ (for Pb)	STPF for As, Cd, Mn, Pb, Zn); wall atomization for the rest of analytes; fast programs possible	Hoenig and Gilissen (1993)
Al, B, Be, Cd, Dy, Ge, P, Se, Sm, Sn	Environmental samples	$Ca(NO_3)_2$	—	Yao and Jiang (1991b)
As, Bi, Cd, Pb, Sb, Se, Sn, Te, Tl	Aq. solutions	2 μg Ir on Zr- or W-treated platform (permanent modifier)	Double peaks for Bi and Te with Ir-W treated platforms; STPF	Tsalev et al. (1995)
Ag, Cd, Co, Fe, Ir, Ni, Mn, Pb, Rh, Ru	Pd, Pt	W-impregnated GT; Pt; $Sr(NO_3)_2$ (for Ag)	Effect of Pd and Pt matrix studied	Arpadjan et al. (1990)
As, Bi, Ga, Ge, In, Pb, Sb, Se, Sn, Te	Aq. solutions	Pd or Pd-albumin	Best sensitivity enhancement for Sn (11 fold), In (4.8 ×), and Sb, Se and Te (2.0 ×)	Katsura et al. (1992)
As, Be, Cd, Co, Mo, Pb, Sb, Se, Sn, Tl, V	Sewage sludge	15 μg Pd-10 μg $Mg(NO_3)_2$	Bomb decomposition; STPF	Bettinelli and Baroni (1990)

As, Bi, Cd, Co, Ni, Pb, Sb, Se, Sn, Te, Tl	Biological samples	Ascorbic acid, $Ni(NO_3)_2$, H_2SO_4	Microwave digestion for ETAAS or ICP-AES	Sedykh et al. (1991)
Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni	Mo_2O_3 (high purity)	Mo_2O_3 matrix (100–250 mg/10 mL)	Slurry sampling; T_{pyr} 900–1000 °C	Docekal and Krivan (1993b)
Ag, Al, As, Be, Cd, Co, Cu, Ga, In, Mn, Pb, Se, V, Y	Aq. solutions	Ascorbic acid, Mg, Pd, PO_4^{3-}	Review; stabilization and atomization mechanisms studied	Styris and Redfield (1993)
As, Bi, Co, Cu, Fe, In, Mn, Ni, Pb, Sb, Se, Sn, Te, Tl	Aq. solutions	Pd, Pd-Zr, Pd-W, Pd-Zr-citric acid, Pd-W-citric acid	T_{vap} tabulated; mechanisms discussed	Havezov et al. (1995)
Al, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Si, Zn	ZrO_2, ZrO_2-Y_2O_3	ZrO_2 matrix; H_3BO_3-HF (for Al); 50 µg $(NH_4)_2HPO_4$-3 µg $Mg(NO_3)_2$ (for Cd); 80 µg $Ca(NO_3)_2$ (for Si)	Slurry vs. liquid sampling; STPF	Schneider and Krivan (1995)
Ag, As, Au, Bi, Cd, Ga, Ge, Hg, In, Mn, Pb, Sb, Se, Sn, Te, Tl	Aq. solutions; river sediment (for Bi, Mn and Pb); coal fly ash (slurried, for Ga and Pb)	Pd, Pd-$Mg(NO_3)_2$, Pd-ascorbic acid	Pd modifiers critically compared; Pd-Mg not recommended because of higher background absorbance, yet similar performance	Shan and Wen (1995)
Ag, As, Au, Bi, Cd, Cu, Ga, Ge, In, Mn, P, Pb, Sb, Se, Sn, Te, Tl, Zn	Aq. solutions	4 µg Pd, Rh or Ru, with or without 200 µg ascorbic acid	T_{vap} higher for As, Ge, In, P, Se, and Tl in the series Ru > Rh > Pd	Tsalev and Slaveykova (1992b)
Ag, As, Au, Bi, Cd, Cu, Ga, Ge, In, Mn, P, Pb, Sb, Se, Sn, Te, Tl, Zn	Aq. solutions	Sc, Y, La, Ce, Ce-Pd, Mo-Pd, W-Pd	Classification of CMs into 3 groups proposed; several new mixed modifiers proposed; T_{pyr} compared for a series of CMs (Sc-Y-La-Ce)	Tsalev et al. (1990c)

(*continued*)

Appendix 3. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Ag, Al, As, Au, Bi, Cd, Cu, Ga, Ge, Hg, In, Mn, P, Pb, Sb, Se, Si, Sn, Te, Tl, Zn	Aq. solutions	32.5 μg $Pd(NO_3)_2$-10 μg $Mg(NO_3)_2$	Thermal stabilization and tolerance to Cl^- and SO_4^{2-} studied	Welz et al. (1992c)
Ag, As, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, Mn, Ni, P, Pb, Sb, Se, Si, Sn, Te, Tl, Zn	Aq. solutions	$(NH_4)_2Ce(NO_3)_6$; Pd-$(NH_4)_2Ce(NO_3)_6$	T_{vap} higher with the mixed modifier	Mandjukov and Tsalev (1990)
Ag, Al, As, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, Mn, Ni, P, Pb, Sb, Se, Si, Sn, Te, Tl, Zn	Fish (As, Cu), hair (Sn), kidney (Se), mussel (As), sediment (Tl)	20 μg V (as NH_4VO_3), 20 μg V-4 μg Pd, 20 μg V-100 μg PO_4^{3-}	Systematic study of V-based modifiers; better thermal stabilization with mixed modifiers	Tsalev et al. (1990a)
Rare earth elements	Aq. solutions	1.8% m/v PTFE slurry	16 rare earth elements studied; vaporization assisted	Huang et al. (1992)
Y, rare earth elements	Aq. solutions	0.3% Freon (CHF_3) in Ar	Systematic ETAAS and ETV-ICP-MS studies; reduced memory effects in the presence of Freon; vaporization mechanisms studied	Goltz et al. (1995c)
17 elements	Biological tissues	Various	Solid sampling for tissues reviewed	Herber (1995)
33 elements	Acids (Cu and Tl only determined)	10 μg Pd or 10 μg Pd + H_2	Pd + 10% H_2-Ar preferred for P and Sn; T_{vap} tabulated; STPF with glassy carbon platforms	Heinrich and Dette (1996)
Many analytes	Various	Pd-based modifiers	Review with 42 references	Matsumoto (1993b)

Note: [a]For literature before 1990, see reviews by Ni and Shan (1987), Tsalev et al. (1990b), and bibliography (Tsalev, 1991).

Appendix 4. Chemical Modification Combined with Preconcentration or Speciation

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Ag	Seawater	In	Ag(I) thiocyanate complex extracted with trioctylmethylammonium chloride-xylene, then back-extracted in dilute HNO_3; LOD 1.3 ng/L;	Shimizu et al. (1994a)
Al	Fe, steel	$MgSO_4$	Acid soluble Al (in H_2SO_4) determined	Naka et al. (1990a, 1990b)
As	Drinking water	Pd (electrodeposited or sputtered) on W, Ta, Mo, or Re platforms	HG-trapping-ETV-ICP-MS; Pd-sputtered W platforms preferred; LOD 0.01 µg/L	Marawi et al. (1995)
As	Environmental waters	Zr; Zr-coated GT; HCl	Both As(III) and As(V) coprecipitated with hydrated Zr(IV) oxide; $AsCl_3$ fractionally volatilized at 1100–1400 °C upon conc. HCl addition; T_{vap} 1400 °C for As(V)	Chen et al. (1993a)
As	Marine sediment	Pd-$Mg(NO_3)_2$ preferred to $LaCl_3$-HNO_3	Slurry sampling; also As(III) speciation after dithiocarbamate extraction	Bermejo-Barrera et al. (1995a)
As	Soil	5 µg Pd-3 µg $Mg(NO_3)_2$	Bomb decomposition with HNO_3-HF-$HClO_4$ vs. aqua regia; APDC-MIBK extraction; T_{pyr} 1000 °C; Cd and Tl also determined in extracts by FAAS	Ivanova et al. (1995)
As	Steel, mine water, river water	$(NH_4)_2MoO_4$	Molybdenoheteropolyacid-MIBK extraction; C_o 1.58 µg/L	Kanke et al. (1991)
As	Urine	20 µg Pd (deposited on platform)	HG-trapping-ETV-ICP-MS; T_{coll} 400 °C; T_{pyr} 1200 °C; LOD 2 ng/L	Marawi et al. (1994)
As	Urine	37.5 µg $Pd(NO_3)_2$-25 µg $Mg(NO_3)_2 \cdot 6H_2O$	Toluene-iodide extraction from ca. 10 M HCl; back-extraction with 1% HNO_3; T_{pyr} 400 and 1300 °C; Zeeman ETAAS; part of a speciation scheme involving also HPLC-ICP-MS	Bavazzano et al. (1996)
As	Urine, urine fractions	Pd-$S_2O_8^{2-}$; $Mg(NO_3)_2$-Triton X-100	"Total", "inorganic" and "organic" fractions separated by cation exchange	Nixon and Moyer (1992)
As	Water	Pd	Speciation of As(III) and As(V)	Qi et al. (1994)

(*continued*)

Appendix 4. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
As	Water (tap, waste, well)	Pd-W-citric acid	As(III)/As(V) separated on $(C_8H_{17})_2SnCl_2$-*n*-decanol modified silica; arsenate eluted with 2 M HCl; T_{pyr} 1200 °C; STPF	Havezov and Russeva (1993); Russeva et al. (1993)
As	Water (river, sea)	Pd	FI-HG-trapping-ETAAS; T_{coll} 200–600 °C; LOD 36 pg	An et al. (1992)
Be	Rain water, seawater	Activated carbon; also tested Al, Ni, Rh (as nitrates)	Preconcentration of Be(II) acetylacetonate on activated carbon; no further improvement by metal modifiers; T_{pyr} 900 °C	Okutani et al. (1993)
Be	Seawater	500 µg/mL Mg^{2+}	Coprecipitation with $Mg(OH)_2$ and Sn(IV) hydroxides; LOD 0.5 ng/L	Hiraide et al. (1994)
Bi	Blood, serum	260 µM $PtCl_4$-26 mM HNO_3	APDC-MIBK extraction	Slikkerveer et al. (1991)
Bi	Mussel, plant leaves, rock, sediment, tea	10 µg Pd	Preconcentration on anion exchange resin Bio-Rad AG 1 X-4; T_{pyr} 600 °C	Kuroda et al. (1991)
Cd	Aq. solutions	5 µg Pd	Vapor generation-trapping-ETAAS; T_{coll} 150 °C; T_{pyr} 800 °C; LOD 60 ng/L; STPF	Goenaga Infante et al. (1996)
Cd	Seawater	Ir-, W-, and W-treated GTs	FI-vapor generation-trapping-ETAAS; T_{coll} 20 °C; Ir coating recommended; m_o 3 pg; LOD 4 ng/L	Bermejo-Barrera et al. (1996g)
Cd	Soil, soil extracts	140 µg PO_4^{3-}-7 µg $Mg(NO_3)_2$	Speciation scheme; T_{pyr} 700 °C; Zeeman STPF	Dubois (1991)
Cd	Zn (high purity)	Various CMs compared (1 µg in 3.2 M H_2SO_4): Ag, Au, Cu, Fe, Ni, Pd, Pt, Zn	After coprecipitation with $Fe(OH)_3$; 400 µg/mL Fe-3.2 M H_2SO_4 in final solutions; T_{pyr} 600 °C	Ashino and Hirokawa (1995)
Co	Water (nuclear reactor coolant)	Ni	Solvent extraction using water-in-oil and oil-in-water emulsions; LOD 10 ng/L	Okamoto et al. (1990)
Cr	Feed	Pd-$Mg(NO_3)_2$	T_{pyr} 1600 °C; total Cr after HNO_3-HCl-HF digestion (LOD 0.53 µg/L); Cr(VI) after leaching with 10 mM NaOH (LOD 0.42 µg/L)	Soares et al. (1993)
Cr	Seawater	Pd-$Mg(NO_3)_2$ and Ta-treated GT	Coprecipitation of Cr(III) with $Ga(OH)_3$ at pH 9.3–10.0; T_{pyr} 1900 °C; LOD 0.02 µg/L	Boughriet et al. (1994)

Cr	Water	$Mg(NO_3)_2$ vs. HNO_3 and Na_2WO_4	Cr(III) speciation after quinolin-8-ol-MIBK extraction; $Mg(NO_3)_2$ preferred; hot injection; T_{pyr} 1400 °C	Beceiro-Gonzalez et al. (1993)
Cu	Flour, plant leaves	Mg(II) oxinate; Ni(II) complexes	Coprecipitation with Mg(II) quinolin-8-ol or Ni(II)-DMG-PAN	Atsuya et al. (1990)
Fe	Cerebrospinal fluid	$Mg(NO_3)_2$	Fe, transferrin and ferritin levels	Gruener et al. (1991)
Fe	Fe oxides mixtures, iron rust	0.5% m/v suspension of carbon black	Differentiation between Fe(II) and Fe(III) in the presence of modifier; T_{pyr} 790 °C	Yoshimura and Huzino (1990)
Ge	Aq. solutions	Pd	FI-HG-trapping-ETAAS	Wang et al. (1995)
Ge	Aq. solutions	Pd-, Zr- and Pd-Zr-coated GTs	Sample injection vs. HG-trapping-ETAAS; T_{coll} 800 °C	Ni and Zhang (1995)
Ge	Coal fly ash, river sediment, soil	Pd-treated GT	HG-trapping-ETAAS; 0.15–0.6 M $HClO_4$ medium; m_o 46 pg; LOD 36 pg	Ni and He (1995)
Ge	Garlic, geol. RMs, ginseng, tap water	Pd-treated GT	FI-HG-trapping-ETAAS; T_{coll} 400 °C; LOD 4 ng/L	Tao and Fang (1993)
Ge	Ginseng	10 µg/mL Ni (as nitrate)	$GeCl_4$ extraction and back extraction; T_{pyr} 700 °C	Bao et al. (1991)
Ge	NaCl	Pd, Pd-$Mg(NO_3)_2$	Direct ETAAS and HG-trapping-ETAAS studied; T_{coll} 800 °C; T_{pyr} 1200 °C; LOD 30 pg	Haug and Ju (1990)
Ge	Plant (ginseng, etc.)	Aqueous NH_3 in Mo-treated GT	After extraction with phenylfluorone-isopropylacetone-*NN*-dimethylformamide; T_{pyr} 900 °C	Bao et al. (1992)
Ge	Rock, sediment, steel	Pd, Ir, Ir-Pd, Pd-$Mg(NO_3)_2$; coatings: Nb, Ta, W, Zr	HG-trapping-ETAAS; T_{coll} 400–500 °C (noble metal) or 500–600 °C (carbide); m_p 10–54 pg	Haug and Liao (1995)
Hg	Blood	15 µg Pd-10 µg $Mg(NO_3)_2$	Diethyldithiocarbamate-toluene extraction; T_{pyr} 250 °C	Emteborg et al. (1992)
Hg	Bone, fish, milk, plant, seawater, sediment, shrimp, soil, water	Ir vs. Pd (permanent modifiers)	CVT-in situ collection-FANES LOD 0.9 ng/L with Ir	Dittrich et al. (1994)
Hg	Cellulose, fish, kidney, sewage sludge, shrimp	Au or Pd permanent modifier	CVT-in situ collection-FANES; T_{vap} 150 °C (Au) or 170 °C (Pd)	Dittrich and Franz (1993)
Hg	Marine tissues	5 mM $Na_2S_2O_3$	Toluene extraction of org. Hg; back extraction into CM solution; T_{pyr} 150 °C, T_{at} 900 °C; Zeeman	Shintsu et al. (1992)

(*continued*)

Appendix 4. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Hg	Water	Ir permanent modifier or Au-Pt gauze	FI-CVT-ETAAS; T_{coll} 150 °C	Sinemus et al. (1993a)
Hg	Water	120 µg Ir permanent modifier	CVT-trapping-ETAAS; T_{coll} 150 °C, T_{at} 900 °C; coating lifetime 500 firings; LOD 70 pg; Zeeman STPF	Sinemus et al. (1993b)
I^-	Aq. solutions	Pd	Ion association complex between Hg(II), I^- and 2,2′ dipyridyl extracted; Hg measured by ETAAS; T_{pyr} 200 °C	Bermejo-Barrera et al. (1995a)
I^-	Tap water	Pd, S^{2-}, air, O_2	Indirect method; Hg_xI_y complex formed, and Hg signal measured by ETAAS; LOD 3 µg/L I^-; m_o 38.8 pg I^-	Bermejo-Barrera et al. (1994c)
In	Aq. solutions	Pd-treated platform	HG-trapping-ETAAS; T_{coll} 800 °C	Liao and Li (1993)
In	Blood, bone, tissues	50 µg/mL Pd	Ion pair extraction of $InCl_4^-$ with Aliquat 336-hexane-MIBK, back extraction with 5% HNO_3-5% CH_3COOH; T_{pyr} 450 and 795 °C	Zheng et al. (1993a)
In	Rock, soil	Cr	Iodide-MIBK extraction; Zeeman	Fang and Shi (1990)
In	Silicate rock	30 µg Ni	Cation exchange on cellulose phosphate; then anion exchange in HCl-NH_4SCN medium; T_{vap} 600 °C	Kuroda et al. (1990b)
In	Water	1.4 µg Pd	In(III) acetylacetonate sorbed on activated carbon at pH 6–8, slurried in 2% glycerol; T_{pyr} 800 °C; LOD 25 ng/L	Wei et al. (1994)
Mn	Zn	Y and Y-treated GT	Coprecipitation with $Y(OH)_3$ at pH 9.0–11.3	Takeda et al. (1994)
Mo	Mo compounds dispersed in water	Carbon black	Differentiation between different compounds attempted	Yoshimura and Huzino (1992)
P	Aq. solutions	PO_4^{3-}	Indirect determination based on the enhancement effect of PO_4^{3-} on Zn	Fukushima et al. (1993)
Pb	Aq. solutions	Pd-treated GT; Zr-treated GT	Direct ETAAS or HG-trapping-ETAAS; kinetics studied	Yan and Ni (1993)

Pb	Aq. solutions	$(NH_4)_2Ce(NO_3)_6$-KI	Plumbane generation and trapping in an absorbing solution containing modifier for ETAAS; T_{pyr} 750 °C; T_{vap} 850 °C; m_p 20 pg	Tsalev et al. (1992)
Pb	Coal fly ash, mussel, tea, water	Zr-treated GT	HG-trapping-ETAAS; T_{coll} 300 °C; m_o 52.8 pg, LOD 242 pg	Yan and Ni (1991)
Pb	Sediment	Ir, Pd-Ir, Ir-Mg, W- and Zr-coatings	HG-trapping-ETAAS; ^{209}Pb study; best sensitivity with Ir; m_o 21 pg; LOD 0.25 ng	Haug (1996)
Pb	Water (riverine, sea), fish, lobster	150 µg Ir (conditioned at 1100 °C)	FI-ethylation with $NaB(C_2H_5)_4$; tetraethyllead trapped at 300 °C; LOD 12 pg; Zeeman STPF	Willie (1994)
Pt	Blood, plasma, plasma ultrafiltrate	Aq. NH_3	Total Pt determined by ETAAS; speciation performed with LC-UV detection	Amorusi et al. (1994)
Se	Aq. solutions	50 µg Ir as permanent modifier	FI-HG-trapping-ETAAS; STPF	Schlemmer and Feuerstein (1993)
Se	Aq. solutions	Pd-Ir-treated platform	HG-trapping-ETAAS; T_{coll} 250 °C; hydride atomization studied; STPF	Dedina et al. (1996)
Se	Aq. solutions (NaCl added)	Pd-$Mg(NO_3)_2$; BN-coated GT	Se(IV), Se(VI) and selenomethionine studied; in-situ preatomization separation of Se(IV) as volatile piazselenol possible	Krivan and Kueckenwaitz (1992)
Se	Blood, blood cells, plasma	Pd-$Mg(NO_3)_2$-H_2O_2	Isolation of cell fractions and Se levels discussed; LOD 50 mmol/L; Zeeman STPF	Ruekgauer et al. (1995)
Se	Bone meal, feed, meat, plant	$Ni(NO_3)_2$	APDC-MIBK extraction	Brown and Zeringue (1991)
Se	Environmental waters	7.5 µg Pd-5 µg $Mg(NO_3)_2$	Anion exchange separation of *i*-Se species; LODs 2.1 and 2.4 µg/L for Se(IV) and Se(VI), resp.	Pyrzynska (1995b)
Se	HPLC effluents	Ni	IC separation of selenite and selenate	Koelbl et al. (1993)
Se	HPLC effluents	200 µg Ni-50 µg $Mg(NO_3)_2$	Anion exchange IC in 10 mM ammonium citrate, pH 3.0 and 7.0 for selenite, selenate, and $(CH_3)_3Se^+$; LOD 1.2 µg/L	Laborda et al. (1993a)
Se	Nutritional supplement formula	50 µg Ir (permanent modifier)	FI-HG-trapping-ETAAS; T_{coll} 250 °C	Hanna et al. (1995)
Se	Sediment, seawater, lake water	2 µg Pd	Preconcentration of Se(IV)-Bismuthiol II complex on activated carbon; slurry sampling	Kubota et al. (1995)

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Appendix 4. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Se	Soil	Pd	HG-trapping-ETAAS; T_{coll} 700 °C; $(CH_3)_2Se$ and $(C_2H_5)_2Se$ also determined; m_o 15 pg	Zhang et al. (1991a)
Se	Soil	Pd-treated GT	GC-trapping-ETAAS for speciation of $(CH_3)_2Se$, $(C_2H_5)_2Se$ and $(CH_3)_2Se_2$ with m_p 18, 12, and 30 pg, resp.; T_{coll} 500, 700, and 700 °C, resp.	Jiang et al. (1992)
Se	Urine	Pd	Ion pair extraction for speciation of $(CH_3)_3Se^+$; LOD 1 µg/L	Tsunoda et al. (1994)
Se	Urine	$PdCl_2$ (dried at 120 °C)	HG-trapping-ETAAS; T_{coll} 400 °C; LOD 20 ng/L or 20 pg	Ni et al. (1993b)
Se	White clover	20 µg $Ni(NO_3)_2$	HPLC-ETAAS speciation of selenocystine, selenomethionine, Se(IV) and Se(VI); T_{pyr} 650 °C	Potin-Gautier et al. (1993)
Sn	Aq. solutions	100 µg Ir permanent modifier	FI-HG-trapping-ETAAS for *i*-Sn and butyltins; T_{coll} 500 °C; isoformation not possible; STPF	Erber et al. (1996)
Sn	Aq. solutions	$(NH_4)_2Ce(NO_3)_6$-KI	SnH_4 generation and trapping in an absorbing solution containing CM for ETAAS; T_{pyr} 900 °C; m_o 29 pg	Mandjukov et al. (1991)
Sn	Fatty foods, food simulants, PVC bottles	Pd-$Mg(NO_3)_2$	Methyltin stabilizers leached; T_{pyr} 250, 700, 730, and 900 °C (stepwise pyrolysis); STPF	Dominic et al. (1993)
Sn	Fruits, vegetables	Mg, Pd, $NH_4H_2PO_4$; Ti- or Zr-coating	Speciation of tricyclohexyltin hydroxide after $CHCl_3$ extraction; Zeeman STPF or Ti-coated tubes	Giordano et al. (1994)
Sn	Ga (high purity)	$AgNO_3$-Mo	SnH_4 generation and trapping in $AgNO_3$ solution; LOD 36 ng/g	Sahayam et al. (1993a)
Sn	Geological RMs, hair, serum, tap water	Pd-treated GT	Fl-on-line enrichment on strongly basic anion exchanger, then HG-trapping-ETAAS; LOD 10 ng/L	Tao and Fang (1995)
Sn	HPLC effluents (water and sediment samples)	Picric acid-tropolone	Butyltins speciation	Astruc et al. (1992b)
Sn	Marine sediments	Pd, $NH_4H_2PO_4$, $K_2Cr_2O_7$, HNO_3	Organotins extracted; Zeeman	Mortensen et al. (1995)

Sn	Minerals, ores, sediments	PO_4^{3-}-$Mg(NO_3)_2$	Trioctylphosphine oxide-MIBK extraction; LOD 10 pg	Elsheimer (1993); Elsheimer and Fries (1990)
Sn	Mussels, sediments	200 μg $NH_4H_2PO_4$-20 μg $Mg(NO_3)_2$	Bis(Bu_2Sn)oxide extracted in *n*-hexane-CH_2Cl_2, purified and back extracted into HNO_3; T_{pyr} 800 °C; Zeeman STPF	Cardelicchio et al. (1992)
Sn	Organic extracts	$PdCl_2(CH_3CN)_2$	Alkyltins thermally stabilized; sensitivity improved by up to 19-fold	Katsura et al. (1990)
Sn	Org. extracts from seawater	$PdCl_2(CH_3CN)_2$, Pd, Pd-albumin, $PdCl_2(C_6H_5CN)_2$, $PdCl_2C_8H_{12}$, $[PdCl(CH_3H_5)]_2$, $Pd(C_5H_7O_2)_2$	Alkyltins extracted with ethylacetate-*n*-hexane (3:2); T_{pyr} 850–1100 °C; $PdCl_2(CH_3CN)_2$ recommended	Matsumoto et al. (1991)
Sn	Seawater	Zr-treated GT	HG-trapping-ETAAS; T_{cell} 500 °C; m_o 14 and 20 pg for i-Sn(II) and Bu_3Sn^+, resp.; Bu_3Sn^+ speciation after extraction in CH_2Cl_2	Ni et al. (1991)
Sn	Sediment	0.04% $K_2Cr_2O_7$-2% HNO_3	HPLC(IC)-ETAAS speciation of BuSn, Bu_2Sn, Bu_3Sn on a strong cation exchanger column; T_{pyr} 850 °C	Pannier et al. (1993)
Sn	Sediment, rock	$(NH_4)_2HPO_4$-$Mg(NO_3)_2$	$LiBO_2$ fusion; TOPO-MIBK extraction	Elsheimer (1993)
Sn	Sediment, water	1% picric acid	HPLC-ETAAS speciation of BuSn, Bu_2Sn, Bu_3Sn, Bu_4Sn tropolone complexes on cyanopropyl bonded silica column; T_{pyr} 750 °C	Astruc et al. (1992a)
Sn	Sewage effluent	Pd	Toluene extractable organotins	Dadfarnia et al. (1994)
Sn	Ship paint leachates	10 μg Pd as $PdCl_2(CH_3CN)_2$ vs. other org. Pd modifiers	Stabilization of alkyltins in ethylacetate-hexane extracts studied; LOD 0.11 ng	Katsura et al. (1991)
Sn	Silicate rocks	80 μg Ca-0.2 M HNO_3	After preconcentration of oxalato complex on strongly basic ion exchange resin Bio-Rad AG 1, X-8(Cl^-); T_{pyr} 700 °C	Kuroda et al. (1990a)
Sn	Silicate rocks	$(NH_4)_2HPO_4$-$Mg(NO_3)_2$	$LiBO_2$ fusion; TOPO-*i*-propylacetone extraction; LOD 10 pg	Elsheimer and Fries (1990)

(*continued*)

Appendix 4. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Te	Aq. solutions	Pd treated platform	H_2Te generated and trapped in Amberlite LA-2	Grotti and Mazzucotelli (1995)
Te	Environmental samples	Pd	APDC-$CHCl_3$-CCl_4 extracts; also speciation of Te(IV)/Te(VI)	Chi et al. (1992)
Te	Geol. materials: minerals, ores, rocks	Ir	Reductive coprecipitation with elemental Hg; LOD 1 ng/g	Kontas et al. (1990)
Te	Geol. samples	2 µg Rh-1 M HCl	MIBK extraction from 4.8 M HCl-1% ascorbic acid solutions	Zhang and Jin (1990)
Te	InP	Pd-$Mg(NO_3)_2$	Bismuthiol II-$CHCl_3$ extracts; T_{pyr} 400 °C (org. phase); 1100 °C (aq. phase)	Taddia et al. (1995)
Te	Ores, concentrates, rocks, sediments	Ni	Preconcentration by coprecipitation and extraction; LOD 8 ng/g	Donaldson and Leaver (1990)
Te	Urine	$PdCl_2$	MIBK extraction from 7 M HCl; multiple injections	Kobayashi and Imaizumi (1990)
Ti	TiO, TiO_2, Ti_2O_3 mixtures	Carbon black suspension	Differentiation between Ti(II), Ti(III), and Ti(IV) oxides attempted	Yoshimura et al. (1993)
Tl	Sediment	Pd-ascorbic acid	Xanthogenate complex adsorbed on activated carbon; slurry sampling	Naganuma and Okutani (1991)
Tl	Urine	Pd-ascorbic acid-Triton X-100	Diisobutylketone extraction from 30% HCl medium; LOD 0.2 µg/L; Zeeman	Collet and Jones (1991)
Al, Mn	Bi_2O_3, ZnO (high purity)	$Mg(NO_3)_2$	Ion pair extraction and back extraction for numerous elements	Karadjova et al. (1991)
Al, Si	Serum	W-treated GT	Anion exchange HPLC-ETAAS for speciation; T_{pyr} 1200 °C	Wrobel et al. (1995)
As, Ge	HCl (for As), seawater (As, Ge), urine (As)	10 µg Pd	HG-trapping-ETAAS; T_{coll} 200–800 and 400–900 °C, resp.	Chaudhry et al. (1991)
As, P	$SiHCl_3$	CuCl	ETV-ICP-MS; sample evaporated on CuCl powder for preconcentration; LODs 0.01 and 0.02 ng/g, resp.	Wei and Yang (1995)

As, Se	Aq. solutions	ZrC coated GT vs. Pd	HG-trapping-ETAAS; T_{coll} 800–900 and 600–800 °C, resp.; m_p 43 and 77 pg, resp.	Garbos et al. (1995)
As, Se	Mineral waters	4 µg Pd	HG-trapping-ETAAS; T_{coll} 300 °C; T_{pyr} 450 °C	Veber et al. (1994)
As, Se	Seawater	Pd-Ir coated GT	Electrochemical HG-trapping-ETAAS	Ding and Sturgeon (1996)
As, Se	Seawater (for As)	Pd-treated GT	HG-trapping-ETAAS	Li et al. (1992)
As, Se	Sulfur	Pd-treated GT	HNO_3 (bomb) digests; HG-trapping-ETV-MIP-AES; LODs 150, and 200 pg, resp.	Matusiewicz and Kurzawa (1991)
Bi, Pb	Ni-base alloys	Pd, EDTA and aq. NH_3 tested	Coprecipitation of Bi(III) with aq. NH_3 and no modifier approach adopted; STPF	Tsai et al. (1994)
Cd, Ni	Protein extracts from bean seeds	Pd-NH_4NO_3 (for Cd)	Separation by ultrafiltration; protein binding capacities and levels discussed	Lange-Hesse et al. (1994)
Cd, Zn	Vegetables	Pd-$Mg(NO_3)_2$ for Cd; $Mg(NO_3)_2$ for Zn	Speciation in various cytosol fractions after Sephadex G-50 separation	Guenther and Waidner (1992)
Cu, Zn	Serum protein fractions	10 µL of 100 mM $(NH_4)_2HPO_4$-20 mM HNO_3 (for Zn)	HPLC on Sephadex-200; T_{pyr} 900 and 1050 °C; LODs 1.6 and 0.64 µg/L, resp.	Gless et al. (1991)
Mo, V	Sediment extracts	2 µg Pd (for Mo); 25 µg $NH_4H_2PO_4$ (for V)	Speciation scheme for 9 elements; T_{pyr} 1750 and 1200 °C, resp.	Davidson et al. (1994)
Ni, V	Sediment extracts	100 µg $NH_4H_2PO_4$	Part of a speciation scheme; T_{pyr} 1200 °C	Belazi et al. (1995)
Se, Te	Alloys (Ni-based, heat resisting superalloys, steel)	Pd	Reductive coprecipitation with ascorbic acid	Ashino and Takada (1995)
Se, Te	Fe (high purity)	Pd	Preconcentration by reductive coprecipitation with Pd; T_{pyr} 1200 °C; LODs 17 and 11 ng/g, resp.	Ashino et al. (1994)
Se, Te	Garlic, mussel, rice flour	Ag-treated vs. Pd-treated GTs	HG-trapping-ETAAS; Ag preferred for lower T_{at} (1800 °C); T_{coll} 200–400 and 200–800 °C, resp.; m_o 17 and 18 pg, resp.	Ni et al. (1993a)
Se, Te	Pb alloys	100 µg $Ni(NO_3)_2 \cdot 6H_2O$	Coprecipitation with As; T_{pyr} 700 and 900 °C, resp; STPF	Fox (1990)
Te,Tl	Ni-base alloys	Ni matrix (for Te); Pd, EDTA, aq. NH_3, etc. tested	T_{pyr} 1000 °C (for Te); coprecipitation for Tl; STPF	Tsai et al. (1993)

(continued)

Appendix 4. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
As, Bi, Sb	Low-alloy steel	Ir, Ir-Mg, lr-Pd; carbide-treated surfaces (Nb, Ta, W, Zr)	FI-HG-ETAAS with in situ trapping on permanently-modified GTs or tubes with integrated platforms; ZrC preferred for lifetime over 400 cycles; m_o 16, 9 and 15 pg and LODs 15, 27, and 10 pg, resp.	Haug and Liao (1996)
As, Bi, Se	Aq. solutions	50 µg Pd-50 µg Ir	FI-HG-ETAAS with in situ trapping; permanent modifier useful up to 300 cycles; m_o 45, 76, and 61 pg, resp.	Shuttler et al. (1992)
As, Sb, Sn	Gold	Pd-citric acid	Au matrix precipitated with hydrazine; STPF or W coil atomizer; tolerance to 1.8 M Cl^-	Ivanova et al. (1990)
Bi, Sb, Sn	Copper	Cu-Mn	Coprecipitation with MnO_2; standards containing Cu and Mn	Kurata et al. (1990)
Cd, Co, Pb	Chlorinated solvents/extracts: CCl_4, $CHCl_3$, $C_2H_2Cl_2$	$PdCl_2(MTOA)_2$-MIBK extracts; W-treated GT	T_{vap} 800 and 1000 °C for Cd and Pb with 20 ng Pd CM; T_{pyr} 500, 1500 and 800 °C with W-treated GTs (recommended)	Tserovsky et al. (1993)
Cd, Cu, Pb	Seawater	Pd	Coprecipitation on elemental Pd (50 × enrichment); T_{pyr} 250, 800 and 800 °C, resp.	Zhuang et al. (1996)
Cd, Cu, Pb	Seawater	Pd-$Mg(NO_3)_2$	Direct ETAAS vs. 50-fold enrichment on Kelex 100-C18; T_{pyr} 800, 1050, and 1200 °C, resp.; Zeeman STPF	Lopez Garcia et al. (1993a)
Ge, Sb, Sn	Fe (high purity)	Pd, Pd-Mg, Pd-Cu, Pd-Fe	Reductive coprecipitation with Pd; T_{pyr} 1400, 1200, and 1600 °C, resp.; LODs 10, 19, and 31 ng/g; Zeeman	Ashino and Takada (1996)
As, Bi, Sb, Sn	Aq. solutions	2 µg Ir on a Zr-treated platform	HG-trapping-ETAAS with permanent modification; effect of L-cysteine on inorganic and organoelement species studied	Tsalev et al. (1996b)
Cd, Cu, Ni, Pb	Seawater, marine interstitial water	$PdCl_2$-dilute HNO_3	APDC extraction and back extraction with modifier solution; 500-fold enrichment	Sachsenberg et al. (1992)
As, Bi, Sb, Se, Sn	Marine sediments RMs	1.25 µg Pd	HG-trapping-ETV-ICP-MS; LODs 2.9, 5, 3.3, 1980, and 54 pg, resp.	Sturgeon and Gregoire (1994)

As, Bi, Sb, Se, Te	Bone, fish, milk, plant leaves, seawater, sediment, shrimp, soil	50 μg Ir (trapping); 0.5 μg Pd or 1 μg Ir (direct ETAAS)	HG-trapping-FANES; T_{coll} 300 °C; LODs 32, 15, 12, 47, and 9 μg/L, resp.	Dittrich et al. (1995)
Cd, Co, Cu, Fe, Ni	Ga (high purity)	25 μg $NH_4H_2PO_4$	APDC-MIBK extraction; PO_4^{3-} improves recoveries for Cd in direct ETAAS but not in org. extracts	Kumar et al. (1990)
As, Bi, Sb, Se, Sn, Te	Plant (Pb only), seawater, sediment	2 μg Ir on Zr- or W-treated platform	Permanent modification; HG-trapping-ETAAS; direct ETAAS (As, Pb); trapping/stabilization of organo As, org. Sn, and org. Se species also studied	Tsalev et al. (1996a)
Cd, Co, Cu, Fe, Ni, Pb	Organic solvents and extracts	W-treated GT; Pd (for Cd and Pb)	Smaller amount of Pd needed for MIBK vs. aqueous solutions: 0.2 vs. 10–15 μg, resp.	Tserovsky and Arpadjan (1991)
Cd, Co, Cu, Ni, Pb, Se	Mineral water	The resin matrix; Pd (for Se)	Preconcentration on chelating resin; slurry sampling; T_{pyr} 650, 800, 800, 800, 700, and 900 °C, resp.	Sedykh et al. (1994)
Ag, Au, Pd, Pt, Rh, Se, Te	Geological RMs	10 μg Ir as $(NH_4)_2IrCl_6$-ascorbic acid (for Ag, Au, Se, Te)	Reductive coprecipitation with 4 mg of Hg; T_{pyr} 800, 1000, 1200, 1200, 1200, 1100, and 1200 °C, resp.; Zeeman STPF	Niskavaara and Kontas (1990)
As, Bi, Cd, Cu, Hg, Pb, Sb	Water	10 μg Pd-0.25 M HCl	Down to 0.1 μg/L of Hg determined after I^--toluene extraction	Shabanova et al. (1990)
As, Bi, Cd, Pb, Sb, Se, Sn, Te	Organic solvents and extracts	$PdCl_4(MTOA)_2$ or $PtCl_6(MTOA)_2$	APDC-MIBK extraction; better thermal stabilization on W-treated GT	Tserovsky et al. (1992)
Be, Cd, Co, Cr, Cu, Fe, Ni, Pb	Water	Zr	Coprecipitation with Zr(IV) hydroxide at pH 9; solid sampling ETAAS; LODs 0.23–2.3 ng/L	Nakamura et al. (1994)

(continued)

Appendix 4. Continued

Analyte	*Matrix*	*Modifier*	*Comments*	*Reference*
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb	Water (river)	200 μg/mL thiourea-0.5 M HBr	After coprecipitation with $In(OH)_3$; $InBr_3$ volatilized in the presence of CM	Chen et al. (1993b)
As, Bi, Ge, Hg, Pb, Sb, Se, Sn, Te	Various	Various	Review on HG in situ-trapping in atomic spectroscopy	Matusiewicz and Sturgeon (1996)
As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	Freshwater sediment	Pd-Ni-$NH_4H_2PO_4$	Fractionation scheme for acid volatile sulfides and pyrite	Huerta Diaz et al. (1993)

REFERENCES

Aadland, E., Aaseth, J., Dahl, K., Radziuk, B., Thomassen, Y. *J. Trace Elem. Electrolytes Health Dis.* **1990**, *4*, 233.

Aggarwal, S.K., Kinter, M., Nicholson, J., Herold, D.A. *Anal. Chem.* **1994**, *66*, 1316.

Akman, S., Doner, G. *Spectrochim. Acta, Part B* **1994**, *49*, 665.

Akman, S., Doner, G. *Spectrochim. Acta, Part B* **1995**, *50*, 975.

Ala-Opas, M., Tahvonen, R. *J. Trace Elements Med. Biol.* **1995**, *9*, 176.

Aller, A.J. *Anal. Chim. Acta* **1993**, *284*, 361.

Aller, A.J. *Anal. Chim. Acta* **1994**, *292*, 317.

Aller, A.J., Garcia-Olalla, C. *J. Anal. At. Spectrom.* **1992**, *7*, 753.

Almeida, A.A., Lima, J.L.F.C. *At. Spectrosc.* **1995**, *16*, 261.

Almeida, A.A., Lourdes Bastos, M., Isabel Cardoso, M., Ferreira, M.A., Lima, J.L.F.C., Elisa Soares, M. *J. Anal. At. Spectrom.* **1992**, *7*, 1281.

Alvarado, J., Cristiano, A.R., Curtius, A.J. *J. Anal. At. Spectrom.* **1995**, *10*, 483.

Alvarado, J.S., Erickson, M.D. *J. Anal. At. Spectrom.* **1996**, *11*, 923.

Alvarez, M.A., Carrion, N., Gutierrez, H. *Spectrochim. Acta, Part B* **1995**, *50*, 1581.

Alvarez, M.A., Carrion, N., Gutierrez, H. *Spectrochim. Acta, Part B* **1996**, *51*, 1121.

Alvarez-Cabal Cimadevilla, E., Wrobel, K., Gayon, G., Sanz-Medel, A. *J. Anal. At. Spectrom.* **1994**, *9*, 117.

Alvarez-Cabal Cimadevilla, E., Wrobel, K., Gayon, G., Sanz-Medel, A. *J. Anal. At. Spectrom.* **1995**, *10*, 149.

Amorusi, P., Lessard, D., Bansal, S.K., Selinger, K., Yocobi, A., Tonelli, A.P. *J. Pharm. Biomed. Anal.* **1994**, *12*, 1023.

An, Y., Willie, S.N., Sturgeon, R.E. *Spectrochim. Acta, Part B* **1992**, *47*, 1403.

Andrey, D., Beugert, H., Ceschi, M., Corvi, C., de Rossa, M., Herrmann, A., Klein, B., Probst-Hensch, N. *Mitt. Geb. Lebensmittelunters. Hyg.* **1992**, *83*, 711.

Anwar, J., Anzano, J.M., Winefordner, J.D. *Talanta* **1991**, *38*, 1071.

Anwari, M.A., Abbasi, H.U., Volkan, M., Ataman, O.Y. *Fresenius J. Anal. Chem.* **1996**, *355*, 284.

Anzano, J.M., Anwar, J., Smith, B.W., Winefordner, J.D. *Spectrosc. Lett.* **1991**, *24*, 837.

Apte, S.C., Comber, S.D.W., Gardner, M.J., Gunn, A.M. *J. Anal. At. Spectrom.* **1991**, *6*, 169.

Araujo, P.W., Gomez, C.V., Marcano, E., Benzo, Z. *Fresenius J. Anal. Chem.* **1995**, *351*, 204.

Araujo, P.W., Marcano, E., Gomez, C.V., Benzo, Z. *Anal. Quim.* **1994**, *90*, 343.

Ari, U., Volkan, M., Aras, N.K. *J. Agric. Food Chem.* **1991**, *39*, 2180.

Arnaud, J., Favier, A., Alary, J. *Lait* **1991**, *71*, 87.

Arpadjan, S., Karadjova, I., Tserovski, E., Aneva, Z. *J. Anal. At. Spectrom.* **1990**, *5*, 195.

Arruda, M.A.Z., Gallego, M., Valcarcel, M. *J. Anal. At. Spectrom.* **1994a**, *9*, 657.

Arruda, M.A.Z., Gallego, M., Valcarcel, M. J. *Anal. At. Spectrom.* **1995a**, *10*, 55.

Arruda, M.A.Z., Gallego, M., Valcarcel, M. J. *Anal. At. Spectrom.* **1995b**, *10*, 501.

Arruda, M.A.Z., Gallego, M., Valcarcel, M. *J. Anal. At. Spectrom.* **1996**, *11*, 169.

Arruda, M.A.Z., Quintela, M.J., Gallego, M., Valcarcel, M. *Analyst* **1994b**, *119*, 1695.

Ashino, T., Hirokawa, K. *Anal. Sci.* **1995**, *11*, 703.

Ashino, T., Takada, K. *Anal. Chim. Acta* **1995**, *312*, 157.

Ashino, T., Takada, K. *J. Anal. At. Spectrom.* **1996**, *11*, 577.

Ashino, T., Takada, K., Hirokawa, K. *Anal. Chim. Acta* **1994**, *297*, 443.

Astruc, A., Astruc, M., Pinel, R., Potin-Gautier, M. *Appl. Organomet. Chem.* **1992a**, *6*, 39.

Astruc, M., Astruc, A., Pinel, R. *Mikrochim. Acta* **1992b**, *109*, 83.

Atsuya, I., Akatsuka, K., Itoh, K. *Fresenius J. Anal. Chem.* **1990**, *337*, 294.

Bannon, D.I., Marashchuk, C., Zapf, C.R., Farfel, M.R., Chisolm, J.J., Jr. *Clin. Chem.* **1994**, *40*, 1730.

Bao, C., Cheng, X., Li, Y., Wei, Y. *Fenxi Huaxue* **1992**, *20*, 429.

Bao, C., Cheng, X., Li, Y., Wei, Y., An, Z. *Guangpuxue Yu Guangpu Fenxi* **1991**, *11* (5), 56.

Barbera, R., Farre, R., Garcia Andion, P. *Nahrung* **1992**, *36*, 202.
Barnett, N., Ebdon, L., Evans, E.H., Ollivier, P. *Microchem. J.* **1991**, *44*, 168.
Bass, D.A., Holcombe, J.A. *Spectrochim. Acta, Part B* **1988**, *43*, 1473.
Bavazzano, P., Perico, A., Rosendahl, K., Apostoli, P. *J. Anal. At. Spectrom.* **1996**, *11*, 521.
Baxter, D.C., Frech, W. *Fresenius J. Anal. Chem.* **1990**, *337*, 253.
Beceiro-Gonzalez, E., Bermejo-Barrera, P., Bermejo-Barrera, A. *Quim. Anal.* **1992**, *11*, 17.
Beceiro-Gonzalez, E., Bermejo-Barrera, P., Bermejo-Barrera, A., Barciela-Garcia, J., Barciela-Alonso, C. *J. Anal. At. Spectrom.* **1993**, *8*, 649.
Becker-Ross, H., Florek, S., Tischendorf, R., Schmecher, G.R. *J. Anal. At. Spectrom.* **1995**, *10*, 61.
Bei, Y., Chen, Y.-j., Dai, L.-m., Tian, L.-q. *Fenxi Shiyanshi* **1995**, *14* (3), 26.
Beinrohr, E., Rapta, M., Taddia, M., Poluzzi, V. *J. Anal. At. Spectrom.* **1991**, *6*, 33.
Beisel, N.F., Dahmen, F.I., Fuchs-Pohl, G.R., Yudelevich, I.G. *J. Anal. Chem.* **1993**, *48*, 877.
Beisel, N.F., Heinrich, G.I., Emrich, G., Yudelevich, I.G. *Vysokochist. Veshchestva* **1991**, *5*, 165.
Beisel, N.F., Korda, T.M., Yudelevich, I.G. *Vysokochist. Veshchestva* **1992**, *3*, 134.
Belazi, A.U., Davidson, C.M., Keating, G.E., Littlejohn, D., McCartney, M. *J. Anal. At. Spectrom.* **1995**, *10*, 233.
Belskii, N.K., Ochertyanova, L.I. *J. Anal. Chem.* **1993**, *48*, 1423.
Belskii, N.K., Timashuk, E.L., Ochertyanova, L.I., Garmash, A.V. *J. Anal. Chem.* **1994**, *49*, 744.
Bendicho, C., de Loos-Vollebregt, M.T.C. *Spectrochim. Acta, Part B* **1990a**, *45*, 679.
Bendicho, C., de Loos-Vollebregt, M.T.C. *Spectrochim. Acta, Part B* **1990b**, *45*, 695.
Bendicho, C., Sancho, A. *At. Spectrosc.* **1993**, *14*, 187.
Benzo, Z., Cecarelli, C., Carrion, N., Alvarez, M.A., Rojas, C., Rosso, M. *J. Anal. At. Spectrom.* **1992**, *7*, 1273.
de Benzo, Z.A., Fraile, R., Carrion, N. *Anal. Chim. Acta* **1990**, *231*, 283.
Berglund, M., Frech, W., Baxter, D.C. *Spectrochim. Acta, Part B* **1991**, *46*, 1767.
Berglund, M., Frech, W., Baxter, D.C., Radziuk, B. *Spectrochim. Acta, Part B* **1993**, *48*, 1381.
Bermejo-Barrera, P., Aboal-Somoza, M., Moreda-Pineiro, Bermejo-Barrera, A. *J. Anal. At. Spectrom.* **1995a**, *10*, 227.
Bermejo-Barrera, P., Aboal-Somoza, M., Soto-Ferreiro, R.M., Dominguez-Gonzalez, R. *Analyst* **1993a**, *118*, 665.
Bermejo-Barrera, P., Barciela-Alonso, M.P., Aboal-Somoza, M., Bermejo-Barrera, A. *J. Anal. At. Spectrom.* **1994a**, *9*, 469.
Bermejo-Barrera, P., Barciela-Alonso, M.C., Ferron-Novais, M., Bermejo-Barrera, A. *J. Anal. At. Spectrom.* **1995b**, *10*, 247.
Bermejo-Barrera, P., Barciela-Alonso, M.C., Moreda-Pineiro, J., Gonzalez-Sixto, C., Bermejo-Barrera, A. *Spectrochim. Acta, Part B* **1996a**, *51*, 1235.
Bermejo-Barrera, P., Beceiro-Gonzalez, E., Bermejo-Barrera, A. *Anal. Chim. Acta* **1990a**, *236*, 475.
Bermejo-Barrera, P., Beceiro-Gonzalez, E., Bermejo-Barrera, A. *Microchem. J.* **1992**, *45*, 90.
Bermejo-Barrera, P., Lorenzo-Alonso, M.P., Aboal-Somoza, M., Bermejo-Barrera, A. *Mikrochim. Acta* **1994b**, *117*, 49.
Bermejo-Barrera, P., Moreda-Pineiro, A., Aboal-Somoza, M., Moreda-Pineiro, J,, Bermejo-Barrera, A. *J. Anal. At. Spectrom.* **1994c**, *9*, 483.
Bermejo-Barrera, P., Moreda-Pineiro, A., Moreda-Pineiro, J., Bermejo-Barrera, A. *Anal. Chim. Acta* **1995c**, *310*, 355.
Bermejo-Barrera, P., Moreda-Pineiro, A., Moreda-Pineiro, J., Bermejo-Barrera, A. *Quim. Anal.* **1995d**, *14*, 201.
Bermejo-Barrera, P., Moreda-Pineiro, A., Moreda-Pineiro, J., Bermejo-Barrera, A. *Talanta* **1996b**, *43*, 35.
Bermejo-Barrera, P., Moreda-Pineiro, A., Moreda-Pineiro, J., Bermejo-Barrera, A. *Talanta* **1996c**, *43*, 77.

Bermejo-Barrera, P., Moreda-Pineiro, A., Moreda-Pineiro, J., Bermejo-Barrera, A. *Talanta* **1996d**, *43*, 1783.

Bermejo-Barrera, P., Moreda-Pineiro, A., Romero-Barbeito, T., Moreda-Pineiro, J., Bermejo-Barrera, A. *Talanta* **1996e**, *43*, 1099.

Bermejo-Barrera, P., Moreda-Pineiro, J., Moreda-Pineiro, A., Bermejo-Barrera, A. *Anal. Chim. Acta* **1994d**, *296*, 181.

Bermejo-Barrera, P., Moreda-Pineiro, J., Moreda-Pineiro, A., Bermejo-Barrera, A. *J. Anal. At. Spectrom.* **1995e**, *10*, 1011.

Bermejo-Barrera, P., Moreda-Pineiro, J., Moreda-Pineiro, A., Bermejo-Barrera, A. *Fresenius J. Anal. Chem.* **1996f**, *355*, 174.

Bermejo-Barrera, P., Moreda-Pineira, J., Moreda-Pineiro, A., Bermejo-Barrera, A. *J. Anal. At. Spectrom.* **1996g**, *11*, 1081.

Bermejo-Barrera, P., Pita-Calvo, C., Bermejo-Barrera, A., Bermejo-Martinez, F. *Fresenius J. Anal. Chem.* **1991**, *340*, 265.

Bermejo-Barrera, P., Pita-Calvo, C., Bermejo-Martinez, F. *Analyst* **1990b**, *115*, 549.

Bermejo-Barrera, P., Pita-Calvo, C., Cocho de Juan, J. A. *Anal. Chim. Acta* **1990c**, *231*, 321.

Bermejo-Barrera, P., Soto-Ferreiro, R.M., Aboal-Somoza, M., Bermejo-Barrera, A. *Quim. Anal.* **1995f**, *13*, 15.

Bermejo-Barrera, P., Soto-Ferreiro, R.M., Bermejo-Barrera, A. *Fresenius J. Anal. Chem.* **1993b**, *345*, 60.

Berryman, N.G., Probst, T.U. *Fresenius J. Anal. Chem.* **1996**, *355*, 783.

Bertram, H.P., Mueller, C. In *Analysis of Hazardous Substances in Biological Materials*; Angerer, J., Schaller, K.H., Eds.; VCH: Weinheim, 1991, p. 171.

Bettinelli, M., Baroni, U. *Intern. J. Environ. Anal. Chem.* **1990**, *43*, 22.

Bettinelli, M., Spezia, S., Baroni, U., Bizzarri, G. *At. Spectrosc.* **1994**, *15*, 115.

Bhattacharyya, S.S. *At. Spectrosc.* **1994**, *15*, 242.

Bhattacharyya, S.S., Chakraborty, R., Das, A.K. *Anal. Lett.* **1993**, *26*, 341.

Bishop, J.K.B. *Anal. Chem.* **1990**, *62*, 553.

Boer, P., Braam, B., Fransen, R., Boer, W.H., Koomans, H.A. *Kidney Int.* **1994**, *45*, 1211.

Boer, P., Fransen, R., Boer, W.H., Koomans, H.A. *J. Anal. At. Spectrom.* **1993**, *8*, 611.

Bogacz, W. *Chem. Anal. (Warsaw)* **1992**, *37*, 635.

Bortoli, A., Dell'-Andrea, E., Gerotto, M., Marin, V., Moretti, G. *Acta Chim. Hung.* **1991**, *128*, 573.

Bosnak, C.P., Bradshaw, D., Hergenreder, R., Kingston, K. *At. Spectrosc.* **1993**, *14*, 80.

Botelho, G.M.A., Curtius, A.J., Campos, R.C. *J. Anal. At. Spectrom.* **1994**, *9*, 1263.

Botha, V.P., Fazakas, J. *Magy. Kem. Foly.* **1993**, *99*, 82.

Boughriet, A., Deram, L., Wartel, M. *J. Anal. At. Spectrom.* **1994**, *9*, 1135.

Bozsai, G., Schlemmer, G., Grobenski, Z. *Talanta* **1990**, *37*, 545.

Bradshaw, D. *At. Spectrosc.* **1991**, *12*, 160.

Brazdes, L., Fazakas, J. *Magy. Kem. Foly.* **1991**, *97*, 128.

Brennfleck, U., Mueller-Vogt, G., Wendl, W. *Spectrochim. Acta, Part B* **1996**, *51*, 1139.

Brodie, K.G., Matousek, J.P. *Anal. Chim. Acta* **1974**, *69*, 200.

Brown, T.F., Zeringue, L.K. *Commun. Soil Sci. Plant Anal.* **1991**, *22*, 399.

Bruno, S.N.F., Campos, R.C., Curtius, A.J. *J. Anal. At. Spectrom.* **1994**, *9*, 341.

Bulska, E., Godlewska, B., Wrobel, K., Hulanicki, A. *Can. J. Appl. Spectrosc.* **1991**, *36*, 89.

Bulska, E., Grobenski, Z., Schlemmer, G. *J. Anal. At. Spectrom.* **1990**, *5*, 203.

Bulska, E., Jedral, W. *J. Anal. At. Spectrom.* **1995**, *10*, 49.

Bulska, E., Kandler, W., Hulanicki, A. *Spectrochim. Acta, Part B* **1996**, *51*, 1263.

Buiska, E., Kandler, W., Paslawski, P., Hulanicki, A. *Mikrochim. Acta* **1995**, *119*, 137.

Bulska, E., Pyrzynska, K. *Fresenius J. Anal. Chem.* **1996**, *355*, 672.

Bulska, E., Wrobel, K., Hulanicki, A. *Fresenius J. Anal. Chem.* **1992**, *342*, 740.

Burguera, J.L., Burguera, M., Carrero, P., Rivas, C., Gallignani, M., Brunetto, M.R. *Anal. Chim. Acta* **1995a**, *308*, 349.

Burguera, M., Burguera, J.L., Rondon, C., Rivas, C., Carrero, P., Gallignani, M., Brunetto, M.R. *J. Anal. At. Spectrom.* **1995b**, *10*, 343.

Burguera, J.L., Villasmil, L.M., Burguera, M., Carrero, P., Rondon, C., Matousek de Abel de la Cruz, A., Brunetto, M.R., Gallignani, M. *J. Trace Elements Med. Biol.* **1995c**, *9*, 160.

Burrini, C., Ghinassi, A., Borghi, G., Fuzzi, G.G. *Ital. Chim. Clin.* **1993**, *18* (1), 27.

Butcher, D.J. *Microchem. J.* **1993**, *48*, 303.

Butcher, D.J., Irwin, R.L., Takahashi, J., Michel, R.G. *J. Anal. At. Spectrom.* **1991**, *6*, 9.

Byrne, J.P., Chakrabarti, C.L., Gilchrist, G.F.R., Lamoureux, M.M., Bertels, P. *Anal. Chem.* **1993a**, *65*, 1267.

Byrne, J.P., Chakrabarti, C.L., Gregoire, D.C., Lamoureux, M.M., Ly, T. *J. Anal. At. Spectrom.* **1992**, *7*, 371.

Byrne, J.P., Gregoire, D.C., Goltz, D.M., Chakrabarti, C.L. *Spectrochim. Acta, Part B* **1994a**, *49*, 433.

Byrne, J.P., Hughes, D.L., Chakrabarti, C.L., Gregoire, D.C. *J. Anal. At. Spectrom.* **1994b**, *9*, 913.

Byrne, J.P., Lamoureux, M.M., Chakrabarti, C.L., Ly, T., Gregoire, D.C. *J. Anal. At. Spectrom.* **1993b**, *8*, 599.

Cabon, J.Y., Le Bihan, A. *J. Anal. At. Spectrom.* **1992**, *7*, 383.

Cabon, J.Y., Le Bihan, A. *J. Anal. At. Spectrom.* **1994**, *9*, 477.

Cabon, J.Y., Le Bihan, A. *Spectrochim. Acta, Part B* **1995**, *50*, 1703.

Cabon, J.Y., Le Bihan, A. *Spectrochim. Acta, Part B* **1996a**, *51*, 619.

Cabon, J.Y., Le Bihan, A. *Spectrochim. Acta, Part B* **1996b**, *51*, 1245.

Cabrera, C., Lorenzo, M.L., Gallego, C., Lopez, M.C., Lillo, E. *J. Agric. Food Chem.* **1992**, *40*, 1631.

Campos, R.C., Moraes, S.S. *At. Spectrosc.* **1993**, *14*, 71.

Cardellicchio, N., Geraci, S., Marra, C., Paterno, P. *Appl. Organomet. Chem.* **1992**, *6*, 241.

Carey, J.M., Evans, E.H., Caruso, J.A., Shen, W.L. *Spectrochim. Acta, Part B* **1991**, *46*, 1711.

Carlosena, A., Prada, D., Andrade, J.M., Lopez, P., Muniategui, S. *Fresenius J. Anal. Chem.* **1996**, *355*, 289.

Carneiro, M.C., Campos, R.C., Curtius, A.J. *Talanta* **1993**, *40*, 1815.

Carnrick, G., Schlemmer, G., Slavin, W. *Am. Lab.* **1991**, *23*, 120.

Cernohorsky, T., Kotrly, S. *J. Anal. At. Spectrom.* **1995**, *10*, 155.

Cervera, M.L., Navarro, A., Montoro, R., de la Guardia, M., Salvador, A. *J. Anal. At. Spectrom.* **1991**, *6*, 477.

Chakrabarti, C.L., Gilmutdinov, A.K., Hutton, J.C. *Anal. Chem.* **1993**, *65*, 716.

Chakrabarti, C.L., Marchand, B., Vandernoot, V., Walker, J., Schroeder, W.H. *Spectrochim. Acta, Part B* **1996**, *51*, 155.

Chakrabarti, C.L., Wan, C.C., Li, W.C., *Spectrochim. Acta, Part B* **1980**, *35*, 93.

Chakraborty, R., Bhattacharyya, S.S., Das, A.K. *Bull. Chem. Soc. Japan* **1993a**, *66*, 2233.

Chakraborty, R., Burguera, M., Burguera, J.L. *Fresenius J. Anal. Chem.* **1993b**, *347*, 233.

Chakraborty, R., Das, A.K. *Fresenius J. Anal. Chem.* **1994**, *349*, 774.

Chakraborty, R., Das, A.K., Cervera, M.L., de la Guardia, M. *J. Anal. At. Spectrom.* **1995**, *10*, 353.

Chakraborty, R., Das, A.K., Cervera, M.L., de la Guardia, M. *Fresenius J. Anal. Chem.* **1996**, *355*, 43.

Chapple, G., Byrne, J.P. *J. Anal. At. Spectrom.* **1996**, *11*, 549.

Chaudhry, M.M., Littlejohn, D. *Analyst* **1992**, *117*, 713.

Chaudhry, M.M., Mouillere, D., Ottaway, B., Littlejohn, D., Whitley, J.E. *J. Anal. At. Spectrom.* **1992**, *7*, 701.

Chaudhry, M.M., Ure, A.M., Cooksey, B., Littlejohn, D., Halls, D.J. *Anal. Proc.* **1991**, *28*, 44.

Chen, G., Jackson, K.W. *Spectrochim. Acta, Part B* **1996**, *51*, 1505.

Chen, S.Y., Zhu, A.-j., Chen, J. *Guangpuxue Yu Guangpu Fenxi* **1992**, *12* (4), 63.

Chen, T., Xu, C. *Fenxi Shiyanshi*, **1991**, *10* (5), 38.

Chen, Y. *Guangpuxue Yu Guangpu Fenxi* **1990**, *10* (5), 66.

Chen, Y. *Guangpuxue Yu Guangpu Fenxi* **1990**, *10* (6), 68.
Chen, Y., Qi, W., Cao, J., Chang, M.-s. *J. Anal. At. Spectrom.* **1993a**, *8*, 379.
Chen, Z.-s., Chen, Y.-I. *Guangpuxue Yu Guangpu Fenxi* **1990**, *10* (3), 69.
Chen, Z.-s., Hiraide, M., Kawaguchi, H. *Bunseki Kagaku* **1993b**, *42*, 759.
Chernyakhovskiy, V., Chernyakhovskaya, S., Cirillo, A. *At. Spectrosc.* **1994**, *15*, 250.
Chi, X.-z., Liu, J.-x., Shi, Y. *Guangpuxue Yu Guangpu Fenxi* **1992**, *12* (5), 95.
Chiba, M., Shinohara, A., Inaba, Y. *Microchem. J.* **1994**, *49*, 275.
Chuang, H., Huang, S.-d. *Spectrochim. Acta, Part B* **1994**, *49*, 283.
Cocho, J.-A., Cervilla, J.R., Rey-Goldar, M.-L., Fdez-Lorenzo, J.-R., Fraga, J.-M. *Biol. Trace Elem. Res.* **1992**, *32*, 105.
Collett, D.L.N., Jones, S.M. *At. Spectrosc.* **1991**, *12*, 69.
Creed, J., Martin, T., Lobring, T., O'Dell, J. *Environ. Sci. Technol.* **1992**, *26*, 102.
Currey, N.A., Benko, W.I., Yaru, B.T., Kabi, R. *Sci. Total Environ.* **1992**, *125*, 305.
Dabeka, R.W. *Anal. Chem.* **1992**, *64*, 2419.
Dabeka, R.W., McKenzie, A.D. *J. AOAC Int.* **1992**, *75*, 954.
Dadfarnia, S., Thompson, K.C., Hoult, G. *J. Anal. At. Spectrom.* **1994**, *9*, 7.
Dahl, K., Thomassen, Y., Martinsen, I., Radziuk, B., Salbu, B. *J. Anal. At. Spectrom.* **1994**, *9*, 1.
Dai, L.J., Xiao, Y.G., Huang, J. *Lihua Jianyan, Huaxue Fence* **1994**, *30*, 15.
Das, D., Chatterjee, A., Mandal, B.K., Samanta, G., Chakraborti, D., Chanda, B. *Analyst* **1995**, *120*, 917.
Davidson, C.M., Thomas, R.P., McVey, S.E., Perala, R., Littlejohn, D., Ure, A.M. *Anal. Chim. Acta* **1994**, *291*, 277.
Deaker, M., Maher, W. *J. Anal. At. Spectrom.* **1995**, *10*, 423.
Dean, S., Tscherwonyi, P.J., Riley, W.J. *Clin. Chem.* **1992**, *38*, 119.
Dědina, J., Matousek, T., Frech, W. *Spectrochim. Acta, Part B* **1996**, *51*, 1107.
Dědina, J., Tsalev, D.L. *Hydride Generation Atomic Absorption Spectrometry*; John Wiley & Sons: Chichester, 1995.
de la Fuente, M.A., Guerrero, G., Juarez, M. *At. Spectrosc.* **1995**, *16*, 219.
Deng, S.-I., Li, X.-f. *Fenxi Huaxue* **1992**, *20*, 985.
Deng, B., Gao, Y.-g. *Spectrochim. Acta, Part B* **1994**, *49*, 537.
Deval, J., Sneddon, J. *Microchem. J.* **1995**, *52*, 96.
Ding, W.-W., Sturgeon, R.E. *Spectrochim. Acta, Part B* **1996**, *51*, 1325.
Dittrich, K., Franz, T. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 875.
Dittrich, K., Franz, T., Wennrich, R. *Spectrochim. Acta, Part B* **1994**, *49*, 1695.
Dittrich, K., Franz, T., Wennrich, R. *Spectrochim. Acta, Part B* **1995**, *50*, 1655.
Dittrich, K., Fuchs H. *J. Anal. At. Spectrom.* **1990**, *5*, 39.
Dobrowolski, R., Mierzwa, J. *Fresenius J. Anal. Chem.* **1993**, *346*, 1058.
Dobrowolski, R., Mierzwa, J. *Analyst* **1996**, *121*, 897.
Docekal, B., Docekalova, H., Komarek, J., Novotny, I. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 123.
Docekal, B., Krivan, V. *J. Anal. At. Spectrom.* **1992**, *7*, 521.
Docekal, B., Krivan, V. *Anal. Chim. Acta* **1993a**, *279*, 253.
Docekal, B., Krivan, V. *J. Anal. At. Spectrom.* **1993b**, *8*, 637.
Docekalova, H., Docekal, B., Komarek, J., Novotny, I. *J. Anal. At. Spectrom.* **1991**, *6*, 661.
Doidge, P.S., McAllister, T. *J. Anal. At. Spectrom.* **1993**, *8*, 403.
Dolinsek, F., Stupar, J., Vrscaj, V. *J. Anal. At. Spectrom.* **1991**, *6*, 653.
Dominic, M.R., Koch, C.P., Mills, J.K. *J. Vinyl Technol.* **1993**, *15* (4), 228.
Donaldson, E.M., Leaver, M.E. *Talanta* **1990**, *37*, 173.
Doner, G., Akman, S. *J. Anal. At. Spectrom.* **1994**, *9*, 333.
Drake, E.N., Hain, T.D. *Anal. Biochem.* **1994**, *220*, 336.

Drews, W. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 553.
Dubois, J.-P. *J. Trace and Microprobe Techniques* **1991**, *9*, 149.
Eaton, A.D. *J. Am. Water Works Assoc.* **1994**, *86*, 100.
Ebdon, L., Fisher, A.S., Hill, S.J. *J. Anal. At. Spectrom.* **1992**, *7*, 511.
Ebdon, L., Fisher, A.S., Hill, S.J. *Anal. Chim. Acta* **1993**, *282*, 433.
Edel, H., Quick, L., Cammann, K. *Anal. Chim. Acta* **1995**, *310*, 181.
Ediger, R.D. *At. Absorpt. Newsl.* **1975**, *14*, 127.
Ediger, R.D., Beres, S.A. *Spectrochim. Acta, Part B* **1992**, *47*, 907.
Elci, L., Dogan, M. *Anal. Lett.* **1991**, *24*, 1047.
Ellen, G., van Loon, J.W. *Food Addit. Contam.* **1990**, *7*, 265.
Eloi, C.C., Robertson, J.D., Majidi, V. *J. Anal. At. Spectrom.* **1993**, *8*, 217.
Eloi, C.C., Robertson, J.D., Majidi, V. *Anal. Chem.* **1995a**, *67*, 335.
Eloi, C.C., Robertson, J.D., Majidi, V. *Nucl. Instr. Methods Phys. Res.* **1995b**, *99*, 468.
Elsheimer, H.N. *Anal. Sci.* **1993**, *9*, 681.
Elsheimer, H.N., Fries, T.L. *Anal. Chim. Acta* **1990**, *239*, 145.
Emteborg, H., Bulska, E., Frech, W., Baxter, D.C. *J. Anal. At. Spectrom.* **1992**, *7*, 405.
Epstein, M.S., Turk, G.C., Yu, L.J. *Spectrochim. Acta, Part B* **1994**, *49*, 1681.
Erber, D., Buscher, W., Cammann, C. In *CANAS'95 Colloquium Analytische Atomspektroskopie*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1996, p. 321.
Ergenoglu, B., Olcay, A. *Fuel Sci. Tech.* **1990**, *8*, 743.
Fagioli, F., Locatelli, C., Vecchietti, R., Torsi, G. *Appl. Spectrosc.* **1991**, *45*, 983.
Fang, Y.-G., Shi, H.-Y. *Yejin Fenxi* **1990**, *10* (3), 23.
Fazakas, J. *Chem. Anal. (Warsaw)* **1990**, *35*, 127.
Fender, M.A., Butcher, D.J. *Anal. Chim. Acta* **1995**, *315*, 167.
Ferng, H.M., Chiou, B.N., Chen, C.C., Kuo, M.S. *Huanjing Baohu (Taipei)* **1991**, *14*, 26.
Ferng, H.-m., Chu, T.-W., Chen, H.-H., Kuo, M.S. *Huanjing Baohu (Taipei)* **1992**, *15*, 29.
Fleischer, M., Schaller, K.H., Angerer, J. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 851.
Florian, K., Nickel, H., Zadgorska, Z. *Fresenius J. Anal. Chem.* **1993**, *345*, 445.
Fonseca, R.W., Miller-Ihli, N.J. *Appl. Spectrosc.* **1995**, *49*, 1403.
Fonseca, R.W., Miller-Ihli, N.J. *Spectrochim. Acta, Part B* **1996**, *51*, 1591.
Fonseca, R.W., Pfefferkorn, L.L., Holcombe, J.A. *Spectrochim. Acta, Part B* **1994a**, *49*, 1595.
Fonseca, R.W., Wolfe, K.I., Holcombe, J.A. *Spectrochim. Acta, Part B* **1994b**, *49*, 399.
Forrer, R., Gautschi, K., Lutz, H. *J. Trace Elem. Electrolytes Health Dis.* **1991**, *5*, 101.
Fox, G.J. *At. Spectrosc.* **1990**, *11*, 13.
Frech, W., Baxter, D.C. *Spectrochim. Acta, Part B* **1996**, *51*, 961.
Frech, W., Li, K., Berglund, M., Baxter, D.C. *J. Anal. At. Spectrom.* **1992**, *7*, 141.
Frech, W., L'vov, B.V. *Spectrochim. Acta, Part B* **1993**, *48*, 1371.
Friese, K.-C., Krivan V. *Anal. Chem.* **1995**, *67*, 354.
Friese, K.-C., Krivan, V., Schuierer, O. *Spectrochim. Acta, Part B* **1996**, *51*, 1223.
Fuchs-Pohl, G.R., Solinska, K. *GIT Fachz. Lab.* **1990**, *34*, 1115.
Fuchs-Pohl, G.R., Solinska, K., Feig, H. *Fresenius J. Anal. Chem.* **1992**, *343*, 711.
Fukushima, K., Nagashima, K., Kamaya, M., Ishii, E. *Bunseki Kagaku* **1993**, *42*, 401.
Fukushima, M., Ogata, T., Haraguchi, K., Nakagawa, K., Ito, S., Sumi, M., Asami, N. *J. Anal. At. Spectrom.* **1995**, *10*, 999.
Funato, Y., Takasaka, M. *Anal. Sci.* **1991**, *7* (Suppl.), 455.
Gailer, J., Irgolic, K.J. *Appl. Organomet. Chem.* **1994**, *8*, 129.
Gao, Y., Deng, B. *Spectrochim. Acta, Part B* **1996**, *51*, 1147.
Gao, Z., Li, Y. *Yeijin Fenxi* **1992**, *2*, 18; *Chem. Abstr.* **1993**, *118*, 204274.
Gao, Z.-z., Li, Y.-q. *Fenxi Shiyanshi* **1995**, *14* (3), 77.

Garbos, S., Walcerz, M., Bulska, E., Hulanicki, A. *Spectrochim. Acta, Part B* **1995**, *50*, 1669.
Garcia, A.L., Gonzalez, E.B., Sanz-Medel, A. *Mikrochim. Acta* **1993**, *112*, 19.
Garcia-Olalla, C., Aller, A.J. *Anal. Chim. Acta* **1991**, *252*, 97.
Garcia-Olalla, C., Aller, A.J. *Fresenius J. Anal. Chem.* **1992a**, *342*, 70.
Garcia-Olalla, C., Aller, A.J. *Anal. Chim. Acta* **1992b**, *259*, 295.
Garcia-Olalla, C., Robles, L.C., Alemany, M.T., Aller, A.J. *Anal. Chim. Acta* **1991a**, *247*, 19.
Garcia-Olalla, C., Robles, L.C., Aller, A.J. *Anal. Sci.* **1991b**, *7*, 611.
Gardiner, P.H.E., Littlejohn, D., Halls, D.J., Fell, G.S. *J. Trace Elements Med. Biol.* **1995**, *9*, 74.
Gilchrist, G.F.R., Chakrabarti, C.L., Byrne, J.P., Lamoureux, M. *J. Anal. At. Spectrom.* **1990**, *5*, 175.
Gilchrist, G.F.R., Chakrabarti, C.L., Cheng, J.G., Hughes, D.M. *J. Anal. At. Spectrom.* **1993**, *8*, 623.
Gilmutdinov, A.Kh., Staroverov, E.A., Gregoire, D.C., Sturgeon, R.E., Chakrabarti, C.L. *Spectrochim. Acta, Part B* **1994**, *49*, 1007.
Gilmutdinov, A.Kh., Zakharov, Yu.A., Ivanov, V.P., Voloshin, A.V. *J. Anal. At. Spectrom.* **1991**, *6*, 505.
Giordano, R., Ciaralli, L., Gattorta, G., Ciprotti, S., Costantini, S. *Microchem. J.* **1994**, *49*, 69.
Giordano, R., Costantini, S., Vernillo, I., Moramarco, A., Rasi, V., Giustolisi, R., Balacco-Gabrieli, C. *Microchem. J.* **1992a**, *46*, 184.
Giordano, R., Musmeci, L., Ciaralli, L., Vernillo, I. Chirico, M., Piccioni, A., Costantini, S. *Mar. Pollut. Bull.* **1992b**, *24*, 350.
Gitelman, H.J., Alderman, F.R. *J. Anal. At. Spectrom.* **1990**, *5*, 687.
Gless, U., Schmitt, Y., Ziegler, S., Kruse-Jarres, J.D. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 813.
Godlewska, B., Hulanicki, A., Abou-Shakra, F.R., Ward, N.I. *Anal. Lett.* **1994**, *27*, 2647.
Goenaga Infante, H., Fernandez Sanchez, M.L., Sanz-Medel, A. *J. Anal. At. Spectrom.* **1996**, *11*, 571.
Golloch, A., Haveresch-Kock, M., Platnikow-Vossgaetter, F. *Spectrochim. Acta, Part B* **1995**, *50*, 501.
Goltz, D.M., Gregoire, D.C., Byrne, J.P., Chakrabarti, C.L. *Spectrochim. Acta, Part B* **1995a**, *50*, 803.
Goltz, D.M., Chakrabarti, C.L., Sturgeon, R.E., Hughes, D.M., Gregoire, D.C. *Appl. Spectrosc.* **1995b**, *49*, 1006.
Goitz, D.M., Gregoire, D.C., Chakrabarti, C.L. *Spectrochim. Acta, Part B* **1995c**, *50*, 1365.
Gomez, M., Rodriguez, I., Camara, C., Palacios, M.A. *Analyst* **1990**, *115*, 553.
Gong, B.-I., Li, H., Ochiai, T., Zheng, L.-t., Matsumoto, K. *Anal. Sci.* **1993**, *9*, 723.
Gong, B., Liu, Y. *At. Spectrosc.* **1990**, *11*, 229.
Gong, B.-I., Liu, Y.-m., Li, Z.-h., Lin, T.-z. *Anal. Chim. Acta* **1995a**, *304*, 115.
Gong, B.-I., Liu, Y.-m., Xu, Y., Li, Z.-h., Lin, T.-z. *Talanta* **1995b**, *42*, 1419.
Granadillo, V.A., Navaro, J.A., Romero, R.A. *Invest. Clin.* **1991a**, *32* (1), 27.
Granadillo, V.A., Romero, R.A. *J. Anal. At. Spectrom.* **1993a**, *8*, 615 and 1049.
Granadillo, V.A., Romero, R.A. *Ciencia* **1993b**, *1* (1), 55.
Granadillo, V.A., Romero, R.A. In *Trace Elements in Man and Animals - TEMA 8*; Anke, M., Meissner, D., Mills, C.F., Eds.; Verlag Media Touristik: Jena, 1993c, p. 86.
Granadillo, V.A., Romero, R.A., Navarro, J.A. *Anal. Sci.* **1991b**, *7* (Suppl.), 1189.
Gregoire, D.C., Al-Maawali, S., Chakrabarti, C.L. *Spectrochim. Acta, Part B* **1992**, *47*, 1123.
Gregoire, D.C., Goltz, D.M., Lamoureux, M.M., Chakrabarti, C.L. *J. Anal. At. Spectrom.* **1994**, *9*, 919.
Gregoire, D.C., Sturgeon, R.E. *Spectrochim. Acta, Part B* **1993**, *48*, 1347.
Grey, P. *Analyst* **1990**, *115*, 159.
Grotti, M., Magi, E., Leardi, R. *Anal. Chim. Acta* **1996**, *327*, 47.
Grotti, M., Mazzucotelli, A. *J. Anal. At. Spectrom.* **1995**, *10*, 325.
Gruener, N., Gozlan, O., Goldstein, T., Davis, J., Besner, T., Iancu, T.C. *Clin. Chem.* **1991**, *37*, 263.
Guenther, K., Waldner, H. *Anal. Chim. Acta* **1992**, *259*, 165.
Guo, J.H., Fang, T., Xu, Z.L., Chen, Y.W. *Guangpuxue Yu Guangpu Fenxi* **1993**, *13* (3), 57.
Hahn, L., Mueller-Vogt, G., Wendi, W. *J. Anal. At. Spectrom.* **1993**, *8*, 223.
Haldimann, M., Venner, T.Y., Zimmerli, B. *J. Trace Elements Med. Biol.* **1996**, *10*, 31.
Halls, D.J. *J. Anal. At. Spectrom.* **1995**, *10*, 169.

Hamid, H.A., Al-Joboury, M.I., Mohammed, A.K. *Anal. Chim. Acta* **1991**, *243*, 239.
Hanna, C.P., Carnrick, G.R., McIntosh, S.A., Guyette, L.C., Bergemann, D.E. *At. Spectrosc.* **1995**, *16*, 82.
Hao, D.-Q., Xiang, P.-P., Tian, G.-J., Liang, L. *Gongye Weisheng Yu Zhiyebing* **1991**, *17*, 99.
Harnly, J.M., Radziuk, B. *J. Anal. At. Spectrom.* **1995**, *10*, 197.
Harrison, I., Littlejohn, D., Fell, G.S. *J. Anal. At. Spectrom.* **1995**, *10*, 215.
Hassell, D.C., Majidi, V., Holcombe, J.A. *J. Anal. At. Spectrom.* **1991**, *6*, 105.
Haug, H.O. *Spectrochim. Acta, Part B* **1996**, *51*, 1425.
Haug, H.O., Liao, Y. *J. Anal. At. Spectrom.* **1995**, *10*, 1069.
Haug, H.O., Liao, Y.-p. *Fresenius J. Anal. Chem.* **1996**, *356*, 435.
Haug, H.O., Ju, C. *J. Anal. At. Spectrom.* **1990**, *5*, 215.
Hauptkorn, S., Krivan, V. *Spectrochim. Acta, Part B* **1996**, *51*, 1197.
Hauptkorn, S., Schneider, G., Krivan, V. *J. Anal. At. Spectrom.* **1994**, *9*, 463.
Havezov, I., Detcheva, A., Rendl, J. *Mikrochim. Acta* **1995**, *119*, 147.
Havezov, I., Iordanov, N., Ortner, H.M. *Fresenius J. Anal. Chem.* **1991**, *339*, 871.
Havezov, I., Russeva, E. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 573.
He, B., Ni, Z.-m. *J. Anal. At. Spectrom.* **1996**, *11*, 165.
He, H.-w. *Fenxi Huaxue* **1994**, *22*, 106.
He, J. *Fenxi Huaxue* **1990**, *13*, 1029.
He, S., Zhang, W., Wang, G., Zhu, P. *Fenxi Ceshi Tongbao* **1991**, *10*, 64.
Heinrich, H.-J., Dette, A. In *CANAS'95 Colloquium Analytische Atomspektroskopie*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1996, p. 109.
Heinrich, H.-J., Emrich, G. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 133.
Heitmann, U., Schuetz, M., Becker-Ross, H., Florek, S. *Spectrochim. Acta, Part B* **1996**, *51*, 1095.
Herber, R.F.M. *Microchem. J.* **1995**, *51*, 46.
Herber, R.F.M., Stoeppler, M., Tonks, D.B. *Fresenius J. Anal. Chem.* **1990a**, *338*, 269.
Herber, R.F.M., Stoeppler, M., Tonks, D.B. *Fresenius J. Anal. Chem.* **1990b**, *338*, 279.
Hernandes Cordoba, M., Lopez Garcia, I. *Talanta* **1991**, *38*, 1247.
Heron, C. *Monitoring of Blood Lead Levels at Mintek*; Mintek Report M409, Johannesburg, 1991, pp. 1–10.
Hewitt, C.D., Winborne, K., Margrey, D., Nicholson, J.R.P., Savory, M.G., Savory, J., Wills, M.R. *Clin. Chem.* **1990**, *36*, 1466.
Hinds, M.W. *J. Anal. At. Spectrom.* **1992**, *7*, 685.
Hinds, M.W., Brown, G.N., Styris D.L. *J. Anal. At. Spectrom.* **1994**, *9*, 1411.
Hinds, M.W., Jackson K.W. *J. Anal. At. Spectrom.* **1990**, *5*, 199.
Hinds, M.W., Kogan, V.V. *J. Anal. At. Spectrom.* **1994**, *9*, 451.
Hinds, M.W., Latimer, K.E., Jackson K.W. *J. Anal. At. Spectrom.* **1991**, *6*, 473.
Hiraide, M., Ishikawa, K., Chen, Z.S., Kawaguchi, H. *Mikrochim. Acta* **1994**, *117*, 7.
Hirano, Y., Nomura, Y., Yasuda, K., Hirokawa, K. *Anal. Sci.* **1992**, *8*, 427.
Hirano, Y., Yasuda, K., Hirokawa, K. *Anal. Sci.* **1994a**, *10*, 481.
Hirano, Y., Yasuda, K., Hirokawa, K. *Bunseki Kagaku* **1994b**, *43*, 105.
Hirano, Y., Yasuda, K., Hirokawa, K. *Bunseki Kagaku* **1994c**, *43*, 813.
Hirano, Y., Yasuda, K., Hirokawa, K. *Bunseki Kagaku* **1995**, *44*, 521.
Hirano, Y., Yasuda, K., Nomoto, S. *Seibutsu Shiryo Bunseki* **1990**, *13*, 191.
Hirokawa, K., Yasuda, K., Takada, K. *Anal. Sci.* **1992**, *8*, 411.
Hoenig, M. *Analusis* **1991**, *19*, 41.
Hoenig, M., Cilissen, A. *Spectrochim. Acta, Part B* **1993**, *48*, 1303.
Hoenig, M., Puskaric, E., Choisy, P., Wartel, M. *Analusis* **1991a**, *19*, 285.
Hoenig, M., Regnier, P., Chou, L. *Analusis* **1991b**, *19*, 163.

Hoenig, M., Regnier, P., de Kersabiec, A.M. *Analusis* **1990**, *18*, 420.
Holden, A.J., Littlejohn, D., Fell, G.S. *Anal. Proc.* **1992**, *29*, 260.
Hong, W. *At. Spectrosc.* **1991**, *12*, 87.
Hosoda, K., Omae, K., Onodera, M., Oda, K., Sakurai, H. *Sangyo Igaku* **1994**, *36*, 102.
Howell, A.G., Koirtyohann, S.R. *Appl. Spectrosc.* **1992**, *46*, 953.
Hu, B., Jiang, Z., Qin, Y., Zeng, Y. *Anal. Chim. Acta* **1996**, *319*, 255.
Hu, B., Jiang, Z., Zeng, Y. *J. Anal. At. Spectrom.* **1991a**, *6*, 623.
Hu, B., Jiang, Z., Zeng, Y. *Fresenius J. Anal. Chem.* **1991b**, *340*, 435.
Hu, B., Jiang, Z.-c., Zeng, Y. *Fenxi Huaxue* **1993a**, *21*, 6.
Hu, B., Jiang, Z.-c., Zeng, Y. *Fenxi Huaxue* **1993b**, *21*, 1139.
Hu, B., Jiang, Z.-c., Zeng, Y. *Yankuang Ceshi* **1993c**, *12* (3), 183.
Hu, B., Jiang, Z.-c., Zeng, Y. *Fenxi Shiyanshi* **1994a**, *13* (2), 16.
Hu, B., Jiang, Z., Zeng, Y. *Anal. Chim. Acta* **1994b**, *296*, 213.
Hu, B., Jiang, Z., Zeng, Y., Zhu, H. *Anal. Sci.* **1991c**, *7*, 433.
Hu, Q. *Fenxi Huaxue* **1991**, *19*, 908.
Huang, M., Jiang, Z., Zeng, Y. *Anal. Sci.* **1991**, *7*, 773.
Huang, M., Jiang, Z., Zeng, Y. *Fenxi Huaxue* **1992**, *20*, 287.
Huang, S.-d., Lai, W.-r., Shih, K.-y. *Spectrochim. Acta, Part B* **1995**, *50*, 1237.
Huang, S.-d., Shih, K.-y. *Spectrochim. Acta, Part B* **1993**, *48*, 1451.
Huang, S.-d., Shih, K.-y. *Spectrochim. Acta, Part B* **1995**, *50*, 837.
Huang, Z.-e. *J. Anal. At. Spectrom.* **1994**, *9*, 11.
Huang, Z.-e. *Spectrochim. Acta, Part B* **1995**, *50*, 1383.
Hub, W., Amphlett, H. *Fresenius J. Anal. Chem.* **1994**, *350*, 587.
Huerta Diaz, M.A., Carignan, R., Tessler, A. *Environ Sci. Technol.* **1993**, *27*, 2367.
Hughes, D.M., Chakrabarti, C.L., Goltz, D.M., Gregoire, D.C., Sturgeon, R.E., Byrne, J.P. *Spectrochim. Acta, Part B* **1995**, *50*, 425.
Hughes, D.M., Chakrabarti, C.L., Goitz, D.M., Sturgeon, R.E., Gregoire, D.C. *Appl. Spectrosc.* **1996a**, *50*, 715.
Hughes, D.M., Chakrabarti, C.L., Lamoureux, M.M., Hutton, J.C., Goltz, D.M., Sturgeon, R.E., Gregoire, D.C., Gilmutdinov, A.Kh. *Spectrochim. Acta, Part B* **1996b**, *51*, 973.
Hulanicki, A., Bulska, E., Dittrich, K. J. *Anal. At. Spectrom.* **1990**, *5*, 209.
Hulanicki, A., Bulska, E., Godlewska, B., Wrobel, K. *Anal. Lett.* **1989**, *22*, 1341.
Hulanicki, A., Bulska, E., Wrobel, K. *Chem. Anal. (Warsaw)* **1992a**, *37*, 93.
Hulanicki, A., Bulska, E., Wrobel, K. *Anal. Sci.* **1992b**, *8*, 405.
Ide, K., Hashimoto, S., Okochi, H. *Bunseki Kagaku* **1995**, *44*, 617.
Ide, K., Kudo, M., Kobayashi, T., Hasegawa, S., Okochi, H. *Bunseki Kagaku* **1994**, *43*, 215.
Ilkov, A. *J. Anal. At. Spectrom.* **1996**, *11*, 313.
Imai, S., Hasegawa, N., Hayashi, Y., Saito, K. *J. Anal. At. Spectrom.* **1996a**, *11*, 515.
Imai, S., Hasegawa, N., Nishiyama, Y., Hayashi, Y., Saito, K. *J. Anal. At. Spectrom.* **1996b**, *11*, 601.
Imai, S., Hayashi, Y. *Anal. Chem.* **1991**, *63*, 772.
Imai, S., Hayashi, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 871.
Imai, S., Ibe, T., Tanaka, T., Hayashi, Y. *Anal. Sci.* **1994**, *10*, 901.
Imai, S., Ishikura, H., Tanaka, T., Saito, K., Hayashi, Y. *Eisei Kagaku*, **1991a**, *37*, 401.
Imai, S., Nishiyama, Y., Tanaka, T., Hayashi, Y. *J. Anal. At. Spectrom.* **1995a**, *10*, 439.
Imai, S., Okuhara, K., Tanaka, T., Hayashi, Y., Saito, K. *J. Anal. At. Spectrom.* **1995b**, *10*, 37.
Imai, S., Saito, K., Hayashi, Y. *Anal. Sci.* **1991b**, *7*, 893.
Imai, S., Tanaka, T., Hayashi, Y. *Anal. Sci.* **1990**, *6*, 913.
Imai, S., Tanaka, T., Saito, K., Hayashi, Y. *Eisei Kagaku* **1991c**, *37* (1), 22.
Imai, S., Tanaka, T., Saito, K., Hayashi, Y. *Anal. Sci.* **1992**, *8*, 99.
Irwin, R., Mikkelsen, A., Michel, R.G., Dougherty, J.P., Preli, F.R. *Spectrochim. Acta, Part B* **1990**, *45*, 903.

Irwin, R.L., Wei, G.-T., Butcher, D.J., Liang, Z., Su, E.G., Takahashi, J., Walton, A.P., Michel, R.G. *Spectrochim. Acta, Part B* **1992**, *47*, 1497.
Isoyama, H., Okuyama, S., Uchida, T., Takeuchi, M., Iida, C., Nakagawa, G. *Anal. Sci.* **1990**, *6*, 555.
Itai, K., Takikawa, S., Tsunoda, H. *Environ. Sci.* **1995**, *3* (2), 113.
Itami, T., Ema, M., Amano, H., Kawasaki, H. *J. Anal. Toxicol.* **1991**, *15*, 119.
Ivanova, E., Gentscheva, G., Stoimenova M., Havezov, I. *Anal. Lab. (Sofia)* **1995**, *4* (1), 14.
Ivanova, E., Havezov, I., Berndt, H., Schaldach, G. *Fresenius J. Anal. Chem.* **1990**, *336*, 320.
Iwamoto, E., Hashimoto, H., Kumamaru, T. *Anal. Sci.* **1992a**, *8*, 389.
Iwamoto, E., Shimazu, H., Yokota, K., Kumamaru, T. *J. Anal. At. Spectrom.* **1992b**, *7*, 421.
Iwamoto, E., Shimazu, H., Yokota, K., Kumamaru, T. *Anal. Chim. Acta* **1993**, *274*, 231.
Jackson, A.P., Alloway, B.J. *Int. J. Environ. Anal. Chem.* **1990**, *41*, 119.
Jackson, J.G., Fonesca, R.W., Holcombe, J.A. *J. Anal. At. Spectrom.* **1994**, *9*, 167.
Jacobson, B. E., Lockitch, G., Quigley, G. *Clin. Chem.* **1991**, *37*, 515.
Jaganathan, J., Aggarwal, I. *Appl. Spectrosc.* **1993a**, *47*, 190.
Jaganathan, J., Aggarwal, I. *Appl. Spectrosc.* **1993b**, *47*, 1169.
Jaganathan, J., Aggarwal, I. *Microchem. J.* **1994**, *50*, 44.
Jaganathan, J., Ewing, K.J., Aggarwal, I. *J. Anal. At. Spectrom.* **1992**, *7*, 1287.
Jaganathan, J., Ewing, K.J., Buckley, E.A., Peitersen, L., Aggarwal, I.D. *Microchem. J.* **1990**, *41*, 106.
Jaganathan, J., Ewing, K.J., Peiterson, L.E., O'Brien, E.A., Aggarwal, I.D. *Spectrochim. Acta, Part B* **1991**, *46*, 669.
Jeng, S.L., Lee, S.J., Lin, S.Y. *J. Dairy Sci.* **1994**, *77*, 945.
Ji, D.-y., Guo, S.-w., Zhao, X.-f., Yuan, H.-w. *Guangpuxue Yu Guangpu Fenxi* **1992**, *12* (5), 101.
Ji, X.P. *Fenxi Huaxue* **1993**, *21*, 492.
Ji, X.P., Ren, J.J. *At. Spectrosc.* **1995**, *16*, 224.
Jiang, G.-b., Ni, Z.-m., Zhang, L., Li, A., Han, H.-b., Shan, X.-q. *J. Anal. At. Spectrom.* **1992**, *7*, 447.
Johannessen, J.K., Gammelgaard, B., Jons, O., Hansen, S.H. *J. Anal. At. Spectrom.* **1993**, *8*, 999.
Johnson, K.E., Treble, R.G. *J. Clin. Lab. Anal.* **1992**, *6*, 264.
Jorhem, L., Sundstrom, B. *At. Spectrosc.* **1995**, *16*, 226.
Julshamn, K., Maage, A., Larsen, E.H. *Fresenius J. Anal. Chem.* **1996**, *355*, 304.
Kalaidjieva, I. *Anal. Lab. (Sofia)* **1995**, *4*, 235.
Kanke, M., Kumamaru, T., Sakai, K., Yamamoto, Y. *Anal. Chim. Acta* **1991**, *247*, 13.
Kantor, T. *Spectrochim. Acta, Part B* **1995**, *50*, 1599.
Kantor, T. *Fresenius J. Anal. Chem.* **1996**, *355*, 606.
Kantor, T., Radziuk, B., Weiz, B. *Spectrochim. Acta, Part B* **1994**, *49*, 875.
Kao, C.-M., Cherng, Y.-J., Wung, M.-H., Tsao, P.-Y., Kuo, M.-S. *J. Chin. Chem. Soc.* **1993**, *40*, 33.
Karadjova, I., Iordanova, L., Arpadjan, S. *Dokl. Bolg. Akad. Nauk* **1991**, *44* (7), 45.
Karadjova, I., Mandjukov, P., Tsakovsky, S., Simeonov, V., Stratis, J.A., Zachariadis, G.A. *J. Anal. At. Spectrom.* **1995**, *10*, 1065.
Katsura, T., Kato, F., Matsumoto, K. *Anal. Sci.* **1990**, *6*, 909.
Katsura, T., Kato, F., Matsumoto, K. *Anal. Chim. Acta* **1991**, *252*, 77.
Katsura, T., Kato, F., Matsumoto, K. *Anal. Sci.* **1992**, *8*, 97.
Kelemen, J., Szakacs, O., Laszstity, A. *J. Anal. Atom. Spectrom.* **1990**, *5*, 377.
Kildahl, B.T., Lund, W. *Fresenius J. Anal. Chem.* **1996**, *354*, 93.
Kim, Y.S., Choi, C.M., Choi, H.S. *Hwahak Sekye* **1992**, *32*, 1161.
Kimura, T., Sugino, K., Tamura, Y., Fukunaga, A. *Yamaguchi Igaku* **1990**, *39*, 601.
Klemm, W., Bombach, G. *Fresenius J. Anal. Chem.* **1995**, *353*, 12.
Klinkenberg, H., Beeren, T., Van Borm, W., van der Linden, F., Raets, M. *Spectrochim. Acta, Part B* **1993**, *48*, 649.
Knutsen, E., Wibetoe, G., Martinsen, I. *J. Anal. At. Spectrom.* **1995**, *10*, 757.
Kobayashi, R., Imaizumi, K. *Anal. Sci.* **1990**, *6*, 83.
Kobayashi, R., Imaizumi, K. *Anal. Sci.* **1991**, *7* (Suppl.), 1197.

Kobayashi, R., Imaizumi, K., Kudo, M. *Anal. Sci.* **1995**, *11*, 267.
Koelbl, G., Kalcher, K., Irgolic, K.J. *Anal. Chim. Acta* **1993**, *284*, 301.
Kolosova, L.P., Ushinskaya, L.A., Kopylova, T.N. *J. Anal. Chem.* **1993**, *48*, 461.
Komarek, J., Ganoczy, M. *Collect. Czech. Chem. Commun.* **1991**, *56*, 764.
Komarek, J., Slaninova, M., Vrestal, J., Sommer, L. *Collect. Czech. Chem. Commun.* **1991a**, *56*, 2082.
Komarek, J., Sommer, L., Dittrich, K. *Scr. Chem. (Brno)* **1991b**, *21*, 23.
Kontas, E., Niskavaara, H., Virtasalo, J. *Geostand. Newsl.* **1990**, *14*, 477.
Koons, R. D., Peters, C.A. *J. Anal. Toxicol.* **1994**, *18*, 36.
Koops, J., Westerbeek, D. *Neth. Milk Dairy J.* **1993**, *47*, 1.
Koreckova, J., Musil, J. *Collect. Czech. Chem. Commun.* **1994**, *59*, 1030.
Koshino, Y., Narukawa, A. *Analyst* **1993a**, *118*, 1027.
Koshino, Y., Narukawa, A. *Talanta* **1993b**, *40*, 799.
Koshino, Y., Narukawa, A. *Analyst* **1994**, *119*, 2473.
Krakovska, E., Pulis, P. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 357.
Krakovska, E., Pulis, P. *Spectrochim. Acta, Part B* **1996**, *51*, 1271.
Krivan, V. *J. Anal. Atom. Spectrom.* **1992**, *7*, 155.
Krivan, V., Koch, B. *Anal. Chem.* **1995**, *67*, 3148.
Krivan, V., Kueckenwaitz, M. *Fresenius J. Anal. Chem.* **1992**, *342*, 692.
Kubota, T., Okutani, T., Inamoto, I., Takimoto, K. *Bunseki Kagaku* **1992**, *41*, 57.
Kubota, T., Suzuki, K., Okutani, T. *Talanta*, **1995**, *42*, 949.
Kumar, S.J., Gangadharan, S. *J. Anal. At. Spectrom.* **1993**, *8*, 127.
Kumar, S.J., Natarajan, S., Arunachalam, J., Gangadharan, S. *Fresenius J. Anal. Chem.* **1990**, *338*, 836.
Kumpulainen, J., Saarela, K.-E. *J. Anal. At. Spectrom.* **1992**, *7*, 165.
Kunwar, U.K., Littlejohn, D., Halls, D.J. *Talanta* **1990**, *37*, 555.
Kurata, N., Harada, Y., Furuno, G. *Bunseki Kagaku* **1990**, *39*, 289.
Kuroda, R., Kitada, K., Oguma, K., Katayama, T. *Fresenius J. Anal. Chem.* **1990a**, *338*, 919.
Kuroda, R., Oguma, K., Mori, Y., Okabe, H., Takizawa, T. *Chromatographia* **1991**, *32*, 583.
Kuroda, R., Wada, T., Soma, T., Itsubo, N., Oguma, K. *Analyst* **1990b**, *115*, 1535.
Kutseva, N.K., Volynskii, A.B., Pirogova, S.V., Kashin, A.N. *Vestn. Mosk. Univ. Ser 2 Khim.* **1993a**, *34*, 185.
Kutseva, N.K., Volynskii, A.B., Pirogova, S.V., Kashin, A.N. *J. Anal. Chem.* **1993b**, *48*, 154.
Laborda, F., Chakraborti, D., Mir, J.M., Castillo, J.R. *J. Anal. At. Spectrom.* **1993a**, *8*, 643.
Laborda, F., Vinuales, J., Mir, J.M., Castillo, J.R. *J. Anal. At. Spectrom.* **1993b**, *8*, 737.
Lai, P., Ma, L., She, X. *Lihua Jianyan, Huaxue Fence* **1991**, *27*, 182.
Lajunen, L.H.J., Kokkonen, P., Karijoki, J., Porkka, V., Saari, E. *At. Spectrosc.* **1990**, *11*, 193.
Lamoureux, M.M., Gregoire, D.C., Chakrabarti, C.L., Goltz, D.M. *Anal. Chem.* **1994**, *66*, 3208.
Lan, C.-r. *Analyst* **1993**, *118*, 189.
Lan, C.r., Alfassi, Z.B. *Analyst* **1994**, *119*, 1033.
Lange-Hesse, K., Dunemann, L., Schwedt, G. *Fresenius J. Anal. Chem.* **1994**, *349*, 460.
Lapointe, S., LeBlanc, A. *At. Spectrosc.* **1996**, *17*, 163.
Larsen, E.H. *J. Anal. At. Spectrom.* **1991**, *6*, 375.
Latino, J.C., Sears, D.C., Portala, F., Shuttler, I.L. *At. Spectrosc.* **1995**, *16*, 121.
LeBlanc, A. *J. Anal. At. Spectrom.* **1996**, *11*, 1093.
Lechotycki, A. *J. Anal. At. Spectrom.* **1990**, *5*, 25.
Li, G.-k., Zhang, Z.-x., Yang, X.-h. *Guangpuxue Yu Guangpu Fenxi* **1995**, *15* (3), 91.
Li, H.-t., Gong, B., Matsumoto, K. *Anal. Chem.* **1996a**, *68*, 2277.
Li, H., Gong, B.-I., Ochiai, T., Matsumoto, K. *Anal. Sci.* **1993a**, *9*, 707.
Li, H.-t., Ma, B.-j. *Guangpuxue Yu Guangpu Fenxi* **1993b**, *13* (1), 127.
Li, H.-t., Nagasawa, H., Matsumoto, K. *Anal. Sci.* **1996b**, *12*, 215.

Li, S.-y., Wang, R.-r., Ni, Z.-m., Zhang, L., Yan, X.-p., He, B., Shan, X.-q., Jing, S.-I., Han, H.-b. *Guangpuxue Yu Guangpu Fenxi* **1992**, *12* (4), 117.
Li, Z., Zhang, Q. *Guangpu Shiyanshi* **1993**, *10* (1), 6.
Liang, C.-s., Huang, M.-y. *Fenxi Ceshi Tongbao* **1992**, *11* (6), 65.
Liang, L., D'Haese, P.C., Lamberts, L.V., De Broe, M.E. *Clin. Chem.* **1991**, *37*, 461.
Liang, Y.-Z., Li, M., Rao, Z. *Anal. Sci.* **1996**, *12*, 629.
Liang, Y.-z., Ni, Z.-m. *Spectrochim. Acta, Part B* **1994**, *49*, 229.
Liang, Z., Lonardo, R.F., Takahashi, J., Michel, R.G., Preli, F.R., Jr. *J. Anal. At. Spectrom.* **1992**, *7*, 1019.
Liao, Y.-p., Li, A.-m. *J. Anal. At. Spectrom.* **1993**, *8*, 633.
Liaw, M.-j., Jiang, S.-j. *J. Anal. At. Spectrom.* **1996**, *11*, 555.
Lin, K., He, Y.-z., Lin, W.-y., Luo, J.-h. *Guangpuxue Yu Guangpu Fenxi* **1993a**, *13* (6), 85.
Lin, K., Lin, W.Y., He, Y.Z., Luo, J.H., Huang, L.J. *Fenxi Shiyanshi* **1993b**, *12* (5), 51.
Lin, W., He, Y., Luo, J., Huang, L., Lin, K., Wu, S., Chen, J. *Fenxi Shiyanshi* **1991**, *10* (1), 30.
Lin, Z.-x., Song, J.-y., Mo, S.-j. *Fenxi Ceshi Xuebao* **1993c**, *12* (4), 32.
Lippo, H., Sarkela, A. *At. Spectrosc.* **1995**, *16*, 154.
Littlejohn, D., Egila, J.N., Gosland, L.M., Kunvar, U.K., Smith, C., Shan, X.-q. *Anal. Chim. Acta* **1991**, *250*, 71.
Liu, Y., Gong, B., Li, Z., Xu, Y., Lin, T. *Talanta* **1996**, *43*, 985.
Liu, Y., Gong, B., Xu, Y., Li, Z., Lin, T. *Anal. Chim. Acta* **1994**, *292*, 325.
Liu, Z., Dai, L., Qian, J., Peng, J. *Fenxi Shiyanshi* **1990**, *9* (6), 60.
Lonardo, R.F., Yuzefovsky, A.I., Yang, K.X., Michel, R.G., Frame, E.S., Barren, J. *J. Anal. At. Spectrom.* **1996**, *11*, 279.
Lopez-Artiguez, M., Soria, M.L., Camean, A., Repetto, M. *Bull. Environ. Contam. Toxicol.* **1993**, *50*, 417.
Lopez Garcia, A., Blanco Gonzalez, E., Sanz-Medel, A. *Mikrochim. Acta* **1993a**, *112*, 19.
Lopez Garcia, I., Arroyo Cortez, J., Hernandez Cordoba, M. *Anal. Chim. Acta* **1993b**, *283*, 167.
Lopez Garcia, I., Hernandez Cordoba, M. *J. Anal. At. Spectrom.* **1990**, *5*, 647.
Lopez Garcia, I., Sanchez Merlos, M., Hernandez Cordoba, M. *Anal. Chim. Acta* **1996a**, *328*, 19.
Lopez-Garcia, I., Sanchez-Merlos, M., Hernandez-Cordoba, M. *J. Anal. At. Spectrom.* **1996b**, *11*, 1003.
Luecker, E. *Fresenius J. Anal. Chem.* **1992**, *343*, 386.
Luguera, M., Madrid, Y., Camara, C. *J. Anal. At. Spectrom.* **1991**, *6*, 669.
Luo, F., Li, X., Wang, M. *At. Spectrosc.* **1990**, *11*, 78.
Lynch, S., Littlejohn, D. *Talanta* **1990**, *37*, 825.
Lytle, D.A., Schock, M.R., Dues, N. R., Doerger, J.U. *J. Am. Water Works Assoc.* **1993**, *85*, 77.
Ma, Y.-p., Wang, B. *Guangpuxue Yu Guangpti Fenxi* **1992**, *12* (4), 67.
Ma, Y.-p., Zhan, G.-I., Chen, Y.-h. *Fenxi Huaxue* **1992a**, *20*, 1227.
Ma, Y.-z., Bai, J., Wang, J.-z., Li, Z.-k., Zhu, L., Li, Y.-q., Zheng, H., Li, B.-w. *J. Anal. At. Spectrom.* **1992b**, *7*, 425.
Ma, Y.-z., Li, Z.-k., Wang, X.-h., Wang, J.-z., Li, Y.-q. *J. Anal. At. Spectrom.* **1994**, *9*, 679.
Maage, A., Julshamn, K., Andersen, K.-J. *J. Anal. At. Spectrom.* **1991**, *6*, 277.
McAllister, T. *J. Anal. At. Spectrom.* **1994**, *9*, 427.
McGahan, M.C., Grimes, A.M. *Ophthalmic Res.* **1991**, *23*, 45.
McMaster, D., Bell, N., Anderson, P., Love, A.H.G. *Clin. Chem.* **1990**, *36*, 211.
Machata, G., Binder, R. Z. *Rechtsmed.* **1973**, *73*, 29.
Mahmood, T.M., Qiao, H.C., Jackson, K.W. *J. Anal. At. Spectrom.* **1995**, *10*, 43.
Majidi, V., Robertson, J.D. *Spectrochim. Acta, Part B* **1991**, *46*, 1723.
Majidi, V., Smith, R.G., Bossio, R.E., Pogue, R.T., McMahon, M.W. *Spectrochim. Acta, Part B* **1996**, *51*, 941.
Manca, D., Lefebvre, M., Trottier, B., Lapare, S., Ricard, A.C., Tra, H.V., Chevalier, G. *Microchem. J.* **1992**, *46*, 249.

Mandjukov, P.B., Djarkova, V., Tsalev, D.L. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 597.
Mandjukov, P.B., Tsakovsky, S.L., Simeonov, V.D., Stratis, J.A. *Spectrochim. Acta, Part B* **1995**, *50*, 1733.
Mandjukov, P.B., Tsalev, D.L. *Microchem. J.* **1990**, *42*, 339.
Mandjukov, P., Vassileva, E., Simeonov, V. *Anal. Chem.* **1992**, *64*, 2596.
Manzoori, J.L., Saleemi, A. *J. Anal. At. Spectrom.* **1994**, *9*, 337.
Marawi, I., Olson, L.K., Wang, J.S., Caruso, J.A. *J. Anal. At. Spectrom.* **1995**, *10*, 7.
Marawi, I., Wang, J., Caruso, J.A. *Anal. Chim. Acta* **1994**, *291*, 127.
Marchante-Gayon, J., Gonzalez, J.M., Fernandez, M.L., Blanco, E., Sanz-Medel, A. *Fresenius J. Anal. Chem.* **1996**, *355*, 615.
Marchante Gayon, J.M., Sanchez Uria, J.E., Sanz-Medel, A. *J. Anal. At. Spectrom.* **1993**, *8*, 731.
Marecek, J., Synek, V. *J. Anal. At. Spectrom.* **1990**, *5*, 385.
Martin, M.-L. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 603.
Martin, M.-L., Gruen, M., Schneider, H. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 141.
Masera, E., Mauchien, P., Lerat, Y. *J. Anal. At. Spectrom.* **1995**, *10*, 137.
Matousek, J.P., Powell, H.K.J. *Spectrochim. Acta, Part B* **1995**, *50*, 857.
Matsumoto, K. *Int. Lab.* **1993a**, *8*, 14.
Matsumoto, K. *Anal. Sci.* **1993b**, *9*, 447.
Matsumoto, K., Katsura, T., Kato, E. *Anal. Sci.* **1991**, *7* (Suppl.), 451.
Matsusaki, K. *Bunseki Kagaku* **1990**, *39*, 823.
Matsusaki, K. *Anal. Chim. Acta* **1991a**, *248*, 251.
Matsusaki, K. *Bunseki Kagaku* **1991b**, *40*, 413.
Matsusaki, K., Harada, Y. *Bunseki Kagaku*, **1992**, *41*, 109.
Matsusaki, K., Izuchi, M. *Anal. Sci.* **1991**, *7*, 159.
Matsusaki, K., Oishi, T. *Anal. Sci.* **1993**, *9*, 381.
Matsusaki, K., Okada, K., Oishi, T., Sata T. *Anal. Sci.* **1994**, *10*, 281.
Matsusaki, K., Sata, T. *Bunseki Kagaku* **1994**, *43*, 641.
Matsusaki, K. , Yamaguchi, T., Yamamoto, Y. *Anal. Sci.* **1996**, *12*, 301.
Matsusaki, K., Yamamoto, T., Oishi, T. *Bunseki Kagaku* **1993**, *42*, 1.
Matthews, M.R., Parsons, P.J. *At. Spectrosc.* **1993**, *14*, 41.
Matusiewicz, H., Kurzawa, Z. *Acta Chim. Hung.* **1991**, *128*, 401.
Matusiewicz, H., Sturgeon, R.E. *Spectrochim. Acta, Part B* **1996**, *51*, 377.
Mazzucotelli, A., Grotti, M. *Spectrochim. Acta, Part B* **1995**, *50*, 1897.
Mazzucotelli, A., Soggia, F., Cosma, B. *Appl. Spectrosc.* **1991**, *45*, 504.
Medeiros, L.C., Belden, R.P., Williams, E.S. *J. Food Sci.* **1993**, *58*, 731.
Mi, R. *Lihua Jianyan, Huaxue Fence* **1990**, *26* (4), 251.
Mihara, Y., Yokota, K. *Ann. Rep. Tohoku Coll. Pharm.* **1990**, *37*, 247.
Mile, B., Rowlands, C.C., Jones, A.V. *J. Anal. At. Spectrom.* **1992**, *7*, 1069.
Mile, B., Rowlands, C.C., Jones, A.V. *J. Anal. At. Spectrom.* **1995**, *10*, 785.
Miller-Ihli, N.J. *J. AOAC Int.* **1994**, *77*, 1288.
Miller-Ihli, N.J. *J. Agric. Food Chem.* **1995**, *43*, 923.
Miller-Ihli, N.J., Greene, F.E. *J. AOAC Int.*, **1992**, *75*, 354.
Miller-Ihli, N.J., Greene, F.E. *At. Spectrosc.* **1993**, *14*, 85.
Millward, C.G., Kluckner, P.D. *J. Anal. At. Spectrom.* **1991**, *6*, 37.
Mindak, W.R. *J. AOAC Int.* **1994**, *77*, 1023.
Mohl, C., Bargouth, I., Duebeck, H.W. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 423.
Monteiro, M.I.C., Curtius, A.J. *J. Anal. At. Spectrom.* **1995**, *10*, 329.

Moreira, M.F.R., Curtius, A.J., de Campos, R.C. *Analyst* **1995**, *120*, 947.
Morishige, Y., Hirokawa, K., Yasuda, K. *Fresenius J. Anal. Chem.* **1994**, *350*, 410.
Morita, Y., Tsukada, H., Isozaki, A. *Bunseki Kagaku* **1993**, *42*, 551.
Mortensen, G., Pedersen, B., Pritzl, G. *Appl. Organomet. Chem.* **1995**, *9*, 65.
Motkosky, N., Kratochvil, B. *Analyst* **1993**, *118*, 1313.
Motoyama, A., Yoshida, M. *Bunseki Kagaku* **1995**, *44*, 231.
Mu, L.-b. *Gongye Weisheng Yu Zhiyebing* **1992**, *18*, 364.
Mueller, M., Anke, M., Illing, H., Hartmann, E. *GIT Fachz. Lab.* **1995**, *39*, 795.
Mueller-Vogt, G., Hahn, L., Mueller, H., Wendl, W., Jacquiers-Roux, D. *J. Anal. At. Spectrom.* **1995**, *10*, 777.
Mueller-Vogt, G., Weigend, F., Wendl, W. *Spectrochim. Acta, Part B* **1996**, *51*, 1133.
Naganuma, A., Okutani, T. *Bunseki Kagaku* **1991**, *40*, 251.
Naka, H., Gregoire, D.C. *J. Anal. At. Spectrom.* **1996**, *11*, 359.
Naka, H., Karayasu, H., Inokuma, Y. *Bunseki Kagaku* **1990a**, *39*, 171.
Naka, H., Karayasu, H., Inokuma, Y. *Sumitomo Kinzoku* **1990b**, *42* (5), 9.
Nakagawa, K., Yonemoto, T., Iwasa, A., Matsubara, I. *Bunseki Kagaku* **1994**, *43*, 557.
Nakamura, T., Oka, H., Ishii, M., Sato, J. *Analyst* **1994**, *119*, 1397.
Nakamura, T., Noike, Y., Koizumi, Y., Sato, Y. *Analyst* **1995**, *120*, 89.
Navarro, J.A., Granadillo, V.A., Salgado, O., Garcia, R., Rodriguez-Iturbe, B., Romero, R.A. In *Trace Elements in Man and Animals*; TEMA-7; Momcilovic, B., Ed.; IMI: Zagreb, 1991, p. 29-10.
Navarro, J.A., Granadillo, V.A., Salgado, O., Rodriguez-Iturbe, B., Garcia, R., Delling, G., Romero, R.A. *Clin. Chim. Acta* **1992**, *211*, 133.
Ni, Z.-m., He, B. *J. Anal. At. Spectrom.* **1995**, *10*, 747.
Ni, Z.-m., Hang, H.-b., Li, A., He, B., Xu, F.-z. *J. Anal. At. Spectrom.* **1991**, *6*, 385.
Ni, Z.-m., He, B., Han, H.-b. *J. Anal. At. Spectrom.* **1993a**, *8*, 995.
Ni, Z.-m., He, B., Han, H.-b. *Can. J. Appl. Spectrosc.* **1993b**, *38*, 11.
Ni, Z.-m., He, B., Han, H.-b. *Spectrochim. Acta, Part B* **1994**, *49*, 947.
Ni, Z.-m., Rao, Z., Li, M. *Anal. Chim. Acta* **1996**, *334*, 177.
Ni, Z.-m., Shan, X.-q. *Spectrochim. Acta, Part B* **1987**, *42*, 937.
Ni, Z.-m., Zhang D.-q. *Spectrochim. Acta, Part B* **1995**, *50*, 1779.
Nickel, H., Zadgorska, Z. *Spectrochim. Acta, Part B* **1995**, *50*, 527.
Nickel, H., Zadgorska, Z., Wolff, G. *Spectrochim. Acta, Part B* **1993**, *48*, 25.
Nikitina, Z.A., Kuznetsova, N.M., Zharkova, I.P., Monakhova, N.G. *J. Anal. Chem.* **1995**, *50*, 90.
Niskavaara, H., Kontas, E. *Anal. Chim. Acta* **1990**, *231*, 273.
Nixon, D.E., Moyer, T.P. *Clin. Chem.* **1992**, *38*, 2479.
Nixon, D.E., Mussmann, G.V., Eckdahl, S.J., Moyer, T.P. *Clin. Chem.* **1991**, *37*, 1575.
Nomura, Y., Okuda, K., Tatsumi, N. *Eur. J. Lab. Med.* **1995**, *3* (1), 55.
Nordahl, K., Radziuk, B., Thomassen, Y., Weberg, R. *Fresenius J. Anal. Chem.* **1990**, *337*, 310.
Ohlsson, K.E.A., Frech, W. *Spectrochim. Acta, Part B*, **1991**, *46*, 559.
Ohta, K., Aoki, W., Mizuno, T. *Mikrochim. Acta* **1990a**, *1*, 81.
Ohta, K., Aoki, W., Mizuno, T. *Chem. Anal. (Warsaw)* **1992a**, *37*, 51.
Ohta, K., Isiyama, T., Yokoyama, M., Mizuno, T. *Talanta* **1995**, *42*, 263.
Ohta, K., Itoh, S., Kaneco, S., Mizuno, T. *Anal. Sci.* **1992b**, *8*, 423.
Ohta, K., Itoh, S., Mizuno, T. *Talanta* **1991a**, *38*, 325.
Ohta, K., Itoh, S., Mizuno, T. *Talanta* **1991b**, *38*, 871.
Ohta, K., Kaneco, S., Itoh, S., Mizuno, T. *Anal. Chim. Acta* **1992c**, *267*, 131.
Ohta, K., Mizutani, K., Itoh, S., Mizuno, T. *Microchem. J.* **1993**, *48*, 184.
Ohta, K., Sugiyama, T., Mizuno, T. *Anal. Chim. Acta* **1990b**, *236*, 479.
Oilunkaniemi, R., Peramaki, P., Lajunen, L.H.J. *At. Spectrosc.* **1994**, *15*, 126.
Oimatsu, T., Manabe, H., Nakahara, T. *Bunseki Kagaku* **1993**, *42*, 599.
Oishi, K., Yasuda, K., Hirokawa, K. *Anal. Sci.* **1991**, *7*, 883.

Okamoto, Y., Kakigi, H., Kumamaru, T. *Anal. Sci.* **1993**, *9*, 105.
Okamoto, Y., Takahashi, T., Isobe, K., Kumamaru, T. *Anal. Sci.* **1990**, *6*, 401.
Okutani, T., Tsuruta, Y., Sakuragawa, A. *Anal. Chem.* **1993**, *65*, 1273.
Omokhodion, F.O., Crockford, G.W. *Sci. Total Environ.* **1991**, *103*, 113.
Osojnik, A., Drglin, T. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 617.
Oster, O. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 861.
Ouishi, K., Yasuda, K., Morishige, Y., Hirokawa, K. *Fresenius J. Anal. Chem.* **1994**, *348*, 195.
Palacios Corvillo, M.A., Gomez Gomez, M., Camara Rica, C. *Talanta* **1990**, *37*, 719.
Pannier, F., Dauchy, X., Potin-Gautier, M., Astruc, A., Astruc, M. *Appl. Organomet. Chem.* **1993**, *7*, 213.
Parsons, P.J., Qiao, H., Aldous, K.M., Mills, E., Slavin, W. *Spectrochim. Acta, Part B* **1995**, *50*, 1475.
Parsons, P.J., Slavin, W. *Spectrochim. Acta, Part B* **1993**, *48*, 925.
Paschal, D.C., Bailey, G.G. *At. Spectrosc.* **1991**, *12*, 151.
Peramaki, P. *At. Spectrosc.* **1991**, *12*, 16.
Perez-Corona, M.T., de la Calle-Guntinas, M.B., Madrid, Y., Camara, C. *J. Anal. At. Spectrom.* **1995**, *10*, 321.
Perez Parajon, J.M., Sanz-Medel, A. *Quim. Anal.* **1993**, *12*, 30.
Perez Parajon, J.M., Sanz-Medel, A. *J. Anal. At. Spectrom.* **1994**, *9*, 111.
Pergantis, S.A., Cullen, W.R., Wade, A.P. *Talanta* **1994**, *41*, 205.
Phuong, D.D.T., Tatar, E., Varga, I., Zaray, G., Cseh, E., Fodor, F. *Microchem. J.* **1995**, *51*, 145.
Pita Calvo, C., Bermejo-Barrera, P., Bermejo Barrera, A. *Quim. Anal.* **1992**, *11*, 35.
Pita Calvo, C., Bermejo-Barrera, P., Bermejo-Barrera, A. *Anal. Chim. Acta* **1995**, *310*, 189.
Pohl, B. *LaborPraxis* **1993**, *17* (9), 44.
Pohl, B., Horstkotte, B., Steeg, U. *LaborPraxis* **1992**, *16*, 230.
Pohl, B., Lange, M. *Lab. Med.* **1994**, *18*, 38.
Pohl, B., Schneider, T. *LaborPraxis* **1990**, *14*, 2.
Popova, S.A., Bratinova S.P. *J. Anal. At. Spectrom.* **1990**, *5*, 35.
Popova, S., Raouf, A., Pankova, M. *Anal. Lab. (Sofia)* **1993**, *2*, 176.
Potin-Gautier, M., Boucharat, C., Astruc, A., Astruc, M. *Appl. Organomet. Chem.* **1993**, *7*, 593.
Prell, L.J., Styris, D.L. *Spectrochim. Acta, Part B* **1991**, *46*, 45.
Prell, L.J., Styris, D.L., Redfield, D.A. *J. Anal. At. Spectrom.* **1991**, *6*, 25.
Probst-Hensch, N., Wagmann, M., Herrmann, A. *Mitt. Geb. Lebensmittelunters. Hyg.* **1991**, *82*, 159.
Pszonicki, L., Essed, A.M. *Chem. Anal. (Warsaw)* **1993a**, *38*, 759.
Pszonicki, L., Essed, A.M. *Chem. Anal. (Warsaw)* **1993b**, *38*, 771.
Pszonicki, L., Skwara, W., Dudek, J. *Chem. Anal. (Warsaw)* **1995**, *40*, 351.
Pyrzynska, K. *Spectrochim. Acta, Part B* **1995a**, *50*, 1595.
Pyrzynska, K. *Analyst* **1995b**, *120*, 1933.
Qi, W.-q., Chen, Y.-l., Zhang, M.-s., Cao, J.-s. *Guangpuxue Yu Guangpu Fenxi* **1994**, *14* (1), 81.
Qian, S., Yang, P. *Fenxi Huaxue* **1990**, *18*, 1064.
Qian, S., Yang, P. *Lihua Jianyan, Huaxue Fence* **1991**, *27* (1), 25.
Qiao, H., Jackson, K.W. *Spectrochim. Acta, Part B* **1991**, *46*, 1841.
Qiao, H., Jackson, K.W. *Spectrochim. Acta, Part B* **1992**, *47*, 1267.
Qiao, H., Mahmood, T.M., Jackson, K.W. *Spectrochim. Acta, Part B* **1993**, *48*, 1495.
Qin, Y., Jiang, Z., Zeng, Y., Hu, B. *J. Anal. At. Spectrom.* **1995**, *10*, 455.
Quan, Z., Ni, Z.-m., Yan, X.-p. *Can. J. Appl. Spectrosc.* **1994**, *39*, 54.
Rademeyer, C.J., Radziuk, B., Romanova, N., Skaugset, N.P., Skogstad, A., Thomassen, Y. *J. Anal. At. Spectrom.* **1995**, *10*, 739.
Radunovic, A., Bradbury, M.W.B., Delves, H.T. *Analyst* **1993**, *118*, 533.
Radziuk, B., Thomassen, Y. *J. Anal. At. Spectrom.* **1992**, *7*, 397.
Ratliff, J. *Anal. Chim. Acta* **1996**, *333*, 285.

Ratliff, J., Majidi, V. *Anal. Chem.* **1992**, *64*, 2743.
Rayson, G.D., Fresquez, M.R. *Can. J. Appl. Spectrosc.* **1993**, *38*, 114.
Rayson, G.D., Johnson, C. *Appl. Spectrosc.* **1991**, *8*, 1305.
Reichardt, M.S. *At. Spectrosc.* **1992**, *13*, 178.
Resto, W., Badini, R.G., Smith, B.W., Stevenson, C.L., Winefordner, J.D. *Spectrochim. Acta, Part B* **1993**, *48*, 627.
Roesick, U., Nowak, F., Melchert, D., Braetter, P. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 49.
Rojas, D. *Spectrochim. Acta, Part B* **1995**, *50*, 1031.
Rojas, D., Olivares, W. *Spectrochim. Acta, Part B* **1992**, *47*, 387.
Rojas, D., Olivares, W. *Spectrochim. Acta, Part B* **1995**, *50*, 1011.
Ronchi, A., Minoia, C., Salgado, P.E.T., Apostoli, P. *Rev. Cienc. Farm. (Araraquara, Braz.)* **1991a**, *13*, 111.
Ronchi, A., Minoia, C., Salgado, P.E.T., Apostoli, P. *Rev. Cienc. Farm. (Araraquara, Braz.)* **1991b**, *13*, 127.
Ruekgauer, M., Zeyfang, A., Uhland, K., Kruse-Jarres, J.D. *J. Trace Elements Med. Biol.* **1995**, *9*, 130.
Ruhnke, G., Ristow, R. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 395.
Russeva, E., Havezov, I., Detcheva, A. *Fresenius J. Anal. Chem.* **1993**, *347*, 320.
Sachsenberg, S., Klenke, T., Krumbein, W.E., Schellnhuber, H.J., Zeeck, E. *Anal. Chim. Acta* **1993**, *279*, 241.
Sachsenberg, S., Klenke, T., Krumbein, W.E., Zeeck, E. *Fresenius J. Anal. Chem.* **1992**, *342*, 163.
Sahayam, A.C., Gangadharan, S. *At. Spectrosc.* **1993**, *14*, 83.
Sahayam, A.C., Gangadharan, S. *Can. J. Appl. Spectrosc.* **1994**, *39*, 61.
Sahayam, A.C., Natarajan, S., Gangadharan, S. *Fresenius J. Anal. Chem.* **1993a**, *346*, 961.
Sahayam, A.C., Tyagi, A.K., Gangadharan, S. *Fresenius J. Anal. Chem.* **1993b**, *347*, 461.
Saho, G.-d., Li, K., Shan, X.-q. *Beijing Keji Daxue Xuebao* **1993**, *15* (4), 429.
Sako, N., Tanaka, H., Toyoda, M., Naka, J., Kuramoto, K. *Bunseki Kagaku* **1994**, *43*, 771.
Sandoval, L., Herraez, J.C., Steadman, G., Mahan, K.I. *Mikrochim. Acta* **1992**, *108*, 19.
Santosa, S.J., Tanaka, S., Yamanaka, K. *Anal. Lett.* **1995**, *28*, 509.
Saraswati, R., Desikan, N.R., Rao, T.H. *J. Anal. At. Spectrom.* **1994**, *9*, 1289.
Sato, M., Nomoto, S. *Seibutsu Shiryo Bunseki* **1990**, *13*, 18.
Schaeffer, U., Krivan, V. *Spectrochim. Acta, Part B* **1996**, *51*, 1211.
Schintu, M., Jean-Caurant, F., Amiard, J.-C. *Ecotoxicol. Environ. Safety* **1992**, *24*, 95.
Schleich, C., Henze, G. *Fresenius J. Anal. Chem.* **1990**, *338*, 140.
Schlemmer, G. *At. Spectrosc.* **1996**, *17*, 15.
Schlemmer, G., Feuerstein, M. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993, p. 431.
Schlemmer, G., Lehman, R., Marschall, A. In *CANAS'95 Colloquium Analytische Atomspektroskopie*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1996, p. 97.
Schlemmer, G., Welz, B. *Spectrochim. Acta, Part B* **1986**, *41*, 1157.
Schneider, G., Krivan, V. *Spectrochim. Acta, Part B* **1995**, *50*, 1557.
Schramel, P., Wendler, I. *Fresenius J. Anal. Chem.* **1995**, *351*, 567.
Sedykh, E.M., Tatsy, Yu.G., Ishmiyarova, G.R., Ostronova, M.M. *At. Spectrosc.* **1994**, *15*, 245.
Sekerka, I., Lechner, J.F. *Anal. Chim. Acta* **1991**, *254*, 99.
Seltner, H., Hermann, G., Heppler, C. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 609.
Sen Gupta, J.G., Bouvier, J.L. *Talanta* **1995**, *42*, 269 and 1345.
Sentimenti, E., Mazzetto, G., Milella, E. *J. Anal. At. Spectrom.* **1993**, *8*, 89.
Shabanova, L.N., Gil'bert, E.N., Bukhbinder, G.L., Rozhina, O.V. *Zh. Anal. Khim.* **1990**, *45*, 1178.
Shan, X.-q., Ni, Z.-m. *Hua Hsuch Hsuch Pao (Acta Chim. Sinica)* **1979**, *37*, 261.

Shan, X., Radziuk, B., Welz, B. In *6 Colloquium Atomspektrometrische Spurenanalytik*; Welz, B., Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1991, p. 99.
Shan, X.-q., Radziuk, B., Welz, B., Sychra, V. *J. Anal. At. Spectrom.* **1992a**, *7*, 389.
Shan, X.-q., Radziuk, B., Welz, B., Vyskocilova, O. *J. Anal. At. Spectrom.* **1993**, *8*, 409.
Shan, X.-q., Wang, W., Wen, B. *J. Anal. Atom. Spectrom.* **1992b**, *7*, 761.
Shan, X.-q., Wen, B. *J. Anal. At. Spectrom.* **1995**, *10*, 791.
Shi, Y., Shen, J.H., Chi, X.Z. *Fenxi Shiyanshi* **1993**, *12* (6), 58.
Shimizu, T., Fukuda, K., Shijo, Y. *Bunseki Kagaku* **1994a**, *43*, 1009.
Shimizu, T., Ohya, K., Shijo, Y. *Bunseki Kagaku* **1994b**, *43*, 971.
Shimmura, T., Nakazaki, M., Shiroishi, K. *Toyama ken Eisei Kenkyusho Nempo* **1990**, *14*, 175.
Shiowatana, J., Siripinyanond, A. *At. Spectrosc.* **1996**, *17*, 122.
Shirasaki, T., Nakamura, H., Hiraki, K. *Bunseki Kagaku* **1994**, *43*, 1149.
Shou, M., Shao, H. *Guangpuxue Yu Guangpu Fenxi* **1990**, *10* (6), 41.
Shuttler, I., Feuerstein, M., Schlemmer, G. *J. Anal. At. Spectrom.* **1992**, *7*, 1299.
Sierraalta, A., de Benzo, Z., Araujo, W., Ruette, F. *J. Molecular Structure (Theochem)* **1992**, *254*, 387.
Silva, I.A., Campos, R.C., Curtius, A.J., Sella, S.M. *J. Anal. At. Spectrom.* **1993**, *8*, 749.
Silva, M.M., Silva, R.B., Krug, F.J., Nobrega, J.A., Berndt, H. *J. Anal. At. Spectrom.* **1994**, *9*, 861.
Sinemus, H.W., Kleiner, J., Radziuk, B., Stabel, H.-H. In *CANAS'93 Colloquium Analytische Atomspektroskopie*; Dittrich, K., Welz, B., Eds.; Univ. Leipzig & UFZ: Leipzig-Halle, 1993a, p. 657.
Sinemus, H.W., Stabel, H.-H., Radziuk, B., Kleiner, J. *Spectrochim. Acta, Part B* **1993b**, *48*, 1719.
Sipos, M., Adamis, T. *Acta Chim. Hung.* **1991**, *128*, 869.
Slaveykova, V.I., Manev, S.G., Lazarov, D.L. *Spectrochim. Acta, Part B* **1995**, *50*, 1725.
Slaveykova, V.I., Manev, S.G., Lazarov, D.L. *React. Kinet. Catal. Lett.* **1997a**, *61*, 139.
Slaveykova, V.I., Manev, S.G., Lazarov, D.L. *Spectrosc. Lett.* **1997b**, *30*, 297.
Slaveykova, V.I., Matanova, E., Draganova, S., Daiev, Ch. *Analytical Lababoratory (Sofia)* **1992**, *1*, 12.
Slaveykova, V.I., Rastegar, F., Leroy, M.J.F. *J. Anal. At. Spectrom.* **1996a**, *11*, 997.
Slaveykova, V.I., Stoimenov, P.K., Manev, S.G., Lazarov, D.L. *Spectrochim. Acta, Part B* **1997c**, *52*, 1259.
Slaveykova, V.I., Tsalev, D.L. In *XXVI Colloquium Spectroscopicum Internationale, Selected Papers*; Tsalev, D.L., Ed.; Sofia, July 2–7 1989, Vol. VII, p. 85.
Slaveykova, V.I., Tsalev, D.L. *Anal. Lett.* **1990**, *23*, 1921.
Slaveykova, V.I., Tsalev, D.L. *Spectrosc. Lett.* **1991**, *24*, 139.
Slaveykova, V.I., Tsalev, D.L. *J. Anal. At. Spectrom.* **1992**, *7*, 365.
Slaveykova, V.I., Tsalev, D.L., Maskill, R. *Ciencia (Maracaibo, Venezuela)* **1996b**, *4*, 165.
Slavin, W., Carnrick, G.R., Manning, D.C. *Anal. Chem.* **1982**, *54*, 621.
Slavin, W., Manning, D.C., Carnrick, G.R. *At. Spectrosc.* **1981**, *2*, 137.
Slavin, W., Miller-Ihli, N.T., Carnrick, G.R. *Am. Lab.* **1990**, *22* (Oct.), 80.
Slikkerveer, A., Helmich, R.B., Edelbroek, P.M., Van der Voet, G.B., De Wolff, F.A. *Clin. Chim. Acta* **1991**, *201*, 17.
Smeyers-Verbeke, J., Yang, Q., Penninckx, W., Vandervoort, F. *J. Anal. At. Spectrom.* **1990**, *5*, 393.
Sneddon, J., Farah, K.S. *Spectrosc. Lett.* **1994**, *27*, 257.
Soares, M.E., Bastos, M.L., Ferreira, M.A. *J. Anal. At. Spectrom.* **1993**, *8*, 655.
Soares, M.E., Bastos, M.L., Ferreira, M.A. *J. Anal. At. Spectrom.* **1994**, *9*, 1269.
Soares, M.E., Bastos, M.L., Ferreira, M.A. *At. Spectrosc.* **1995a**, *16*, 256.
Soares, M.E., Bastos, M.L., Ferreira, M.A. *Analyst* **1995b**, *120*, 2367.
Sommer, L., Komarek, J., Burns, D.T. *Pure Appl. Chem.* **1992**, *64*, 213.
Sramkova, J., Kotrly, S., Dolezalova, K. *J. Anal. At. Spectrom.* **1995**, *10*, 763.
Stalikas, C.D., Pilidis, G.A., Karayannis, M.I. *J. Anal. At. Spectrom.* **1996**, *11*, 595.
Stobbaerts, R.F.J., Ieven, M., Deelstra, H., De Leeuw, I. Z. *Ernaerungswiss.* **1992**, *31*, 138.
Streck, S., Pawlik, H. *CLB, Chem. Labor Betr.* **1995**, *46* (2), 68.
Struebel, G., Rzepka-Glinder, V., Grobecker, K.H., Jarrar, K. *Fresenius J. Anal. Chem.* **1990**, *337*, 316.

Stupar, J., Dolinsek, F. *Spectrochim. Acta, Part B* **1996**, *51*, 665.
Sturgeon, R.E., Gregoire, D.C. *Spectrochim. Acta, Part B* **1994**, *49*, 1335.
Sturgeon, R.E., Willie, S.N. *J. Anal. At. Spectrom.* **1992**, *7*, 339.
Sturgeon, R.E., Willie, S.N., Luong, V.T., Berman, S.S. *J. Anal. At. Spectrom.* **1991**, *6*, 19.
Styris, D.L., Prell, L.J., Redfield, D.A. *Anal. Chem.* **1991a**, *63*, 503.
Styris, D.L., Prell, L.J., Redfield, D.A., Holcombe, J.A., Bass, D.A. *Anal. Chem.* **1991b**, *63*, 508.
Styris, D.L., Redfield D.A. *Spectrochim. Acta Rev.* **1993**, *15*, 71.
Sun, X.-j. *Lihua Jianyan, Huaxue Fence* **1996**, *32* (2), 86.
Sun, X., Huang, F.-x., Mei, W.-d. *Guangpuxue Yu Guangpu Fenxi* **1994**, *14* (4), 97.
Suzuki, Y., Marumo, Y. *Bunseki Kagaku* **1993**, *42*, 417.
Taddia, M., Bellini, A., Fornari, R. *J. Anal. At. Spectrom.* **1995**, *10*, 433.
Taddia, M., Bosi, M., Poluzzi, V. *J. Anal. At. Spectrom.* **1993**, *8*, 755.
Tahan, J.E., Granadillo, V.A., Romero, R.A. *Anal. Chim. Acta* **1994**, *295*, 187.
Tahvonen, R., Kumpulainen, J. *Food Addit. Contam.* **1994a**, *11*, 415.
Tahvonen, R., Kumpulainen, J. *J. Anal. At. Spectrom.* **1994b**, *9*, 1427.
Takeda, K., Akamatsu, C., Ishikawa, Y. *Anal. Chim. Acta* **1994**, *298*, 375.
Takeo, M., Tsunekage, N., Takata, E., Maeda, Y. *Bunseki Kagaku* **1995**, *44*, 697.
Tan, G., Liu, M. *Lihua Jianyan, Huaxue Fence* **1991**, *27* (1), 7.
Tan, Y., Blais, J.-S., Marshall, W.D. *Analyst* **1996a**, *121*, 1419.
Tan, Y., Marshall, W.D., Blais, J.-S. *Analyst* **1996b**, *121*, 483.
Tang, S., Parsons, P.J., Slavin, W. *J. Anal. At. Spectrom.* **1995**, *10*, 521.
Tang, S., Parsons, P.J., Slavin, W. *Analyst* **1996**, *121*, 195.
Tao, G.-h., Fang, Z.-I. *J. Anal. At. Spectrom.* **1993**, *8*, 577.
Tao, G.-h., Fang, Z.-I. *Talanta* **1995**, *42*, 375.
Tao, R., Peng, X. *Guangpu Shiyanshi* **1993**, *10* (1), 1.
Teissedre, P.L., Cabanis, M.T., Cabanis, J.C. *Analusis* **1993**, *21*, 249.
Temminghoff, E.J.M. *J. Anal. At. Spectrom.* **1990**, *5*, 273.
Terui, Y., Yasuda, K., Hirokawa, K. *Anal. Sci.* **1991a**, *7*, 397.
Terui, Y., Yasuda, K., Hirokawa, K. *Anal. Sci.* **1991b**, *7*, 593.
Terui, Y., Yasuda, K., Hirokawa, K. *Anal. Sci.* **1991c**, *7*, 599.
Thomaidis, N.S., Piperaki, E.A. *Analyst* **1996**, *121*, 111.
Thomaidis, N.S., Piperaki, E.A., Efstathiou, C.E. *J. Anal. At. Spectrom.* **1995a**, *10*, 221.
Thomaidis, N.S., Piperaki, E.A., Polydorou, C.K., Efstathiou, C.E. *J. Anal. At. Spectrom.* **1996**, *11*, 31.
Thomaidis, N.S., Piperaki, E.A., Siskos, P.A. *Mikrochim. Acta* **1995b**, *119*, 233.
Tian, L.-c., Peng, F., Wang, X.-r. *Anal. Sci.* **1991**, *7* (Suppl.), 1155.
Tinggi, U., Reilly, C., Hahn, S., Capra, M.J. *Sci. Total Environ.* **1992**, *125*, 15.
Tittarelli, P., Biffi, C. *J. Anal. At. Spectrom.* **1992**, *7*, 409.
Tittarelli, P., Biffi, C., Kmetov, V. *J. Anal. At. Spectrom.* **1994**, *9*, 443.
Tompuri, K., Tummavuori, *J. Anal. Commun.* **1996**, *33*, 283.
Tsai, S.-J.J., Bae, Y.-L. *Analyst* **1993**, *118*, 297.
Tsai, S.-J.J., Jan, C.C. *Analyst* **1993**, *118*, 1183.
Tsai, S.-J.J., Jan, C.C., Chang, L.L. *Spectrochim. Acta, Part B* **1994**, *49*, 773.
Tsalev, D.L. *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice, Vol. II: Determination of Individual Elements*; CRC Press: Boca Raton, FL, 1984.
Tsalev, D.L. *At. Spectrosc.* **1991**, *12*, 169.
Tsalev, D.L. *J. Anal. At. Spectrom.* **1994**, *9*, 405.
Tsalev, D.L. *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice, Vol. III: Progress in Analytical Methodology*; CRC Press: Boca Raton, FL, 1995.
Tsalev, D.L. In *Encyclopedia of Environmental Analysis and Remediation*; Meyers, R.E., Ed.; Wiley: New York, 1998, Vol. 3 (in press).
Tsalev, D.L., Dimitrov, T.A., Mandjukov, P.B. *J. Anal. At. Spectrom.* **1990a**, *5*, 189.

Tsalev, D.L., D'Ulivo, A., Lampugnani, L., Di Marco, M., Zamboni, R. *J. Anal. At. Spectrom.* **1995**, *10*, 1003.
Tsalev, D.L., D'Ulivo, A., Lampugnani, L., Di Marco, M., Zamboni, R. *J. Anal. At. Spectrom.* **1996a**, *11*, 979.
Tsalev, D.L., D'Ulivo, A., Lampugnani, L., Di Marco, M., Zamboni, R. *J. Anal. At. Spectrom.* **1996b**, *11*, 989.
Tsalev, D.L., Mandjukov, P.B., Draganova, D. *Spectrosc. Lett.* **1992**, *25*, 943.
Tsalev, D.L., Mandjukov, P.B., Stratis, J.A. *J. Anal. At. Spectrom.* **1987**, 2, 135.
Tsalev, D.L., Slaveykova, V.I. *J. Anal. At. Spectrom.* **1992a**, *7*, 147.
Tsalev, D.L., Slaveykova, V.I. *Spectrosc. Lett.* **1992b**, *25*, 221.
Tsalev, D.L., Slaveykova, V.I., Georgieva, R.B. *Anal. Lett.* **1996c**, *29*, 73.
Tsalev, D.L., Slaveykova, V.I., Mandjukov, P.B. In *5. Colloquium Atomspectrometrische Spurenanalytik*; B. Welz, Ed.; Bodenseewerk Perkin-Elmer GmbH: Ueberlingen, 1989, p. 178.
Tsalev, D.L., Slaveykova, V.I., Mandjukov, P.B. *Spectrochim. Acta Rev.* **1990b**, *13*, 225.
Tsalev, D.L., Slaveykova, V.I., Mandjukov, P.B. *Chem. Anal. (Warsaw)* **1990c**, *35*, 267.
Tsalev, D.L., Tserovski, E.I., Raitcheva, A.I., Barzev, A.I., Georgieva, R.G., Zaprianov, Z.K. *Spectrosc. Lett.* **1993**, *26*, 331.
Tserovsky, E., Arpadjan, S. *J. Anal. At. Spectrom.* **1991**, *6*, 487.
Tserovsky, E., Arpadjan, S., Karadjova, I. *Spectrochim. Acta, Part B* **1992**, *47*, 959.
Tserovsky, E., Arpadjan, S., Karadjova, I. *J. Anal. At. Spectrom.* **1993**, *8*, 85.
Tsunoda, K., Takano, Y., Matsumoto, K., Kawamoto, H., Akaiwa, H. *Microchem. J.* **1994**, *49*, 282.
Tummalapalli, C.M., Williams, J.C., Stern, T.N. *Anal. Lett.* **1994**, *27*, 2091.
Turunen, M., Peraniemi, S., Ahlgren, M., Westerholm, H. *Anal. Chim. Acta* **1995**, *311*, 85.
Ulrich, A., Dannecker, W., Meiners, S., Voellkopf, U. *Anal. Proc.* **1992**, *29*, 284.
Ure, T.A.M., Butler, L.R.P., L'vov, B.V., Rubeska, I., Sturgeon, R. *Pure Appl. Chem.* **1992**, *64*, 253.
Ure, A.M., Thomas, R., Littlejohn, D. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 65.
Ursinyova, M., Hladikova, V., Sovcikova, E. *Chem. Listy* **1995**, *89*, 388.
Ursinyova, M., Palusova, O., Hladikova, V. *Chem. Listy* **1994**, *88*, 252.
Usenko, S.I., Prorok, M.M. *Zavod. Lab.* **1992**, *58*, 6.
Van Cauwenbergh, R., Robberecht, H., Van Dael, P., Deelstra, H. *J. Trace Elem. Electrolytes Health Dis.* **1990**, *4*, 127.
Van Dael, P., Van Cauwenbergh, R., Robberecht, H., Deelstra, H. *At. Spectrosc.* **1995**, *16*, 251.
van Dalen, G. *J. Anal. At. Spectrom.* **1996**, *11*, 1087.
van Dalen, G., de Galan, L. *Spectrochim. Acta, Part B* **1994**, *49*, 1689.
Vasikaran, S.D., Patel, S., O'Gorman, P. *Ann. Clin. Biochem.* **1992**, *29*, 220.
Veber, M., Cujes, K., Gomiscek, S. *J. Anal. At. Spectrom.* **1994**, *9*, 285.
Vinas, P., Campillo, N., Lopez Garcia, I., Hernandez Cordoba, M. *Food Chem.* **1994a**, *50*, 317.
Vinas, P., Campillo, N., Lopez Garcia, I., Hernandez Cordoba, M. *Analyst* **1994b**, *119*, 1119.
Vinas, P., Campillo, N., Lopez Garcia, I., Hernandez Cordoba, M. *Fresenius J. Anal. Chem.* **1994c**, *349*, 306.
Vinas, P., Campillo, N., Lopez Garcia, I., Hernandez Cordoba, M. *At. Spectrosc.* **1995a**, *16*, 86.
Vinas, P., Campillo, N., Lopez Garcia, I., Hernandez Cordoba, M. *Talanta* **1995b**, *42*, 527.
Vinas, P., Campillo, N., Lopez Garcia, I., Hernandez Cordoba, M. *Fresenius J. Anal. Chem.* **1995c**, *351*, 695.
Volynsky, A.B. *Zh. Anal. Khim.* **1987**, *42*, 1541.
Volynsky, A.B. *J. Anal. Chem.* **1995**, *50*, 2.
Volynsky, A.B. *Spectrochim. Acta, Part B* **1996**, *51*, 1573.
Volynsky, A.B., Krivan, V. *J. Anal. At. Spectrom.* **1996**, *11*, 159.
Volynsky, A.B., Krivan, V., Tikhomorov, S.V. *Spectrochim. Acta, Part B* **1996**, *51*, 1253.
Volynsky, A.B., Sedykh, E.M., Bannykh, L.N. *Talanta* **1991a**, *38*, 761.
Volynsky, A.B., Tikhomirov, S.V., Elagin, A. *Analyst* **1991b**, *116*, 145.

Volynsky, A.B., Tikhomirov, S.V., Senin, V.G., Kashin, A.N. *Anal. Chim. Acta 1993, 284*, 367 and 288, 287.
Volynsky, A.B., Valedinskaya, O.R., Kutseva, N.K. *Zh. Anal. Khim.* **1992**, *47*, 493.
Voth-Beach, L.M., Shrader, D.E. *Spectroscopy* (Springfield, Oregon) **1986**, *1*, 49.
Voth-Beach, L.M., Shrader, D.E. *J. Anal. At. Spectrom.* **1987**, *2*, 45.
Wagner, H. *J. Am. Soc. Brew. Chem.* **1995**, *53*, 141.
Wagner, H.P., Dalglish, K., McGarrity, M.J. *J. Am. Soc. Brew. Chem.* **1991**, *49*, 28.
Wagner, H.P., McGarrity, M.J. *J. Am. Soc. Brew. Chem.* **1991**, *49*, 151.
Wagner, H.P., McGarrity, M.J. *J. Am. Soc. Brew Chem.* **1992**, *50*, 142.
Walcerz, M., Garbos, S., Bulska, E., Hulanicki, A. *Fresenius J. Anal. Chem.* **1994**, *350*, 662.
Wan, A.T., Conyers, R.A.J., Coombs, C.J., Masterton, J.P. *Clin. Chem.* **1991**, *37*, 1683.
Wang, A.-x., Wang, F.-I., Wang, Z.-x. *Fenxi Ceshi Xuebao* **1995**, *14*, 72.
Wang, J.-p., Deng, B. *Spectrochim. Acta, Part B* **1992a**, *47*, 711.
Wang, J.-p., Deng, B. *Guangpuxue Yu Guangpu Fenxi* **1992b**, *12* (3), 83.
Wang, P., Holcombe, J.A. *Appl. Spectrosc.* **1994**, *48*, 713.
Wang, S.T., Demshar, H.P. *Analyst* **1992**, *117*, 959.
Wang, Y., Lu, C., Xiao, Z., Wang, G., Kuan, S.S., Rigsby, E.J. *J. Agric. Food Chem.* **1991**, *39*, 724.
Wanner, B., Richner, P., Magyar, B. *Spectrochim. Acta, Part B* **1996**, *51*, 817.
Watling, R.J., Haines, J. *Lab. Pract.* **1990**, *39* (6), 56.
Wegener, S., Pohl, B., Folz, M., Jansen, A. *Fresenius J. Anal. Chem.* **1992**, *343*, 153.
Wei, J.-s., Liu, Q., Okutani, T. *Anal. Sci.* **1994**, *10*, 465.
Wei, W.-C., Yang, M.-H. *Fresenius J. Anal. Chem.* **1995**, *353*, 167.
Welz, B., Bozsai, G., Sperling, M., Radziuk, B. *J. Anal. At. Spectrom.* **1992a**, *7*, 505.
Welz, B., Schlemmer, G., Mudakavi, J.R. *J. Anal. At. Spectrom.* **1992b**, *7*, 499.
Welz, B., Schlemmer, G., Mudakavi, J.R. *J. Anal. At. Spectrom.* **1992c**, *7*, 1257.
Welz, B., Schlemmer. G., Voellkopf, U. *Spectrochim. Acta, Part B* **1984**, *39*, 501.
White, M.A., O'Hagan, S.A., Wright, A.L., Wilson, H.K. *J. Esposure Anal. Environ. Epidemiol.* **1992**, *2* (2), 195.
Wieteska, E., Drzewinska, A. *Chem. Anal. (Warsaw)* **1995**, *40*, 207.
Wieteska, E., Zioek, A., Drzewinska, A. *Anal. Chim. Acta* **1996**, *330*, 251.
Wifladt, A.-M., Bye, R., Lund, W. *Fresenius J. Anal. Chem.* **1992**, *344*, 541.
Willie, S.N. *At. Spectrosc.* **1994**, *15*, 205.
Wiltshire, G.A., Bolland, D.T., Littlejohn, D. *J. Anal. At. Spectrom.* **1994**, *9*, 1255.
Winnefeld, K., Schroeter, H., Weiland, G. *GIT Fachz Lab.* **1993**, *37*, 989.
Wrobel, K., Gonzalez, E.B., Wrobel, K., Sanz-Medel, A. *Analyst* **1995**, *120*, 809.
Wu, M., Carnahan, J.W. *Appl. Spectrosc.* **1990**, *44*, 673.
Wu, Z., Yao, J., Wang, B. *Guangpuxue Yu Guangpu Fenxi* **1990**, *10* (4), 50.
Xu, D.-q. *Guangpuxue Yu Guangpu Fenxi* **1994**, *14* (6), 77.
Xu, D.-q., Guo, G.-p., Sun, H.-w. *J. Anal. At. Spectrom.* **1995**, *10*, 753.
Xu, N., Majidi, V., Ehmann, W.D., Markesbery, W.R. *J. Anal. At. Spectrom.* **1992**, *7*, 749.
Xuan, W. *Fenxi Huaxue* **1992a**, *20*, 209.
Xuan, W. *Spectrochim. Acta, Part B* **1992b**, *47*, 545.
Xuan, W.-k., Cai, B.-h. *Yejin Fenxi* **1992**, *12* (3), 23.
Xuan, W., Li, J. *Spectrochim. Acta, Part B* **1990**, *45*, 669.
Yan, X.-p., Ni, Z.-m. *J. Anal. At. Spectrom.* **1991**, *6*, 483.
Yan, X.-p., Ni, Z.-m. *Spectrochim. Acta, Part B* **1993**, *48*, 1315.
Yan, X.-p., Ni, Z.-m., Yang, X.-t., Hong, G.-q. *Talanta* **1993a**, *40*, 1839.
Yan, X.-p., Ni, Z.-m., Yang, X.-t., Hong, G.-q. *Spectrochim. Acta, Part B* **1993b**, *48*, 605.
Yang, G.-y., Xu, D.-x., Jin, R.-x. *Analyst* **1995**, *120*, 1657.
Yang, J., Dai, L. *Yankuang Ceshi* **1990**, *9* (1), 44.
Yang, J., Su, R. *Lihua Jianyan, Huaxue Fence* **1990**, *26* (1), 36.

Yang, P. *Guangpuxue Yu Guangpu Fenxi* **1992a**, *12* (1), 116.
Yang, P.-y., Ni, Z.-m., Zhuang, Z.-x., Xu, F.-c., Jiang, A.-b. *J. Anal. At. Spectrom.* **1992**, *7*, 515.
Yang, Q., Smeyers-Verbeke, J. *Clin. Chim. Acta* **1991**, *204*, 23.
Yang, W.-m., Ni, Z.-m. *Spectrochim. Acta, Part B* **1994**, *49*, 1067.
Yang, W.-m., Ni, Z.-m. *J. Anal. At. Spectrom.* **1995**, *10*, 493.
Yang, W.-m., Ni, Z.-m. *Spectrochim. Acta, Part B* **1996**, *51*, 65.
Yang, X.-H., Li, G.-K., Tang, B.-Y., Zhang, Z.-X. *Redai Haiyang* **1991**, *10* (3), 101.
Yang, Y.J. *Yankuang Ceshi* **1992b**, *11* (4), 310.
Yao, J., Ji, Y. *Guangpuxue Yu Guangpu Fenxi* **1992**, *12* (3), 93.
Yao, J.-y., Jiang, Y.-q. *Fenxi Ceshi Tongbao* **1990**, *9* (3), 35.
Yao, J., Jiang, Y. *Fenxi Ceshi Tongbao* **1991a**, *10* (5), 56.
Yao, J., Jiang, Y. *Guangpuxue Yu Guangpu Fenxi* **1991b**, *11* (3), 45.
Yao, J., Song, J., Zhou, J. *Guangpuxue Yu Guangpu Fenxi* **1990a**, *10* (1), 27.
Yao, J., Song, J., Zhou, J., Wei, Y. *Fenxi Shiyanshi* **1990b**, *9* (1), 16.
Yao, J., Wu, Z., Zhi, G. *Fenxi Huaxue*, **1991**, *19*, 471.
Yao, J., Yang, Q. *Fenxi Huaxue* **1992**, *20*, 183.
Yao, J.-y., Yun, Z.M., Duan, H.F., Xiang, R.Y. *Fenxi Huaxue* **1993**, *21*, 846.
Yasuda, K., Hirano, Y., Hirokawa, K., Kamino, T., Yaguchi, T. *Anal. Sci.* **1993**, *9*, 529.
Yasuda, K., Hirano, Y., Kamino, T., Hirokawa, K. *Anal. Sci.* **1994**, *10*, 623.
Yasuda, K., Hirano, Y., Kamino, T., Yaguchi, T., Hirokawa, K. *Anal. Sci.* **1995**, *11*, 437.
Yasuda, K., Hirano, Y., Kamino, T., Yaguchi, T., Hirokawa, K. *Anal. Sci.* **1996**, *12*, 659.
Yoo, K.-s., Kim, C.-b., Kwon, J.-k. *Anal. Sci. Technol.* **1995**, *8*, 9.
Yoo, K.S., Kwon, J.K. *Anal. Sci. Technol.* **1992**, *5*, 349.
Yoshimura, C., Fujino, T. *Chem. Express* **1991**, *6*, 305.
Yoshimura, C., Fujino, T., Murata, S. *Nippon Kagaku Kaishi* **1992**, (5), 575.
Yoshimura, C., Fujino, T., Yamakoshi, T. *Nippon Kagaku Kaishi* **1993**, (3), 259.
Yoshimura, C., Huzino, T. *Chem. Express* **1990**, *5*, 129.
Yu, Z., Vandecasteele, C., Desmet, B., Dams, R. *Mikrochim. Acta* **1990**, *1*, 41.
Yuan, H.-J., Yang, Z.-Q. *Shanghai Keji Daxue Xuebao* **1990**, *13* (3), 17.
Yudelevich, I.G., Petrova, N.I., Buyanova, L.M. *Vysokochistye Veshchestva* **1993**, *2*, 83.
Yue, F., Wu, X., Lin, S., Zhang, R. *Guangpuxue Yu Guangpu Fenxi* **1991**, *11* (3), 23.
Yuzefovsky, A.I., Michel, R.G. *J. Anal. At. Spectrom.* **1994**, *9*, 1203.
Zachariadis, G.A., Stratis, J.A., Kaniou, I., Kalligas, G. *Mikrochim. Acta* **1995**, *119*, 191.
Zaray, G., Kantor, T. *Spectrochim. Acta, Part B* **1995**, *50*, 489.
Zeng, D. *Fenxi Huaxue* **1991a**, *19* (7), Back cover.
Zeng, D. *Guangpuxue Yu Guangpu Fenxi* **1991b**, *11* (4), 47.
Zeng, D.-g. *Lihua Jianyan, Huaxue Fence* **1993**, *29* (1), 23.
Zeng, X., You, Q., Zhong, Y. *Guangpuxue Yu Guangpu Fenxi* **1991**, *11* (4), 39.
Zhang, B.-c. *Henliang Fenxi* **1993**, *9* (1–2), 42.
Zhang, L., Carnrick, G., Slavin, W. *Spectrochim. Acta, Part B* **1993**, *48*, 1435.
Zhang, L., Ni, Z.-m., Shan, X-q. *Can. J. Appl. Spectrosc.* **1991a**, *36*, 47.
Zhang, J., Guo, S. *Analyst* **1995**, *120*, 1661.
Zhang, P., Jin, Y. *Yankuang Ceshi* **1990**, *9* (2), 128.
Zhang, Z., Huang, Z., Li, G., Yang, X. *Fenxi Ceshi Tongbao* **1991b**, *10* (4), 1.
Zhao, J., Jiang, S., Chen, S., Jiang, D., Chakraborti, D. *Fresenius J. Anal. Chem.* **1990**, *337*, 877.
Zheng, W., Sipes, I.G., Carter, D.E. *Anal. Chem.* **1993a**, *65*, 2174.
Zheng, Y.-s. *Spectrosc. Lett.* **1994**, *27*, 353.
Zheng, Y.-s., Su, X.-g. *Can. J. Appl. Spectrosc.* **1993b**, *38*, 109.
Zheng, Y., Su, X. *Talanta* **1993**, *40*, 347.
Zheng, Y.-s., Su, X.-g. *Mikrochim. Acta* **1994**, *112*, 237.
Zheng, Y.-s., Su, X.-q., Quan, Z. *Appl. Spectrosc.* **1993c**, *47*, 1222.

Zheng, Y.-s., Wang, Y.-q. *Spectrosc. Lett.* **1994**, *27*, 817.
Zheng, Y.-s., Wang, Y.-q. *Talanta* **1995**, *42*, 361.
Zheng, Y., Xiang, Y. *Fenxi Huaxue*, **1990**, *18*, 676.
Zheng, Y., Zhang, D. *Anal. Chem.* **1992**, *64*, 1656.
Zheng, Y.-s., Zhou, C.-j. *Yankuang Ceshi* **1992**, *11* (3), 236.
Zhou, C.Y., Wong, M. K., Koh, L.L., Wee, Y.C. *Talanta* **1996**, *43*, 1061.
Zhou, H.-g., Peng, X.-y., Tao, R. *Guangpuxue Yu Guangpu Fenxi* **1992**, *12* (3), 97.
Zhou, J., She, Y.M. *Lihua Jianyan, Huaxue Fence* **1992**, *28* (6), 360.
Zhou, M.J., Tang, S.M., Wang, Q. *Guangpuxue Yu Guangpu Fenxi* **1993**, *13* (1), 117.
Zhu, X.P., Cai, S.Q., Wang, K. *Fenxi Shiyanshi* **1993**, *12* (4), 23.
Zhuang, Z., Yang, P., Luo, J., Wang, X., Huang, B. *Can. J. Appl. Spectrosc.* **1991**, *36*, 9.
Zhuang, Z., Yang, C., Wang, X., Yang, P., Huang, B. *Fresenius J. Anal. Chem.* **1996**, *355*, 277.
Zhuang, Z., Yang, P., Wang, X., Deng, Z., Huang, B. *J. Anal. At. Spectrom.* **1993**, *8*, 1109.
Zilliacus, R., Likonen, J. *Appl. Spectrosc.* **1992**, *46*, 1828.
Zolotovitskaya, E.S., Potapova, V.G., Grebenyuk, N.N., Blank, A.B. *J. Anal. Chem.* **1995**, *50*, 914.
Zong, Y.Y., Parsons, P.J., Slavin, W. *Spectrochim. Acta, Part B* **1994**, *49*, 1667.
Zong, Y.Y., Parsons, P.J., Slavin, W. *J. Anal. At. Spectrom.* **1996**, *11*, 25.
Zu, L.-I., Li, A.-m. *Guangpuxue Yu Guangpu Fenxi* **1993**, *13* (5), 85.
Zurera-Cosano, G., Moreno-Rojas, R., Amaro-Lopez, M.A. *Food Addit. Contam.* **1994**, *11* (1), 91.

RECENT DEVELOPMENTS IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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I. INTRODUCTION

This chapter discusses some of the recent and interesting developments in graphite furnace atomic absorption spectrometry (GFAAS). These include the development of a portable atomic absorption spectrometer (Sanford, 1996); a paper describing the use of thermal methods and laser desorption time of flight mass spectrometry to characterize surface interactions between metals and substrates (Majidi, 1996); a new method to extend the nonlinear region of calibration graphs (Lonardo, 1996); a Monte Carlo program to model GFAAS absorption profiles on a desktop personal computer (Histen, 1996); two papers involving GFAAS interferences, one introducing "wall-to-platform" and "two-platform" methods to characterize chemical interferences (Mahmood, 1996) and the other regarding a high-resolution spectrometer to characterize Zeeman spectral interferences (Heitmann, 1996); a new system to determine metals in air by impaction-GFAAS (Lee, 1996); and the use of scanning tunneling microscopy to study graphite substrates for GFAAS (Vandervoort, 1996). These papers are viewed by the author as representative of the current GFAAS literature. The goal of this chapter was not to be comprehensive, but rather to consider some of the interesting papers recently published. I apologize in advance to the authors of the many significant papers whose work was not discussed in this chapter.

II. PORTABLE, TUNGSTEN COIL ATOMIC ABSORPTION INSTRUMENT

A recent trend in analytical instrumentation is the development of field instruments that can do analysis at remote locations. These instruments may reduce the risk of contamination during the transport of samples, and allow nearly simultaneous sample collection and analysis. The high sensitivity and selectivity of GFAAS would appear to make the technique well suited for field instrumentation. The major limitation is the complexity of instrumentation, specifically the large power requirements for the graphite furnace, a high-quality detector to measure the transient signals obtained, and an accurate method of background correction.

Sanford et al. (1996) designed an instrument meeting these requirements for lead determination that has been marketed commercially by Leeman Labs, Inc. (Lowell, MA). A tungsten coil, originally produced for the halogen bulbs of photo-projectors, was employed as the atom cell. Its power requirements were relatively modest (a temperature of 3200 K is obtained at 15 V and 10 A) and were met by an automobile battery. Sample volumes up to 50 μL were accommodated by this atom cell. The coil was enclosed in a glass cell that was purged with 10% H_2/Ar. The hydrogen maintained a reducing atmosphere to prevent oxidation of the tungsten coil. A typical atomization cycle consisted of dry and atomization steps, achieved by two adjustable power resistors (0–4 Ω and 0–2 Ω, respectively).

The detection system was a miniature 1024-element charge-coupled device (CCD) mounted on a PC card in an expansion slot of a Pentium computer. The entrance aperture for the system was the end of a 200 μm fiber optic cable, which provided a 90 nm wavelength range with a resolution of 0.8 nm. A conventional lead hollow cathode lamp (HCL) served as the light source operating in the dc mode. A dc–dc converter was used to convert 12 V from the automobile battery to 300 V for the HCL. The HCL emission was collected by a lens and focused 2 mm above the tungsten coil. The transmitted light was then collected by a second lens and focused onto the fiber optic. The output of the CCD was sent to an analog-to-digital board. Spectra were obtained at a rate of 5 Hz during the atomization step.

Background correction was achieved by the use of the near-line (two-line) correction technique. In this technique, it is assumed that the background is the same at the analytical wavelength and at a second emission line from the HCL, which is not absorbed by the analyte, used to measure background. This technique will not correct for structured background, unlike the more recently developed Zeeman method (Slavin, 1988; Dulude, 1992). Even when the background is continuous, better accuracy is obtained when the second line is within a few nanometers of the analytical wavelength, as some variation in background levels is expected. Sanford et al. (1996) cited two disadvantages with the original near-line correction method: analytical and background measurements were made sequentially, generally minutes apart, and large wavelength differences were employed. These two drawbacks led to significant errors and the eventual disappearance of this method. However, these authors claimed that the combination of a multichannel detector to simultaneously measure the analytical and background signals with the low-background tungsten coil atomizer will allow accurate correction by the near-line method.

For lead, the resonance wavelength of 283.3 nm is surrounded by lines at 280.2 and 287.3 nm suitable for background correction. It was shown that the best accuracy was obtained by measuring the background at both wavelengths and using linear regression to estimate the background at the analytical wavelength. Uncorrected spectral profiles for these three wavelengths are shown in Figure 1.

Analytical figures of merit were obtained for lead. A detection limit of 20 pg was obtained, which was virtually identical with the value obtained with a commercial GFAAS instrument with Zeeman background correction (18 pa). A linear calibration curve was obtained at masses up to 4000 pg, and the RSD for standard solutions was typically 5%.

The ability of the system to determine lead in National Institute of Standards and Technology (NIST) paint and blood standard reference materials (SRMs) was investigated and compared to results obtained by Zeeman GFAAS, and the results are given in Table 1. The SRMs were microwave-digested with nitric acid before analysis. The tungsten coil analyses were performed with calibration graphs and by standard addition. With the former calibration method, the tungsten coil system had an accuracy of 95% and an RSD of 5%. The method of standard addition

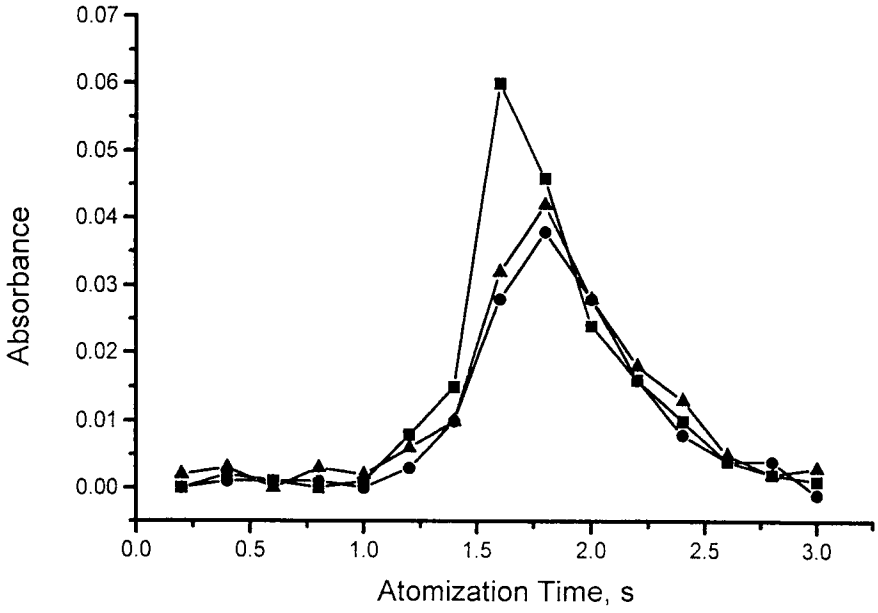

Figure 1. Uncorrected absorbance measured at 280.2 (▲), 283.3 (■), and 287.3 nm (●) during the atomization of a digested blood sample containing 51 ng/mL lead. The atomization current was 5.9 A (Sanford, 1996).

improved the accuracy and RSD to 97% and 3%. The Zeeman GFAAS method gave small improvements in accuracy (98%) and precision (2%). These results demonstrate the potential of this system for real sample analysis.

In the author's opinion, this system has considerable potential for practical analysis. In my mind, there are several questions to be addressed. (1) Can near-line background correction be widely used for real sample analysis? This question must

Table 1. Lead Determination in National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) by Tungsten Coil and Zeeman Graphite Furnace AAS[a]

		Tungsten Coil System		
SRM	*Certified Value*	*Calibration Graph*	*Standard Addition*	*Zeeman GFAAS Calibration Graph*
SRM 1579a, powdered lead paint	11.995 ± 0.031%	11.41 ± 0.56	11.66 ± 0.33	11.75 ± 0.25
SRM 955a-4, lead in blood	54.43 ± 0.38 µg/dL	50.9 ± 3.3	56.3 ± 2.0	55.5 ± 1.1

Note: [a]Sanford, 1996.

be answered by a number of applications of the instrument. (2) Can this system be used for a variety of elements, or is it limited to volatile elements? Chemical interferences with a coil atomizer may be severe for more involatile elements. (3) Will the dc operation of the instrument be a disadvantage? This is expected to be a problem for involatile elements where atom cell emission will be higher. With these limitations stated, this instrument has already been shown to be extremely useful for volatile element determination, and may be useful for less volatile elements as well. It provides a low-cost alternative to other portable instruments, e.g. X-ray fluorescence.

III. OBSERVATION OF PREATOMIZATION EVENTS ON ELECTROTHERMAL ATOMIZER SURFACES

Majidi and coworkers (1996) provided original data and a literature summary of surface chemistry in electrothermal atomizers. The properties of pyrolytically coated graphite were discussed. Graphite may exist in different crystal forms that may interconverted by heating or pressure. Numerous surface defects (approximately 0.1%) are present in pristine graphite substrates, and the number of defects is increased by heating cycles and some chemical modifiers. Metals and metal compounds may migrate into the graphite with the water solvent, forming intercalcation compounds. Previous Rutherford backscattering spectrometry (RBS) work from these authors (Majidi, 1991; Eloi, 1993; Eloi, 1995) has shown the presence of metals at depths up to 2 μm from the surface. As the solvent is removed, the metal may remain in the graphite or move back to the surface.

The differences in melting points of metals as a function of sample size were discussed using gold as an example. Melting points of 1609 °C and 973 °C were reported for gold in the bulk and nanophase, respectively. This discussion led into a description of the surface density of metals on graphite following solvent removal. In the case where the analyte strongly interacts with surface defects, one would expect the analyte to congregate around the defects as solvent is removed, resulting in nonbulk behavior. In a second scenario, the analyte is assumed to have weak interaction with graphite defects, and one would expect the concentration of a soluble analyte to increase as solvent is removed. The analyte will concentrate into a small volume until crystallization begins, and one would expect the analyte to behave like the bulk material. It was emphasized that most analyses will behave between these extreme cases.

Laser desorption time-of-flight mass spectrometry (LD-TOF-MS) was used to illustrate differences in chemical properties of various types of carbon and tantalum. The MS fragments observed are summarized in Table 2. Carbon black gave a variety of fragments, consisting of carbon fragments with chemisorbed hydrogen and physisorbed water. Reactor-grade graphite gave a range of carbon clusters. Pyrolytically coated graphite also gave a variety of carbon clusters, but the spectrum was dominated by the base peak (C_{16}^+). A C_{70} fullerene sample had a single peak

Table 2. Substrate Fragments Observed for Various Carbon and Graphite Compounds by Laser Desorption Time-of-Flight Mass Spectrometry (LD-TOF-MS)[a]

Substrate	*Major Fragments Observed*[b]	*Comments*
Carbon black	$C_{21}H_2^+$, $C_{20}H_2^+$, $C_{13}H_2O^+$, $C_{12}H_2O^+$, $C_9H_2O^+$, C_8H_2O	Hydrogen probably chemisorbed; water probably physisorbed
Reactor grade graphite	C_6^+, C_7^+, C_8^+, C_9, C_{10}^+, C_{11}^+, C_{12}^+, C_{13}^+, C_{14}^+, C_{15}^+, C_{16}^+, C_{17}^+, C_{18}^+, C_{19}^+	Widest variety of fragments
Pyrolytically coated graphite	C_{12}^+, C_{16}^+	Other carbon fragments observed in low intensity
C_{70} fullerene	C_{70}^+	Only fragment observed
Diamond	C_6^+, C_7^+, C_8^+, C_9^+, C_{10}^+, C_{11}^+	Difficult to obtain because the sample is transparent
Tantalum	Ta^+, TaO^+	Surface impurities observed below 100 amu

Notes: [a]Majidi, 1996.

due to the molecular ion (C_{70}^+). Diamond was transparent to the laser and difficult to analyze. Several low molecular weight graphite clusters were observed. Tantalum gave a simple spectrum consisting of the metal and the oxide. This experiment demonstrated that the various grades of carbon have different chemical properties at their surfaces.

Thermal analysis (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to evaluate the surface reactions which occur on graphite and metal surfaces for silver nitrate and cadmium nitrate. Studies showed that platinum and aluminum substrates gave similar results; aluminum was used for the DSC work because of its lower cost. The results for silver are summarized in Table 3. The TGA data showed that silver nitrate decomposed

Table 3. Summary of Thermal Analysis Data for Silver Nitrate on Graphite and Metal Surfaces[a]

Technique	*Substrate*	*Observed Thermal Changes*
Thermogravimetric analysis	Platinum	414 °C to 511 °C—decomposition of silver nitrate
Thermogravimetric analysis	Graphite	256 °C to 345 °C—decomposition of silver nitrate 610 °—mass loss
Differential scanning calorimetry	Aluminum	170 °C, 214 °C—melt stages 474 °C–endothermic decomposition of silver nitrate
Differential scanning calorimetry	Graphite	173 °C, 216 °C—melt stages 345 °C—exothermic decomposition of silver nitrate 515 °C—exothermic process

Note: [a]Majidi, 1996.

150 °C lower on graphite than on platinum. The DSC results showed melt stages around 200 °C and an endothermic decomposition of silver nitrate on platinum, but an exothermic decomposition on graphite. The authors suggested that a new compound was formed on the surface by a highly exothermic process. These data demonstrate that graphite is chemically involved in the chemical decomposition of silver nitrate. Thermal data for cadmium nitrate showed that the substrate affected the decomposition of this salt.

In previous work, these authors investigated the migration of silver and cadmium into graphite by RBS (Eloi, 1993). Silver was shown to diffuse into graphite at ambient temperatures, and remained in the substrate bulk at temperatures up to 590 °C prior to desorption. A new approach to characterize the surface chemistry involved the use of LD-TOF-MS. Analyte was introduced onto a substrate and the solvent was removed. LD-TOF-MS was employed to characterize the condensed phase species present on graphite and tantalum surfaces at 25, 200, 400, and 600 °C.

As in the previous studies, silver and cadmium nitrates were evaluated, and the results observed for the former are summarized in Table 4. The LD-TOF-MS data showed relatively few species on graphite compared to tantalum, which is probably caused by diffusion of silver into graphite (RBS data). At 200 °C, a melting stage had occurred (DSC data, Table 3) without decomposition of silver nitrate (TGA data, Table 3), and similar ions were observed by LD-TOF-MS on tantalum and graphite. This seems to imply that the melting causes a more uniform distribution of silver nitrate on graphite. At 400 °C, TGA data showed silver nitrate decomposition on graphite, but not platinum. The LD-TOF spectra contained a variety of silver nitrate compounds on tantalum, but primarily metal oxides on graphite,

Table 4. Summary of Laser Desorption Time-of-Flight Mass Spectra for Silver Nitrate on Graphite and Metal Surfaces[a]

Substrate	*Temperature (°C)*	*Mass Fragments Observed (amu)*[b]
Graphite	25	AgO^+, $Ag_2(NO_3)_2^+$
Graphite	200	**AgO^+**, $Ag(NO_3)_2^+$, $Ag_2(NO_3)_2^+$, $Ag_2O(NO_3)_2^+$
Graphite	400	AgO^+ plus substrate peaks
Graphite	600	AgO^+, $Ag_2O_2^+$ plus substrate peaks
Tantalum	25	**Ag^+**, AgO^+, $Ag(NO_2)^+$, $Ag_2(NO_3)(NO_2)^+$, $Ag_2(NO_3)_2^+$ plus substrate peaks
Tantalum	200	Ag^+, **AgO^+**, $Ag(NO_2)_2^+$, Ag_2^+ plus substrate peaks
Tantalum	400	Ag^+, **Ag_2O^{2+}**, AgO^+, AgO_2^+, $Ag(N_2O_2)^+$, $Ag(NO_3)^+$, Ag_2^+, $Ag_2(NO_2)^+$ plus substrate peaks
Tantallum	600	Ag^+, **Ag_2O^{2+}**, AgO_2^+, $Ag_2O_2^+$, $Ag_2O_3^+$, $AgTa^+$, $Ag_3O_4^+$, plus substrate peaks

Notes: [a]Majidi, 1996.

[b]The largest mass fragments are listed in **bold**.

verifying this chemical change. At 600 °C, TGA data showed decomposition on both surfaces, and LD-TOF-MS showed silver oxides and reduced silver. The oxides were attributed to contamination during the sample transfer. The TGA, DSC, and LD-TOF-MS data for cadmium nitrate were employed to characterize the preatomization events as well.

This review describes innovative approaches to the investigation of surface chemistry. The results establish the chemical form of metals and confirm the distribution of metals between the surface and bulk previously reported by RBS. Thermal analysis and LD-TOF-MS provide new tools for the investigation of surface phenomena in electrothermal atomizers.

IV. MONTE CARLO SIMULATION OF ELECTROTHERMAL ATOMIZATION ON A DESKTOP COMPUTER

Monte Carlo techniques employ a stochastic approach to simulate chemical and physical properties. They are best suited for complex problems for which they may provide an easier route to a solution than simpler problems that may be solved analytically. Holcombe and coworkers (Black, 1986; Güell, 1988, 1989, 1990, 1991, 1992) have employed Monte Carlo techniques to model electrothermal atomization processes. Supercomputers or mainframes were required in previous studies to obtain results in a reasonable period of time.

However, the development of more powerful desktop computers has reduced a reliance on supercomputers and mainframes. Histen et al. (1996) published a Monte Carlo simulation program which is designed to run on a 486 or higher personal computer under DOS or Windows™. The former version also allows the import of experimental data to allow comparison with simulated profiles. A summary of the variable parameters is listed in Table 5.

Geometric dimensions of the furnace include its length and diameter, the size of the dosing hole, the diameter and position of deposition site, and the number of particles introduced. These provide the user with considerable flexibility regarding the type of electrothermal atomizer employed. The kinetic parameters are defined by this reaction,

$$M_{(c)} \xrightarrow{k_1} M_{(g)} \underset{k_3}{\overset{k_2}{\rightleftarrows}} M'_{(c)} \tag{1}$$

where $M_{(c)}$ and $M'_{(c)}$ are the analyte in condensed states and k_i is the rate constant. It is assumed that $M'_{(c)}$ is only formed by adsorption from the gas phase. The rate constant k_i is given by,

$$k_i = \sigma^n \nu \, e^{-\frac{E}{RT}} \tag{2}$$

where σ is the number of particles, n is the order of release, ν is a preexponential factor, E is the energy barrier for desorption or adsorption onto the surface, R is the gas constant, and T is the absolute temperature. For some elements, the sites of desorption due to sample deposition and adsorption are similar ($M_{(c)} = M'_{(c)}$), and hence the preexponentials and activation energies for desorption are identical (e.g. $k_1 = k_3$). Other elements adsorb on different sites during sample deposition and gas-phase interaction, requiring the input of different preexponential and activation energy values.

The final set of parameters is the furnace temperature. The initial, final, and heating rate may be specified.

This program provides a convenient approach investigate fundamental studies of electrothermal atomization processes. Comparison of experimental and simulated data may be used to validate atomization mechanisms. The significance of varying any of the parameters in Table 5 may be quickly visualized, demonstrating its influence upon the analytical signal.

Table 5. Geometric and Kinetic Parameters that may be Varied in the PC-Based Monte Carlo Program[a]

Variable Category	*Variable*	*Possible Extent of Variation*
Geometric	Tube diameter	$0 \rightarrow \infty$
Geometric	Tube length	$0 \rightarrow \infty$
Geometric	Dosing hole diameter	$0 \rightarrow$ Tube length
Geometric	Position of deposition site	Any where along furnace length
Geometric	Diameter of deposition site	$0 \rightarrow$ Tube length
Geometric	Number of particles	$0 \rightarrow \infty$
Kinetic	Desorption energy #1, kJ/mol	$0 \rightarrow \infty$
Kinetic	Desorption energy #2, kJ/mol	$0 \rightarrow \infty$
Kinetic	Pre-exponential factor #1, s^{-1}	$0 \rightarrow \infty$
Kinetic	Pre-exponential factor #2, s^{-1}	$0 \rightarrow \infty$
Kinetic	Order #1	$0 \rightarrow \infty$
Kinetic	Order #2	$0 \rightarrow \infty$
Kinetic	Readsorption energy, kJ/mol	$0 \rightarrow \infty$
Kinetic	Sticking coefficient	≥ 0 and ≤ 1
Kinetic	Diffusion order	$0 \rightarrow \infty$
Kinetic	Diffusion coefficient at 287 K, $cm^2\ s^{-1}$	$0 \rightarrow \infty$
Temperature	Initial temperature, K	$0 \rightarrow \infty$
Temperature	Final temperature, K	$0 \rightarrow \infty$, > initial temperature
Temperature	Heating rate, $K\ s^{-1}$	$0 \rightarrow \infty$

Note: [a]Histen, 1996.

V. IMPROVEMENT OF THE WORKING RANGE IN ZEEMAN GFAAS BY CORRECTION FOR STRAY LIGHT WITH NONLINEAR CALIBRATION

Calibration graphs for GFAAS have relatively short working ranges, with linear ranges of 1 to 2 orders of magnitude and nonlinear working ranges between 3 and 4 orders of magnitude. Several recent papers have attempted to linearize calibration graphs by correction of each absorbance measurement in a temporal profile for stray light (L'vov, 1992; Su, 1993; Su, 1994; Lonardo, 1996; Yuzefovsky, 1996). Stray light is nonabsorbable light that may include scatter off of instrument components, nonabsorbing nearby analyte lines, and lines due to impurities in the source cathode.

The relative merits of various linearization schemes were reviewed by Lonardo et al. (1996) who developed a three-step routine to extend the nonlinear working range of Zeeman GFAAS. The first component was the pseudo-Newton method reported by Yuzefovsky et al. (1996). This method had the advantage of working accurately at high-background-corrected absorbances. Although the slopes at these higher values were lower than the slopes in the linear region, they were higher than in previously reported methods. The pseudo-Newton method had a common disadvantage with other linearization methods, which is failure at masses above the rollover region of a calibration graph.

Rollover of a calibration graph is characterized by a dip in the temporal absorbance profile. L'vov and coworkers (1992) developed a "dip-correction" method to correct absorbance measurements within the dip of the profile. Lonardo et al. (1996) employed the pseudo-Newton method before the first maximum. In the second step of the linearization scheme, the pseudo-Newton with dip correction was used within the dip region.

Best fit nonlinear calibration graphs through peak areas were generated by the algorithm of Barnett (1984) based on the following function,

$$C = \frac{K_0 (K_1 A + K_3 A^2)}{K_2 A - 1} \tag{3}$$

where C is the concentration, A is absorbance, K_1, K_2, and K_3 are coefficients evaluated during construction of the calibration graph, and K_0 is a constant to compensate for changes in sensitivity. Barnett (1984) used computer modeling to show that this formula better fit nonlinear data than other commercial fitting routines. The degree of fit between the nonlinear calibration graph and data was evaluated by the correlation coefficient and relationships proposed by Miller-Ihli et al. (1984). The correlation coefficient was defined to be,

$$r = \sqrt{1 - \left(\sum_{1}^{n} (C - \hat{C})^2 / \sum_{1}^{n} (C - \bar{C})^2\right)} \tag{4}$$

where n is the number of determinations, C is the mass, $\hat{C}$ is the calculated mass, and $\overline{C}$ is the average entered mass. The sum of the squares of the percentage deviation (SSPD) is defined as,

$$\text{SSPD} = \sum_{i=1}^{n} \left(\frac{\text{actual mass} - \text{calculated mass}}{\text{actual mass}} \right) \times 100\% = \sum_{i=1}^{n} (\text{Delta } \%)^2 \quad (5)$$

where delta % values represent deviations associated with particular standards. The root mean square percentage deviation (RMS) is given by:

$$\text{RMS} = \sqrt{\frac{\text{SSPD}}{n}} \quad (6)$$

Initial studies regarding this routine were conducted on lead, and the results are shown in Figure 2. Four calibration graphs are displayed: five-point smoothed data; data corrected by the pseudo-Newton method without dip correction; data corrected with dip correction; and data corrected by the pseudo-Newton method with dip

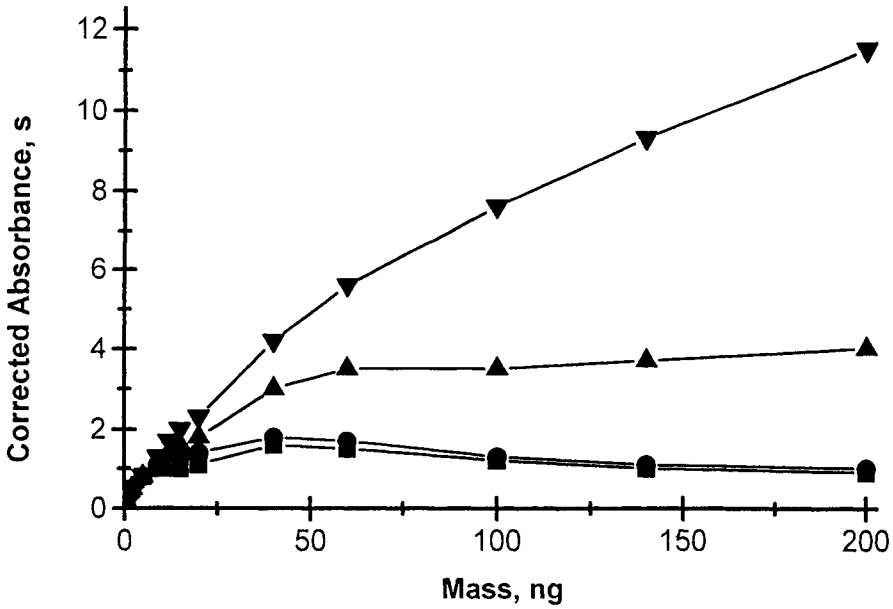

Figure 2. Calibration graphs obtained by (■) five-point smoothed data (nonlinear working range, 0.02–16 ng); (●) data corrected by the pseudo Newton method without dip correction (nonlinear working range, 0.02–12 ng); (▲) data corrected by dip correction (nonlinear working range, 0.02–20 ng); and (▼) data corrected by the pseudo-Newton method with dip correction (nonlinear working range, 0.02–200 ng) (Lonardo, 1996).

Table 6. Comparison of Five-Point Smoothed Data without Dip Correction with Data Subjected to the Pseudo-Newton Method with Dip Correction[a]

	Five Point Smoothed Data without Dip Correction				*Data Subjected to Pseudo-Newton Method with Dip Correction*			
Element	*Nonlinear Range*	*Correlation Coefficient*	*Number of Standards*	*RMS*	*Nonlinear Range*	*Correlation Coefficient*	*Number of Standards*	*RMS*
Pb	0.02–16	0.9623	13	14	0.02–200	0.9991	19	8.8
Ag	0.008–4	0.9973	12	5.9	0.008–100	0.9973	19	7.8
Cr	0.008–40	0.9924	18	9.6	0.008–60	0.9998	19	5.9
Cu	0.016–20	0.9876	15	7.7	0.016–100	0.9920	18	8.8
Mn	0.002–4	0.9898	13	13	0.002–4	0.9932	13	8.0
Tl	0.02–30	0.9986	13	2.7	0.02–300	0.9991	19	3.8
Ni	0.04–240	0.9995	19	2.2	0.04–240	0.9998	19	2.9
Cd	0.002–1	0.9981	12	3.9	0.002–10	0.9989	17	4.2

Note: [a]Lonardo, 1996.

correction. The data demonstrated the ability of the dip-correction routine to extend the linear range, and the ability of the pseudo-Newton method to extend a curve beyond the rollover region, although the curve is nonlinear. The combination of the pseudo-Newton routine with dip correction gave a nonlinear calibration graph between 0.02 and 200 ng, which was 2 orders of magnitude better than the smoothed data and 1 order of magnitude better than the use of only one of the two routines.

Table 6 shows results from eight test elements for the extension of nonlinear working range. The original five-point smoothed data and data subjected to the pseudo-Newton method with dip correction were fitted with the Barnett function (Eq. 3). For all elements, the correlation coefficient was better with the linearization algorithm. The nonlinear working range was increased by 0.5–1.5 orders of magnitude for lead, silver, copper, thallium, and cadmium. No significant effect on the RMS was observed for these elements. The RMS was decreased by a factor of 2 for chromium and manganese, with no effect on the nonlinear working range. Neither the rms nor working range were improved for nickel. The involatility of chromium and nickel induced significant tailing at high masses that produced non-Gaussian profiles that inhibited the performance of the algorithm. The use of higher atomization temperatures or longer integration times to alter the profiles was not investigated.

A small discontinuity was present between the non-dip corrected and dip corrected data. A large value of delta % was observed for the highest non-dip corrected standard that degraded the RMS of the fitting function. Discontinuities were not observed for manganese and nickel, which was expected based on the inability of the algorithm to extend their nonlinear working ranges.

The conclusion of the study was an investigation of the routine with the use of three to five standards to construct the nonlinear calibration routine, and the others used as samples. In general, the nonlinear working range and precision using a few standards were comparable to these shown in Table 6.

The authors suggested that this algorithm has considerable application for multielement GFAAS instrumentation. For example, this algorithm could be used to estimate the factor by which a sample must be diluted to overlap the linear dynamic range of analyses.

VI. WALL-TO-PLATFORM AND TWO-PLATFORM METHODS TO INVESTIGATE THE MECHANISM OF CHLORIDE INTERFERENCE ON THALLIUM

Chloride interferences have been one of the most widely reported interferences in GFAAS (Slavin, 1984; Varma, 1990; Haswell, 1991). At least four mechanisms have been proposed for this interference. One pathway involves gas-phase reaction of analyte with chloride, followed by diffusion from the tube prior to dissociation (Byrne, 1993). An alternative involves condensed-phase reaction, followed by loss from the furnace (Qiao, 1993). Expulsion mechanisms involve rapid expansion of

matrix components which expel analyte from the furnace (Akman, 1994). A final mechanism involves occlusion of analyte in chloride-containing crystals which are forced from the furnace without decomposition (Akrnan, 1994). Mahmood and Jackson (1996) developed procedures called "wall-to-platform" and two-platform migration that were used to elucidate information regarding the mechanism of chloride interferences for thallium. Thallium was chosen for this study because of the severity of the interference and the variety of mechanisms proposed in the literature.

"Wall-to-platform" atomization involved introduction of sample on the wall of a graphite tube in the absence of a platform. The solvent was removed with a conventional dry step, and the tube was allowed to cool. A clean platform was inserted, and a conventional furnace program was executed.

First, thallium absorbance signals for wall, platform, and wall-to-platform atomization were compared on the basis of appearance time. As expected, the platform signal was delayed compared to wall atomization because of the lower heating rate of the platform. The wall-to-platform signal had a similar appearance and peak maximum compared to the platform signal. These results indicate that thallium migrated from the wall to the platform during the pyrolysis step, and was atomized from the platform.

Pyrolysis curves of platform and wall-to-platform methods for 1 ng thallium and 1 ng thallium with 10 μg sodium chloride were obtained. Similar pyrolysis curves for the two methods are observed in the presence of analyte alone. Pyrolysis curves obtained in the presence of sodium chloride showed that the interference was reduced using wall-to-platform atomization. Investigation of temporal absorption profiles for platform and wall-to-platform migration shows that very small overlap or insignificant overlap of the thallium absorption signal with the sodium chloride background signal (Figure 3). The authors suggested vapor-phase interferences or expulsion could not occur (wall-to-platform) or occurred to a small extent (platform) because the analyte and interferent were not simultaneously present in the gas phase, or present simultaneously to a small degree. Occlusion interferences were expected to be independent of pyrolysis temperature, and seemed to be unlikely to be significant because of the signal degradation at high pyrolysis temperatures.

"Two-platform" atomization involved sample introduction on the wall, solvent removal, and cooling of the tube (Figure 4). Platform 1 was introduced into the furnace and dry and char steps were executed. Platform 1 was removed from the furnace, and replaced by a clean platform (Platform 2). Platform 2 was then subjected to a complete heating cycle. The integrated absorbance measured at this step represents the analyte that remained on the wall following the first pyrolysis step (Figure 4, curve A). Platform 1 was then reinserted in the tube and subjected to a complete heating cycle. The integrated absorbance measured with platform 1 represents the analyte that was transferred to the platform in the first pyrolysis step (Figure 4, curve B). The sum of curves A and B were added to give curve C, which was compared to the signal obtained with platform atomization (curve D) to verify the absence of loss of analyte during the transfer of platforms in and out of the tube.

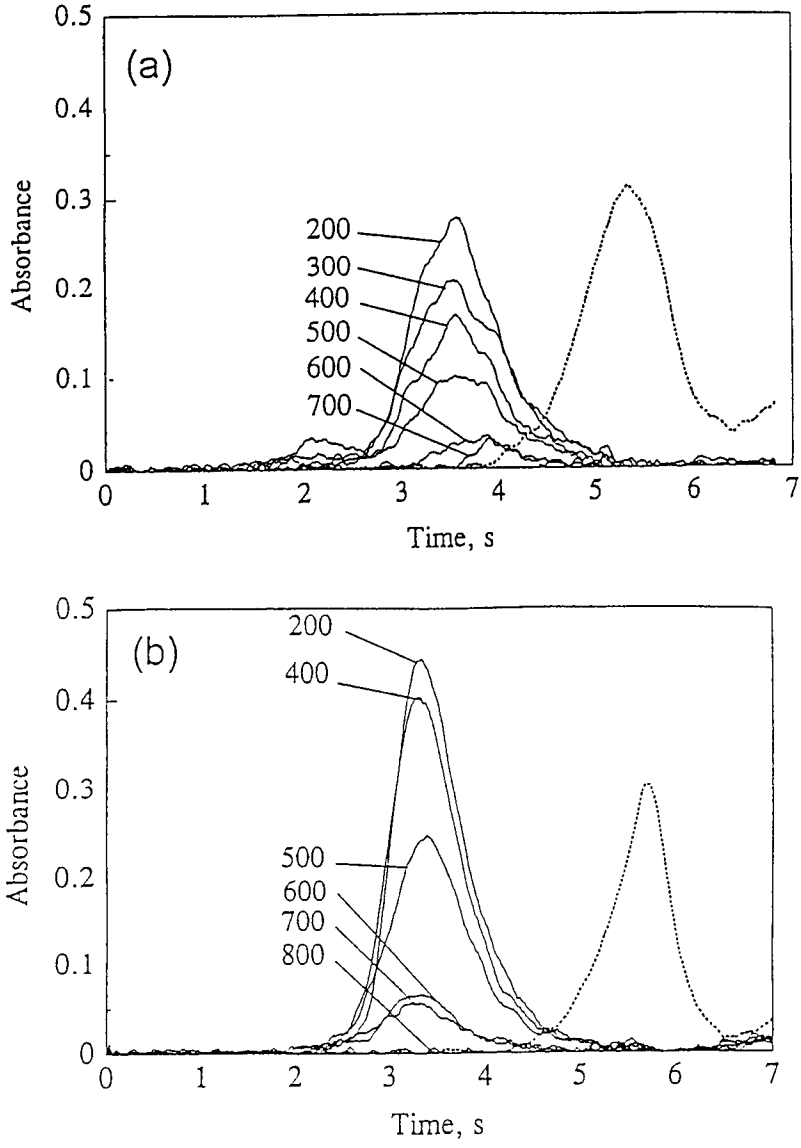

Figure 3. Thallium atomic absorption (____) and background absorption (. . .) signals at the pyrolysis temperatures indicated (°C): (**a**) platform atomization and (**b**) wall-to-platform atomization. Taken with permission from Mahmood, 1996.

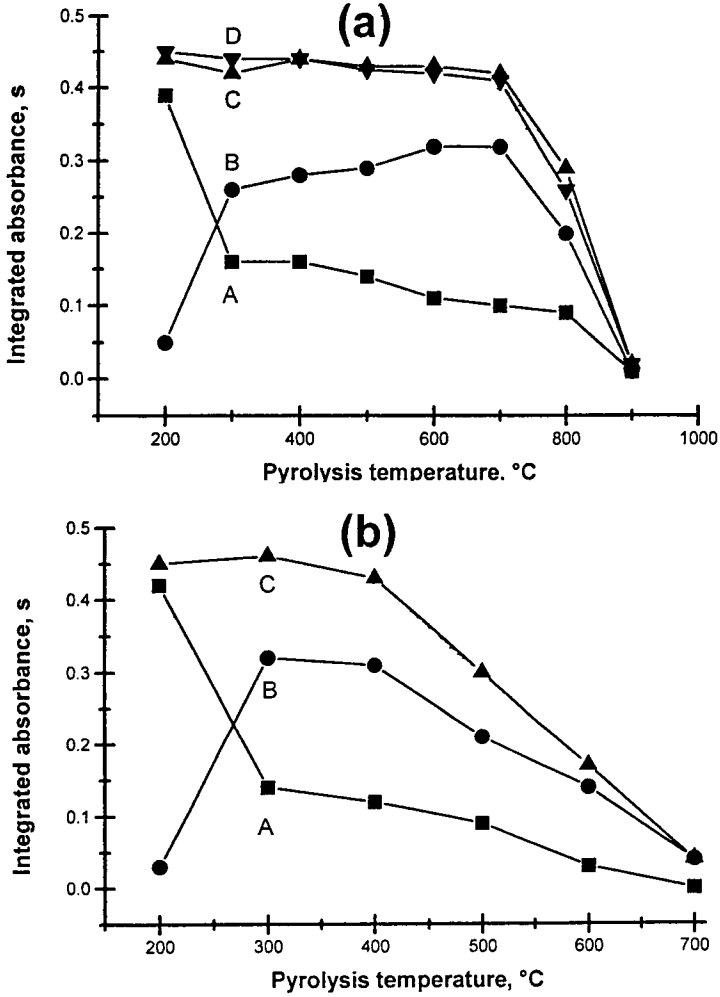

Figure 4. Pyrolysis curves for (a) 1 ng thallium and (b) 1 ng thallium with 10 µg sodium chloride using the two-platform method. (A) platform #2 - analyte remaining on wall; (B) platform #1 - analyte that migrated to a platform; (C) sum of (A) and (B); (D) 1 ng thallium with platform atomization (Mahmood, 1996).

Figure 4a shows pyrolysis curves for platform-to-platform atomization of 1 ng thallium. As expected curves C and D are almost identical, demonstrating no loss of analyte during the transfer process. At 200 °C, most of the analyte is present in curve A compared to curve B, indicating that little wall to platform migration of analyte has occurred. However, above 300 °C, a relatively large signal was observed in curve B, demonstrating significant migration of thallium occurs to the platform.

Figure 4b shows pyrolysis curves for platform-to-platform atomization of 1 ng thallium with 10 μg sodium chloride. As in Figure 4a, significant migration of thallium from the wall to the platform was observed above 300 °C. However, sodium chloride did not migrate under these conditions because its vaporization temperature is 800–900 °C. Comparison of curves C shows that no chloride interference was observed at 300–400 °C. At higher temperatures (500–700 °C), loss of thallium was observed which increased with pyrolysis temperature. The loss of thallium before vaporization of sodium chloride indicates that the interference occurred between condensed-phase thallium and condensed-phase sodium chloride.

This review describes a valuable tool for the investigation of interferences in GFAAS. Wall-to-platform and two-platform techniques have the potential to be used to study various chemical interferences.

VII. HIGH-RESOLUTION MEASUREMENTS OF ZEEMAN SPLITTING OF ATOMIC LINES

Several background correction errors have been reported for inverse Zeeman-effect background correction used with GFAAS (Slavin, 1988; Dulude, 1992). An ac

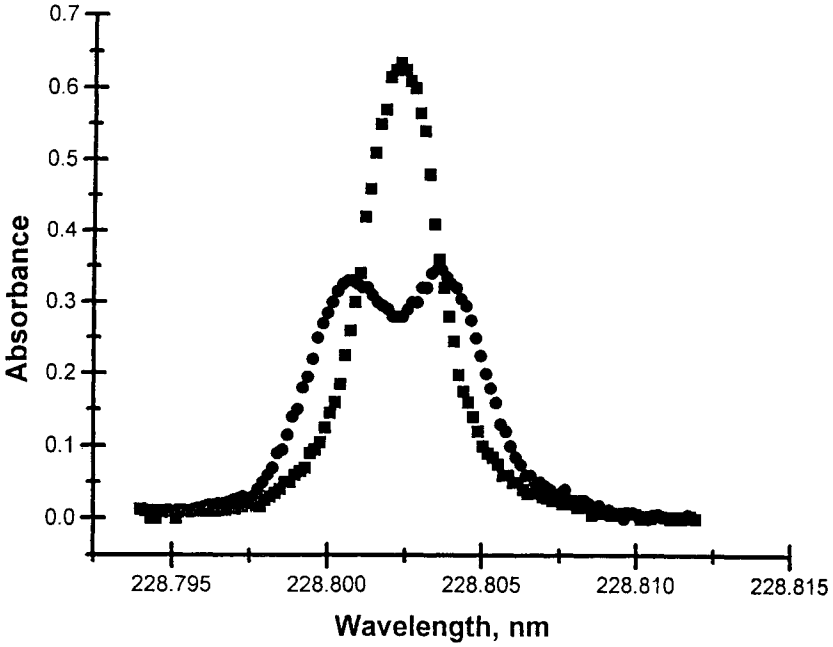

Figure 5. Experimental absorption profile with and without a longitudinal magnetic field (610 mT) for the normal Zeeman effect of the $^1S_0 \rightarrow {}^1P_1$ transition (Heitmann, 1996).

magnetic is placed around the graphite furnace. When the magnetic field is off, signal-plus background is measured; when the magnetic field is on, background is measured. Subtraction of the two measurements provides a background corrected signal. In order for accurate background correction, the assumption is made that the background signal is unaffected by the magnetic field. If this assumption is not met, then inaccurate background correction will result.

Heitmann and coworkers (1996) constructed a high-resolution spectrometer to measure Zeeman splitting of atomic lines and molecular bands in a graphite furnace. The continuum source/Zeeman GFAAS instrument was composed of a xenon arc, a commercial longitudinal Zeeman graphite furnace, a double-echelle monochromator (DEMON), and a linear CCD array. The theoretical instrument bandwidth was calculated to be 1.8 pm at 200 nm and 8.6 pm at 900 nm. The spectral resolution was experimentally determined to be approximately 110,000.

Initial experiments involved high-resolution measurements of atomic lines of standard solutions in the absence and presence of a magnetic field. The experimental results were then compared with theoretical calculations of the positions and intensities of each of the Zeeman components. Figure 5 shows experimental

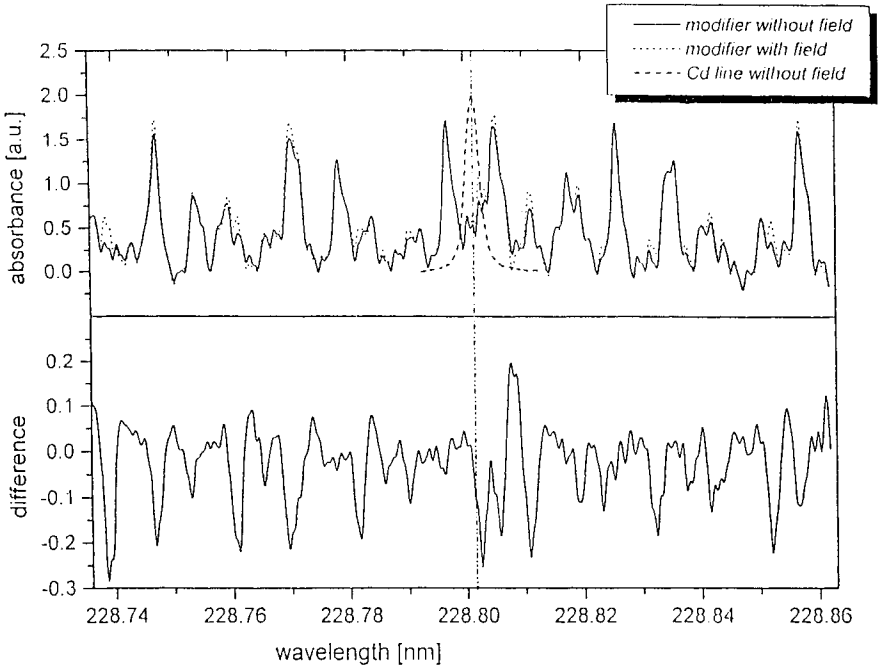

Figure 6. (**a**) High-resolution absorption spectrum of magnesium nitrate and ammonium dihydrogen phosphate with and without magnetic field in comparison to the cadmium absorption profile, and (**b**) difference of field-off – field-on absorption spectra. Taken with permission from Heitmann, 1996.

absorption profiles of the cadmium $^1S_0 \rightarrow {}^1P_1$ cadmium transition (228.8 nm) with and without a magnetic field. The experimental data were shown to compare well with theoretical calculations.

The principal goal of the project was to investigate a Zeeman-effect background correction interference between cadmium (228.8 nm) and $Mg(NO_3)_2 + NH_4H_2PO_4$, a commonly chemical modifier for GFAAS. Conventional Zeeman-effect GFAAS measurements showed the presence of overcorrection. Time and wavelength absorption spectra of cadmium and $Mg(NO_3)_2 + NH_4H_2PO_4$ demonstrated the presence of structured background around the cadmium line. Spectra also were obtained of the modifier mixture in the absence and presence of a magnetic field (Figure 6). The spectrum is clearly modified by the magnetic field, and a negative signal was observed at the cadmium wavelength, resulting in the overcorrection error. Although the authors were unable to positively identify the molecule responsible for the absorption spectrum, they suggested that it might be PO, based on previous assignments of this molecule in this spectral region.

This instrument has demonstrated considerable potential for the characterization of spectral interferences. It may be possible to use this system to generate correction factors for some interferences. For example, in the example discussed above, it may be possible to quantify the phosphate interference at the cadmium wavelength and a develop a correction factor.

VIII. SIMULTANEOUS, MULTIELEMENT DETERMINATION OF FOUR ELEMENTS IN AIR SAMPLES BY IMPACTION-GFAAS

Impaction techniques are used to determine metals in air by passing an aerosol from a jet impinges on a surface, inducing deposition of particles. Lee et al. (1996) described an improved version of a single stage impactor with collection in a commercial graphite tube. The system was constructed from nylon to minimize metal contamination. Jets of 0.5, 1.0, and 1.5 mm inside diameter were constructed for optimization of the system. A turret was present in the system with positions for four graphite tubes to allow four consecutive, identical experiments to be performed.

Theoretical calculations were performed to evaluate the particle size at which 50% of the particles are collected (d_{50}),

$$d_{50} = \sqrt{\frac{9S_{tk}\,\mu D}{\rho U C_c}} \tag{7}$$

where S_{tk} is the Stokes number (0.226); μ is the density of the particles (1 g mL^{-1}); D is the diameter of the jet (mm); ρ is the viscosity of air (1.81×10^{-4} g cm^{-1} s^{-1}); U is the average jet exit flow velocity (cm s^{-1}); and C_c is the Cunningham correction

factor (≈ 1). This equation shows that as the flow rate increases and the jet diameter decreases, smaller particle sizes are collected.

Aqueous standards were introduced into the impaction system at a known flow rate and collected on the graphite tube. Experimental calibration curves for chromium under different flow rates are shown in Figure 7. An increase in calibration sensitivity is observed at flow rates up to 10 L min^{-1}. Little variation in slope was observed between 10 and 15 L min^{-1}. The calculation of metal concentrations in air (C_M) was performed by the following relationship:

$$C_M = \frac{M_m}{V_a} = \frac{C_{std} V_{std}}{F_r S_t} \tag{8}$$

where M_m is the mass of metal in air (ng); V_a is the volume of air sampled (m^3); C_{std} is the concentration of standard (mg mL^{-1}); V_{std} is the volume of standard (mL); F_r is the flow rate (m^3 min^{-1}); and S_t is the sampling time (min).

The performance of this system was investigated for the determination of cadmium, chromium, lead, and manganese in air and air containing cigarette smoke. A significant increase in these metals was observed in air containing cigarette smoke compared to uncontaminated air. The authors suggested that the accuracy

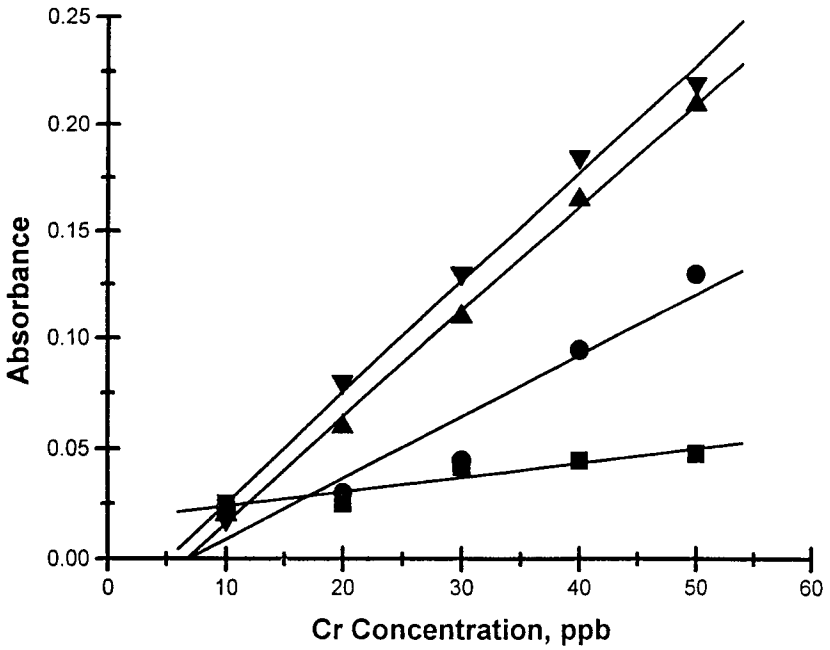

Figure 7. The effect of flow rate on the calibration graph for aqueous solutions of chromium collected and determined by impaction-GFAAS: (▼) 15 L min^{-1}; (▲) 10 L min^{-1}; (●) 5 L min^{-1}; (■) 1 L min^{-1} (Lee, 1996).

of the analyses were difficult to assess, and concluded that the system was best suited to semi-quantitative analysis. This system provides a fast, convenient method to simultaneously monitor four elements in a near real-time manner. Compared to previous impaction designs, the system is easier to use and has a lower risk of contamination.

IX. SCANNING TUNNELING MICROSCOPE IMAGES OF GRAPHITE SUBSTRATES EMPLOYED IN GFAAS

Surface properties that determine interactions between graphite substrates and analytes (e.g. type and abundance of surface defects) are significant in GFAAS. Welz and coworkers (1989) have investigated graphite morphologies by scanning electron microscopy (SEM). Although significant information was obtained in these studies, the resolution of SEM is insufficiently high to image structures at the atomic scale. Images of GFAAS substrates (polycrystalline and pyrolytically coated polycrystalline tubes, solid pyrolytic platforms) were obtained with a scanning tunneling microscope (STM) in order to characterize the surface of substrates to the subnanometer level and obtain information about the atomic-scale defect structure (Vandervoort, 1996). Images were also obtained of highly oriented pyrolytic graphite (HOPG), a material commonly studied by STM.

HOPG is characterized by a high degree of alignment in the vertical axis, as shown in Figure 8a. This 400×400 nm^2 topographic surface image of the surface shows large atomically flat areas, with the exception of diagonal lines which represent monolayer steps. A height distribution histogram of the surface showed that the steps were separated by 0.34 ± 0.02 nm, which is consistent with the half-unit cell spacing between adjacent layers. A two-dimensional gray-scale image of a much smaller area of HOPG is shown in Figure 8b, with lighter shades representing higher features, and darker shades representing lower features. The well-ordered hexagonal structure has maxima separated by 0.25 ± 0.01 nm, which is consistent with a sublattice containing every second atom. Atomic resolution of this quality is normally observed for STM images on HOPG.

A typical 1.1×1.1 μm^2 STM topographic surface image of polycrystalline graphite is shown in Figure 9. Little or no crystalline order was observed and vertical variations exceeding 100 nm are present. Six scans were obtained of this substrate, and the average vertical spread was 160 ± 90 nm, indicating its roughness. In general, it was difficult observe any structural order on this material, even at reduced scales. Atomic imaging was not achieved because of the roughness of the substrate. However, one image showed a crystallite protruding from a disordered area. The microscale images demonstrated a rough, heavily oxidized surface, which correlates with the reactivity of this material and its insuitability as a substrate for many elements.

In general, similar types of features were observed on pyrolytically coated pyrolytic tubes and solid pyrolytic platforms. Relatively rough regions were ob-

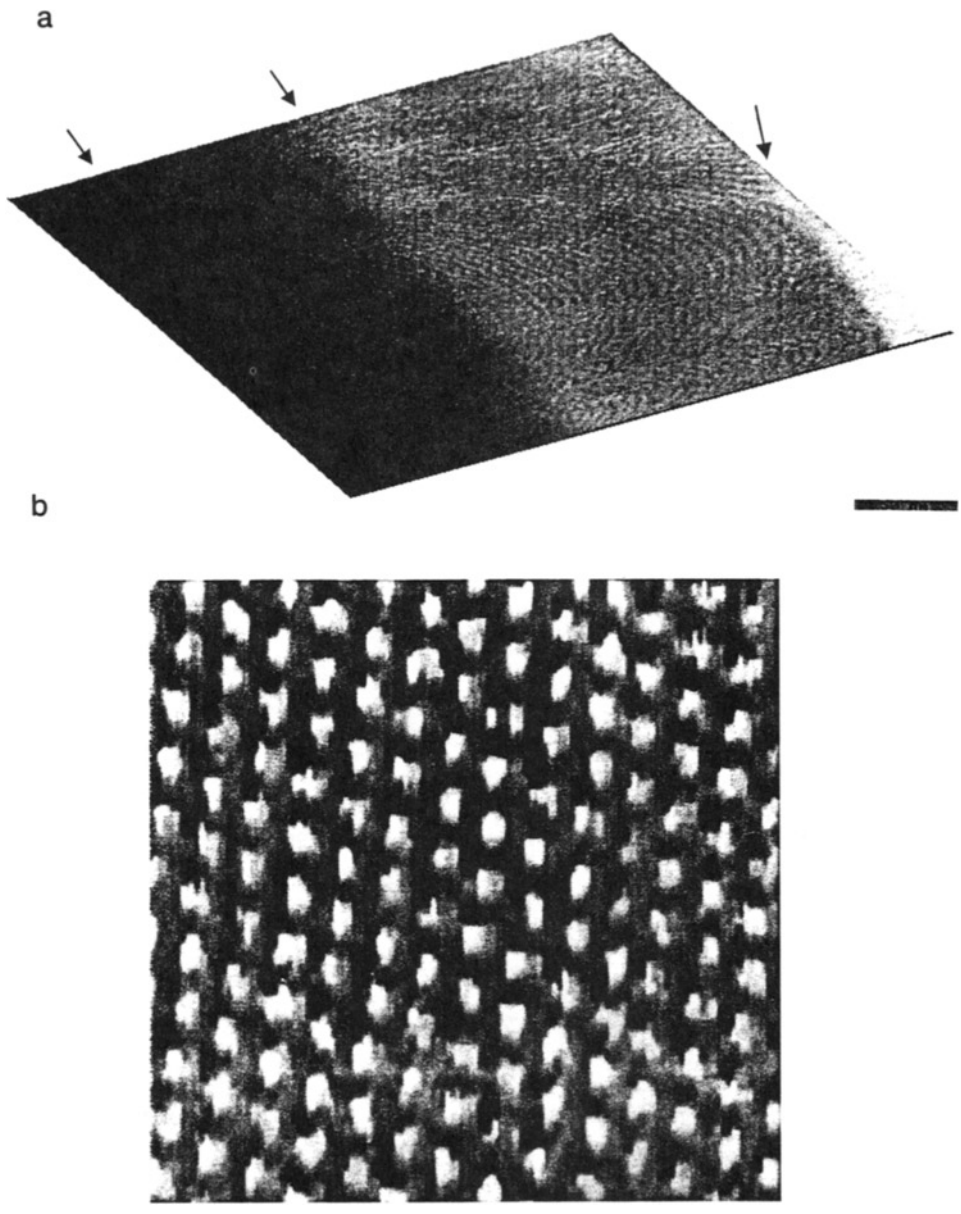

Figure 8. (**a**) A 400 × 400 nm^2 area surface of highly oriented pyrolytic graphite. (**b**) A 2.8 × 2.8 nm^2 area atomic resolution image of highly oriented pyrolytic graphite. Every other atomic site is imaged because of the asymmetry in the local electronic density of states between carbon sites. Taken with permission from Vandervoort, 1996.

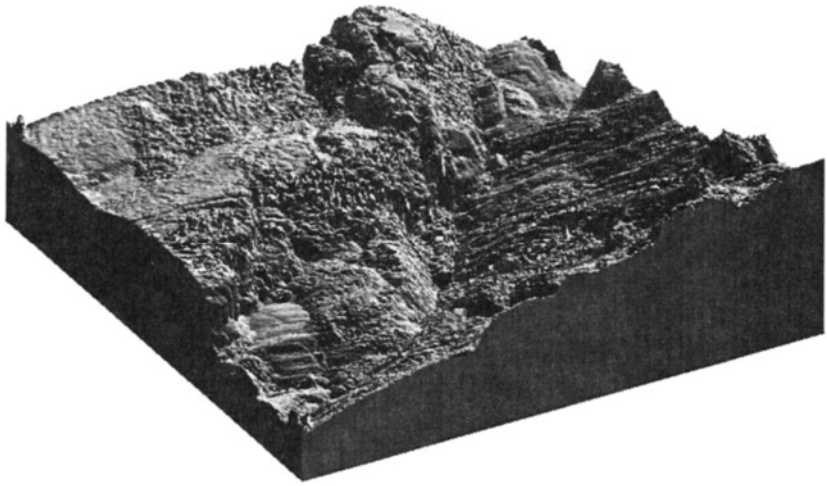

Figure 9. A 1.1 × 1.1 μm^2 area surface of a polycrystalline graphite tube. Taken with permission from Vandervoort, 1996.

served on approximately half of the scans on pyrolytically coated tubes that were characterized by rough scaled structures and columnar islands. For 10 scan regions obtained on this substrate, the average height spread was 74 ± 40 nm, which is comparable to the roughness of the polycrystalline tubes. Approximately 50% of scans on pyrolytically coated tubes and pyrolytic platforms showed areas with

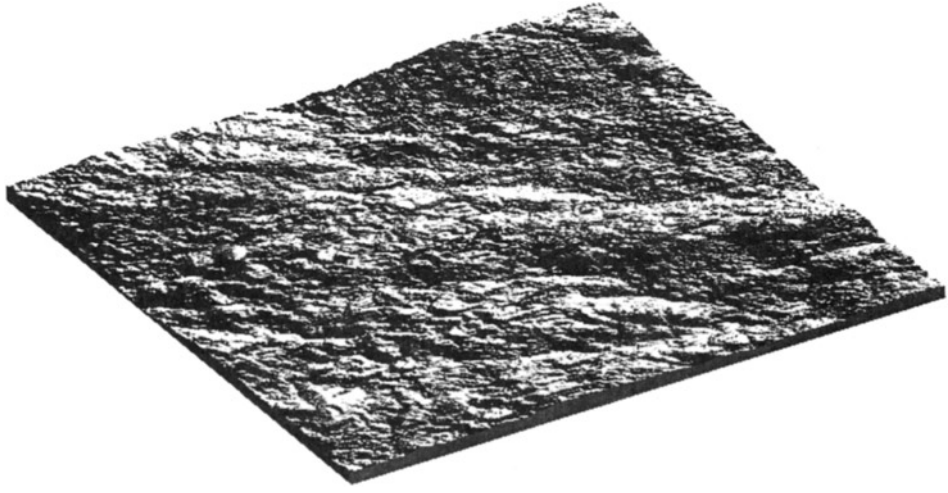

Figure 10. (a) 1.1 × 1.1 μm^2 area surface of a pyrolytically coated graphite tube exhibiting smoothly varying contours.

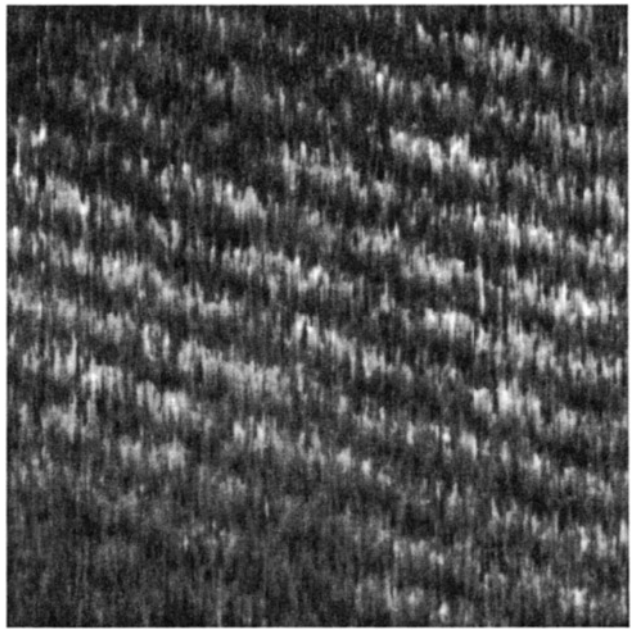

Figure 10. (b) A 2.5 × 2.5 nm^2 area image displaying atomic rows on a pyrolytically coated graphite tube. Taken with permission from Vandervoort, 1996.

exposed edge grains. These more jagged regions probably correspond to chemically active regions towards metals. However, the other 50% of the scans showed relatively smooth varying contours, as shown in Figure 10a. The vertical spread on this 1.1 × 1.1 μm^2 area is 18 nm, and consists of several small, circular bumps of ~15 nm width and 2 nm height. Atomic imaging of these areas was possible, as shown in Figure 10b. Resolution in the y-direction was not achieved, probably because of noise produced by variations in tip height. These relatively ordered regions are expected to be much less reactive towards metals.

STM has been shown to be a powerful tool to characterize graphite substrates for atomic absorption. More work in this area is expected in the future.

REFERENCES

Akman, S., Döner, G. *Spectrochim. Acta, Part B* **1994**, *49B*, 665.

Barnett, W.B. *Spectrochim. Acta, Part B* **1984**, *39B*, 829.

Black, S.S., Riddle, M.R., Holcombe, J.A. *Appl. Spectrosc.* **1986**, *40*, 925.

Byrne, J.P., Lamoureux, M.M., Chakrabarti, C.C., Ly, T., Grégoire, D.C. *J. Anal. Atom. Spectrom.* **1993**, *8*, 599.

Dulude, G. *Advances in Atomic Spectroscopy*, Sneddon, J. Ed.; Jai Press: Stamford, CT, Vol. 1, 1992, p. 125.
Eloi, C., Robertson, J.D., Majidi, V. *J. Anal. Atom. Spectrom.* **1993**, *8*, 217.
Eloi, C.C., Robertson, J.D., Majidi, V. *Anal. Chem.* **1995**, *67*, 335.
Güell, O.A., Holcombe, J.A. *Spectrochim. Acta, Part B* **1988**, *43B*, 459.
Güell, O.A., Holcombe, J.A. *Spectrochim. Acta, Part B* **1989**, *44B*, 185.
Güell, O.A., Holcombe, J.A. *Anal. Chem.* **1990**, *62*, 529A.
Güell, O.A., Holcombe, J.A. *Appl. Spectrosc.* **1991**, *45*, 1171.
Güell, O.A., Holcombe, J.A. *Spectrochim. Acta, Part B* **1992**, *47B*, 1535.
Güell, O.A., Holcombe, J.A. *J. Anal. Atom. Spectrom.* **1992**, *7*, 135.
Haswell, S.J. (Ed.). *Atomic Absorption Spectrometry: Theory, Design, and Applications*. Analytical Spectroscopy Library. Elsevier: Amsterdam, 1991.
Heitmann, U., Schütz, M., Becker-Roß, H., Florek, S. *Spectrochim. Acta, Part B* **1996**, *51*, 1095.
Histen, T.E., Güell, O.A., Chavez, I.A., Holcombe, J.A. *Spectrochim. Acta, Part B* **1996**, *51B*, 1279.
Lee, Y.-I., Smith, M.V., Indurthy, S., Deval, A., Sneddon, J. *Spectrochim. Acta, Part B* **1996**, *51B*, 109.
Lonardo, R.F., Yuzefovsky, A.I., Zhou, J.X., McCaffrey, J.T., Michel, R.G. *Spectrochim. Acta, Part B* **1996**, *51B*, 1309.
L'vov, B.V., Polzik, L.K., Fedorov, P.F., Slavin, W. *Spectrochim. Acta, Part A* **1992**, *47B*, 1411; L'vov, B.V., Polzik, L.K., Kocharova, N.V., Nemets, Y.A., Novichikhin, A.V. *Spectrochim. Acta, Part B* **1992**, *47B*, 1187.
Mahmood, T.M., Jackson, K.W. *Spectrochim. Acta, Part B* **1996**, *51*, 1155.
Majidi, V., Robertson, J.D. *Spectrochim. Acta, Part B* **1991**, *46B*, 1723.
Majidi, V., Smith, R.G., Bossio, R.E., Pogue, R.T., McMahon, M.W. *Spectrochim. Acta, Part B* **1996**, *51B*, 941.
Miller-Ihli, N.J., O'Haver, T.C., Harnly, J.M. *Spectrochim. Acta, Part B* **1984**, *39B*, 1603.
Qiao, H., Mahmood, T.M., Jackson, K.W. *Spectrochim. Acta, Part B* **1993**, *48B*, 1495.
Sanford, C.L., Thomas, S.E., Jones, B.T. *Appl. Spectrosc.* **1996**, *50*, 174.
Slavin, W. *Graphite Furnace AAS: A Source Book*; Perkin-Elmer Corporation: Norwalk, CT, 1984.
Slavin, W., Carnrick, G.R. *CRC Crit. Rev. Anal. Chem.* **1988**, *19*, 95.
Su, E.G., Yuzefovsky, A.I., Michel, R.G., McCaffrey, J.T., Slavin, W. *Microchem. J.* **1993**, *48*, 278.
Su, E.G., Yuzefovsky, A.I., Michel, R.G., McCaffrey, J.T., Slavin, W. *Spectrochim. Acta. Part B* **1994**, *49B*, 367.
Vandervoort, K.G., Butcher, D.J., Brittain, C.T., Lewis, B.B. *Appl. Spectrosc.* **1996**, *50*, 928.
Varma, A. *CRC Handbook of Furnace Atomic Absorption Spectrometry*; CRC Press: Boca Raton, FL, 1990.
Welz, B., Schlemmer, G., Ortner, H.M., Wegscheider, W. *Prog. Anal. Spectrosc.* **1989**, *12*, 111.
Yuzefovsky, A.I., Lonardo, R.F., Zhou, J.X., Michel, R.G., Koltracht, I. *Spectrochim. Acta, Part B* **1996**, *51B*, 713.

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RECENT DEVELOPMENTS IN FLOW-INJECTION ATOMIC SPECTROSCOPY

M. D. Luque de Castro and L. Gámiz-Gracia

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I. INTRODUCTION

Flow injection (FI) is a simple, inexpensive technique the high flexibility of which affords the implementation of analytical process steps of widely variable complexity (Valcárcel and Luque de Castro, 1987; Ruzicka and Hansen, 1988; Karlberg and Pacey, 1989). The use of FI as a means for introducing samples into a detector results in dramatically increased throughput, and dramatically reduces sample and reagent consumption. Even more interesting is the use of FI for implementing on-line derivatization reactions or continuous separation processes, monitoring evolving systems on-line, conducting multideterminations or preconcentration steps, and performing a number of sample handling modes to optimize sample for detecting one or several species. All of these steps or operating modes significantly enhance some valuable analytical properties (e.g. sensitivity, selectivity, expeditiousness, precision, and scope of application) of the ensuing analytical methods.

Depending on the particular role to be played by FI as an interface between samples and instruments, it can be incorporated in various ways into analytical processes, namely:

1. As a simple means for introducing samples into instruments.
2. As a means for automatic development of chemical reactions before the reaction products are introduced into the measuring instrument.
3. As a way to implement nonchromatographic separation techniques with increased selectivity and sensitivity (Valcárcel and Luque de Castro, 1991).
4. As a tool for developing continuous separation processes involving chemical reactions.
5. As a way to develop new kinetic modes based on reaction-rate measurements or otherwise.

As shown by Luque de Castro et al. (1995), FI came of age when it started to be coupled with high discrimination instruments. The earliest FI coupling in this context was the FI-ICP-AES triad. The multidetermination capacity of ICP-AES has been boosted in various respects by FI since the early 1980s. The connection between an FI system and a high-resolution detector decisively influences the performance of the hyphenated system in terms of quality-related as analytical properties such as reproducibility, accuracy, sensitivity, and selectivity. The main advantages of FI-atomic spectroscopy systems (FI-AS) are as follows:

1. Requires little human participation.
2. Allow large numbers of samples to be processed or several reagents to be manipulated simultaneously.
3. Afford a high throughput.
4. Allow handling unstable reagents and products.

5. Overcome the drawbacks of some types of detectors, e.g. high salt contents in AAS.
6. Allow the reliable implementation of nonchromatographic continuous separation techniques and facilitate coupling with chromatographs.
7. Reduce analytical costs.
8. Afford automatic calibration by the standard addition method in the normal or reversed-FI mode.
9. Allow the automatic amplification of the analyte concentration range by dilution or preconcentration.
10. Enable speciation analysis.
11. Facilitate on-line solid sample treatment.
12. Afford convenient, indirect automated determinations.

The many advantages of the FI-AA coupling have aroused widespread acceptance by the scientific community, which has explored it in a large number of papers (about 750 publications in the 1990s), and in several reviews (Tyson et al., 1990, 1991, 1992; Fang et al., 1992, 1996; Trojanowicz et al., 1992; Giné et al., 1994; Mentasti, 1995) and books (Sneddon, 1992; Fang, 1995), all of which testify to the excellence of these hybrid assemblies. However, the ceaseless flow of new developments and applications has raised the need for an overview of the most recent contributions in this area in the form of a book on atomic techniques.

This chapter discusses the main types of FI-AS couplings, namely: FI-atomic absorption spectrometry (FI-AAS), which the most widely used type of atomic spectroscopic assembly; FI-flame emission spectroscopy (FI-FES); FI-atomic fluorescence spectroscopy (FI-AFS); and FI-inductively coupled plasma-atomic emission spectroscopy (FI-ICP-AES). Special emphasis is placed on new instrument devices, coupling with other techniques and the use of FI to improve existing atomic methods.

II. FROM THE BASIC FLOW-INJECTION MANIFOLD

The basic, most simple possible flow-injection manifold has been altered in various ways to fit the FI-AS coupled system to the particular problem. The changes, which affect one or several basic FI units, are illustrated schematically in Figure 1.

A. Pumps

Some computer-controlled peristaltic pumps have been devised to aspirate preset volumes of sample solution that afford automated sample introduction and controlled-dispersion flow injection (Wu et al., 1994). This type of pump is widely used for calibration (by sequential injection of portions of the standard); also, it provides a convenient means for expanding the dynamic range of atomic methods by diluting samples. The use of variable dilution factors allows one to alter the rectilinear

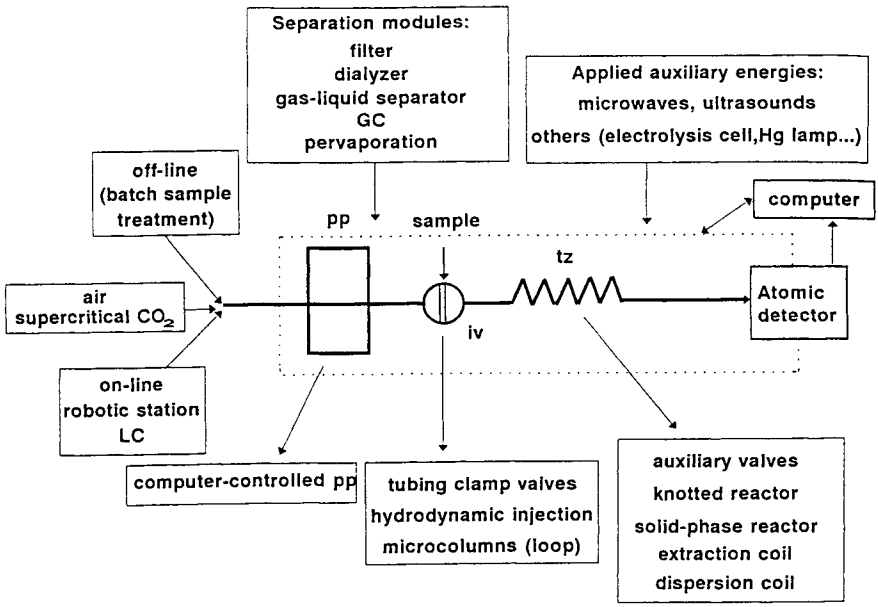

Figure 1. Alterations of the basic units of a flow injection manifold for adjustment to the specific analytical steps to be developed. Separation modules can be located in, and auxiliary energies applied to, any zone of the manifold. pp: peristaltic pump; iv: injection valve; tz: transport zone.

working range and to carry out automatic calibration, thus ensuring a high throughput (about 100 samples/h), as demonstrated by Fang et al. (1993, 1996) and by Lopez-García et al. (1994), among others.

B. Valves

FI devices for AAS are usually equipped with a six-port valve consisting of two PTFE cylinders. One shortcoming of this type of valve is clogging by suspended matter in the liquid stream. This conventional valve can be substituted by an inexpensive assembly of tubing clamp valves that can be readily inserted into the manifold as suggested by Elsholz (1996). A FAAS microsampling system using hydrodynamic injection has also been reported. It used air-transported sample loading and hydrodynamic injection. An augmenting water stream between the sample loop and nebulizer avoids interferences from nebulizer suction during sample loading (Xu and Fang, 1995). Injection valves have been modified for preconcentration or separation by using microcolumns inserted in the sample loop.

C. Carriers

The use of air-forced liquid delivery for sample introduction (Jiménez et al., 1993) provides a number of advantages including easier automation, lower reagent consumption, decreased contamination, and the ability to use the peristaltic pump as the air drive. Supercritical carbon dioxide has been used by Bysouth and Tyson (1992) as carrier for sample introduction in AAS. Also, packed microcolumn SFC coupled with ICP-AES detection has been used by Jinno et al. (1990) to investigate complex stability under supercritical conditions.

D. Transport Zone

This is the manifold part that has undergone the greatest changes. Among others, it has been furnished with sorption, ion-exchange, and chelating microcolumns for preconcentration or separation, with additional injection valves for inserting the eluent prior to the column or placing the microcolumn itself (thus affording elution the opposite direction to retention). Figure 2 illustrated the gradual changes introduced in the flow injection manifold in order to circumvent the problems posed by the inclusion of a solid minicolumn. The manifold in Figure 2a is an earlier design subject to the following problems: (a) poor sample-carrier mixing that resulted in pH differences throughput in the injected plug; (b) increased compaction of the packed material; and (c) passage of the sample plug through the detector. All these problems are circumvented by the manifold in Figure 2b, the automated version of which uses two peristaltic pumps as shown in Figure 2c. Finally, the use of a secondary injection valve (siv in Figure 2d) provides a more simple solution to the above-mentioned shortcomings.

The initial reactor has been replaced by a knotted reactor (for preconcentration), a solid-phase reactor (for implementing on-line selective reactions in order to increase selectivity), an extraction coil followed by a phase separator (for liquid–liquid extraction), a dispersion coil (for dilution), etc.

Various types of separation modules other than microcolumns have been coupled on-line with the FI manifold, namely: dialyzers (for preconcentration and increased selectivity); on-line filters (for precipitation and coprecipitation); and gas–liquid separators (for hydride and cold vapor generation). One other membrane-based separation technique, pervaporation, has also been coupled to FI and used for the speciation of Hg in solid samples. All these units and their different applications are discussed at large in the following section.

E. Instrument Control

The interface for instrument control in the Perkin Elmer FI Mercury system (for the determination of Hg by AAS) has been discussed and the process outlined by Barnett et al. (1994). Also, an overview of this commercially available system has been published by Scheneider et al. (1994).

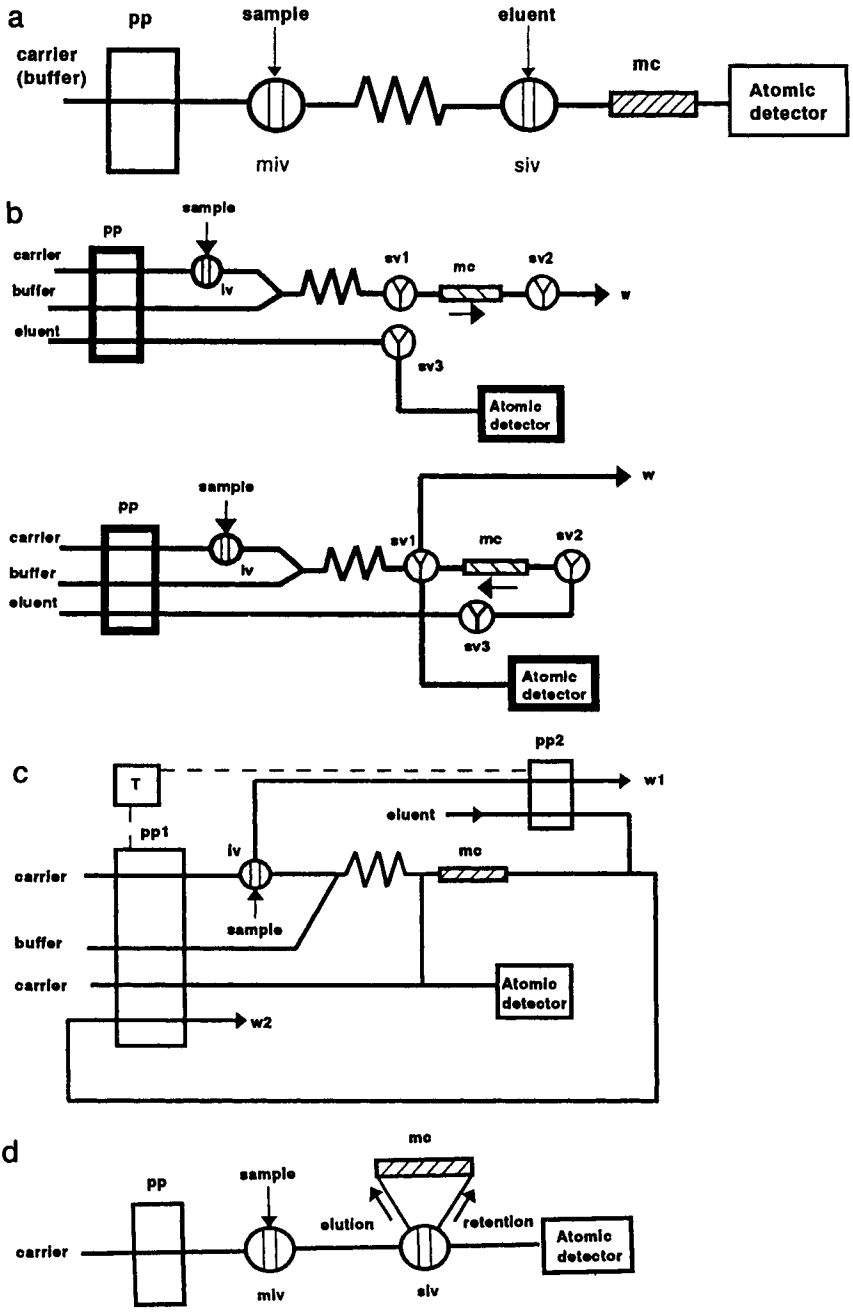

Figure 2. Changes in the solid minicolumn-flow injection coupling introduced in order to circumvent some of its drawbacks (for details see text). pp: peristaltic pump; miv: main injection valve; siv: secondary injection valve; mc: microcolumn; sv: selection valve; w: waste; T: timer.

F. Other FI-AS System Tools

In addition to these modifications of the FI manifold, the following tools have been used with or coupled to an FI-AS system for different purposes:

Robotic Stations

Discreet (robotic) and continuous (flow injection) approaches have been coupled by Torres et al. (1995) for the fully automated treatment of solid samples prior to introduction into an atomic detector (e.g. soil samples for the determination of heavy metals). The ensuing method includes microwave-assisted digestion, which is done in a focused microwave digestor controlled by the robot. After digestion, the sample is aspirated into a valve loop in the FI system, and diluted as required (depending on the concentration of the metal concerned) before it is transferred into the AAS detector for measurement.

Chromatography

Chromatographic separation techniques have been used to separate several analytes prior to detection by AS. One example is the separation of several organo–Hg compounds by gas chromatography (Bryce et al., 1997) or ion-exchange chromatography, after which the fraction of As species is collected and transferred to a FI-hydride generation-AAS system for subsequent treatment and monitoring (Jiménez de Blas et al., 1994).

Auxiliary Energy Devices

Devices that provide auxiliary energies for developing specific steps have also been coupled to FI-AS. Thus, on-line digestions of cocoa powder have been carried out in a double FI manifold incorporating a *resistively heated oven* for the AAS determination of Cu and Fe. Also, an FI system operating in the stopped-flow mode was devised for on-line digestion by Gluodenis and Tyson (1992, 1993) in a microwave oven, followed by FAAS or ICP-AES determination.

An *Hg lamp* has been used for on line photooxidation in the determination of organo–As compounds by AAS. The sample is passed through a reaction coil wrapped around the lamp and driven along the FI manifold for continuous arsine generation (Atallah and Kalman, 1991).

An *electrolysis cell* consisting of a PTFE block with an Au film cathode, separated from the alloy sample (which acted as an anode) by a piece of silicone rubber with a central slot, was included in an FI system for the on-line electrolytic dissolution of solid metal samples in the FAAS determination of Cu and Al (Yuan et al., 1991).

An *electrically heated pyrex column* containing a roller of metallic Al was incorporated into an FI manifold by Burguera et al. (1992) to reduce As(III) to AsH_3, which was transferred to a gas–liquid separator and collected into a liquid-N-cooled trap before its determination by FAAS.

Microwaves, whether focused or multimode, are the most extensively used type of auxiliary energy, particularly for mineralization and digestion. Thus, on-line microwave-assisted mineralization with a PTFE reaction coil inside a microwave oven has been applied to the determination of toxic and nontoxic As species in urine (López-Gonzalvez et al., 1995); in the determination of lead in biological materials, where digestion is usually followed by gas diffusion prior to introduction of arsine into a GF-AAS detector; and in the quantitation of Fe and Zn in adipose tissue, which was subjected to assisted-microwave mineralization after introduction into an FI-GF-AAS assembly (Burguera et al., 1993, 1995).

Two *in vivo sample uptakes* with on-line measurements of Co, Zn, and Cu in whole blood by FI-AAS after microwave-assisted mineralization have also been developed by Burguera et al. (1993, 1995), using an automatically controlled timed injector.

Microwave-assisted digestion is a simple, fast sample pretreatment. It has been used by Welz et al. (1992) for the determination of Hg in water and urine by FI-cold vapor AAS, using a system comprising an autosampler, a microwave digestor, a hydride generation system, and an amalgamation accessory. This analyte was also determined in blood by using the same atomic technique (Guo and Baasner, 1993). An automated on-line microwave digestor for sample preparation in FI-AAS that operates in a fast (2–3 min) and continuous way has been reported by Lofty (1992). An automated dual-channel FI manifold for determining heavy metals in sewage sludge has been reported by Bordera et al. (1996); the sample is loaded into a digestion coil that is subjected to microwave radiation and ICP-AES detection. Slurried samples have been analyzed by using an FI-AAS approach based on an on-line microwave digestor, a cooling loop, and a back-pressure regulator (Haswell and Barclay, 1992). Solid samples (e.g. sludge, artichokes) have also been treated in a closed FI system for on line microwave digestion with AAS detection, using digestion times from 2 to 4 min (Carbonell et al., 1992). An on-line microwave digestor and an ice bath were included in an FI-hydride generation AAS system by Cabrera et al. (1994) aimed at reducing the amount of water vapor in the determination of lead in beer, juice, and slurries.

III. OBJECTIVES OF FLOW-INJECTION–ATOMIC DETECTOR (FI-AD) COUPLINGS

Recent approaches to the joint use of FI and atomic detectors are aimed at endowing analytical methods with one or several of the following features: *higher sensitivity and/or selectivity*, which are the chief result of a continuous separation step carried out in the FI manifold, of a chemical or biochemical derivatization reaction, or of the synergistic effect of both; *better precision*, which is a consequence of minimizing or avoiding the shortcomings of atomic techniques by intelligent manipulation of reactants and products along the previous FI manifold; *flexible sensitivity*, intended to avoid dilution and/or concentration steps and hence to save time;

speciation analysis, which can be accomplished by suitable manipulation of the analytes in the continuous system; *partial or full automation*, which encompasses sample treatment, introduction into the spectrometer; and *calibration*. One additional asset of automation is easier, more expeditious data processing. The previous achievements were reported in the last few years and are commented on below.

A. Increased Sensitivity and/or Selectivity

This is the most usual aim of the FI-AD coupling, as reflected the large number of papers and reviews (Fang et al., 1991, 1996; Carbonell et al., 1992; Welz, 1992; Wang et al., 1995) published on this topic. As a rule, FI methods are less sensitive than their manual counterparts because chemical equilibrium has not been attained by the time detection occurs (owing to the short reaction times involved), and because of physical dispersion or dilution of the sample plug in the carrier. Nevertheless, the high flexibility of the FI technique allows sensitivity to be boosted by introducing appropriate modifications in the manifold.

There are two general ways of mixing dissolved reactants. In the normal FI mode, the sample is injected into the stream containing the reagents; in the reversed mode (rFI), the reagent is injected into the sample stream. In the latter case, the amount of sample in the reagent zone increases with increased dispersion. The sensitivity is thus clearly increased, albeit at the expense of using a large sample volume (Yebra et al., 1993).

On-line *preconcentration and separation* are among the most important contributions of FI to atomic spectrometry. The most usual way of enacting them is by implementing a non-chromatographic continuous separation technique in the FI configuration using different types of interface, namely: (1) liquid–solid (sorption, ion exchange, precipitation); (2) liquid–liquid (extraction, dialysis); and (3) gas–liquid (hydride generation, cold vapor generation, pervaporation). The preconcentration efficiency depends on the ratio of sample to acceptor volume, which is occasionally proportional to that between the flow rates (e.g. in liquid–liquid extraction) (Valcárcel and Luque de Castro, 1990). FI on-line preconcentration systems for FAAS and ICP-AES feature high operating efficiencies (10 to 100 times higher than with conventional sample aspiration) and throughputs up to of 60 samples/h. As shown by Carbonell et al. (1992), the extent to which the sensitivity is increased is related to sample size and column features.

Liquid–Solid Techniques

Liquid–solid interfaces are very common in FI-AD, particularly with sorption systems, but also with on-line precipitation in some instances.

On-Line Liquid–Solid Preconcentration and Separation. So far this has been the most extensively used mode due to its operating convenience and automatability. The system uses sorption minicolumns packed with ion-exchange or

chelating resins (both of them involve a chemical reaction between the analyte and the solid column), or adsorptive extraction of either the analytes or the interferents. The tool was first coupled to FAAS and later to ETAAS. The minicolumn can be placed at several points in the FI manifold (Figure 3), namely:

1. Before the injection system (whether in the carrier or in the sample stream) in order to remove reagent impurities or release the reagent required for matrix interference removal or preconcentration purposes.
2. In the loop of the injection valve, for preconcentration.
3. Between the injection and detection units, which the most usual location for solid reactors in an FI manifold.

The performance and efficiency preconcentration minicolumns can be enhanced in various ways. Thus, performance can be improved by loading the column in the opposite direction to elution (viz. by placing the column in the loop of the injection valve), thus avoiding the shortcomings derived from increased compaction of the packed material and from the appearance of parasitic signals due to the sample matrix, which can be sent directly to waste (Luque de Castro, 1992). Higher efficiency can be achieved by using conical rather than cylindrical columns that must be arranged in the FI manifold in such a way that sample loading takes place from the narrower to the broader end. One inexpensive way to build these columns is by using of micropipette tips. Retained analytes must be eluted in the opposite direction to retention in order to minimize dispersion in the column, which can be accomplished by using a time-based injection technique. The dimensions and configuration of the reaction coil between the sample–reagent merging point and

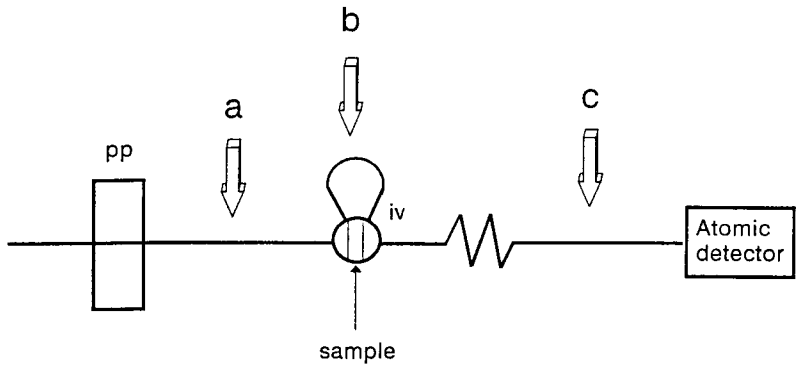

Figure 3. Possible locations of a minicolumn in the flow injection manifold: (**a**) before the injection system (for removal of impurities or interferences from the reagents and sample, respectively); (**b**) in the loop of the injection valve (for preconcentration); (**c**) in the transport zone (for preconcentration or interference removal). pp: peristaltic pump; iv: injection valve.

injector (which incorporates the sorbent column) have a significant effect on the enrichment factor. The shortest connection with the shortest residence time will give the highest enrichment factors (Fang et al., 1991).

One shortcoming of this preconcentration system is the long time required to achieve a large enrichment factor (2–3 min or even 20 min preconcentration times have been reported). The typically low throughput hinders calibration in routine applications. The adverse effect of the preconcentration step on throughput can be avoided by using several columns arranged in parallel and have them operate simultaneously and alternately to deliver the eluates sequentially to the flow manifold (Luque de Castro and Tena, 1993). One other constraint of this technique is the relatively large sample volumes used in each determination. Depending on both analyte concentration and the enrichment factor to be achieved, the sample volume can range from 2 to 100 mL, which is far from the microliter volume range typical of FI. Attempts at circumventing these pitfalls include the use of short, small-bore conduits and knotted reactors, both to restrict dispersion of the eluted sample zone and to improve precision. Low elution flow rates have been used against high nebulizer uptake rates to increase the efficiency of sample usage and make the system easily adaptable to ICP-AES. In general, the efficiency of the system can be improved by more careful control of the dispersion and reduction of the sample loading period. It is also advisable not to go for the highest enrichment factor at the expense of long preconcentration times and high sample consumption.

In order to adapt the final volume of eluate introduction into a graphite furnace, the capacity of preconcentration columns used in ET-AAS has been reduced by Fang et al. (1996) to less than 20 μL, thus restricting the sample volume loaded on the column to a few milliliters. Extensive efforts have been made in order to reduce the eluate volume while maintaining relatively high enrichment factors (e.g. by decreasing dispersion mainly through isolation of the eluant zones with air) (Azeredo et al., 1993).

Microcolumns also increase selectivity indirectly through the isolation of analytes from the sample matrix, or directly, by using a support suited to the species to be retained that allows the matrix to be removed, thus avoiding interferences on the analytical signal and its passage through the detector, which is of paramount importance in cases of insufficient capability. The use of switching valves facilitates disposal of unwanted species following separation and before they can pass by the detection point. Jin et al. (1996) used various serially arranged ion-exchange columns to enact simultaneous separation and preconcentration.

On-line column preconcentration can be fully computer controlled by means of a flow injection accessory for atomic spectrometry in which rotation of the pump, its stop and go intervals, actuation of the valves, and the time at which the thermal program of the atomic absorption measurement is started are automatically controlled by a computer (Sung et al., 1997).

Table 1 shows the different materials used for packing minicolumns as well as the underlying principle for the retention, the detection system and other data of

Table 1. Solid Supports Used in Microcolumns for Preconcentration and Separation in FI-Atomic Techniques

Material	*Retention Principle*	*Analyte*	*Sample*	*Prec. Factor*	*LOD**	*Detector*	*Other Aspects*	*Ref.*
RP-C-18	Adsorption	As(III), total As	Seawater	7.6	0.32, 0.43 (ng)	GF-AAS	Separation and	Sperling, 1991
		Cr(VI), total Cr	Natural water	—	16, 18 (ppt)	GF-AAS	Preconcentration	Sperling, 1992
		Ni, Co, Mn	Certified water	10	70	GF-AAS	—	Ma, 1995
		Pb	Biological, vegetable	—	3	FAAS	—	Lima, 1996
		Trace elements	Drinking water	50	—	HP-FAAS	High perform.–AS	Berndt, 1993
		Mo	Seawater	—	5	FAAS	—	Iyer, 1994
		Cu	Seawater	—	0.16	MPT-AES	Microwave plasma torch–AES	Madrid, 1993
		Cd, Cu, Pb, Ni	Natural water	—	0.8, 17, 6.5, 36 (ppt)	ET-AAS	Microscale system	Sperling, 1991
		Co	Seawater	210	1.7 (ppt)	ET-AAS	—	Sperling, 1991
		Cd, Cu, Pb	Estuarine waters and fertilizers	—	0.003, 0.05, 0.04	GF-AAS	—	Ma, 1996
		Fe(II), Fe(III)	—	—	—	FAAS	—	Krekler, 1994
		Cd, Cu	Biological ref. mat.	20	0.15, 0.2	FAAS	—	Xu, 1992
		Pb	Sea and river water	26	3 (ppt)	GF-AAS	—	Welz, 1990
		Cd, Cu, Pb, Ni	Natural waters	—	0.6, 8.5, 4, 21 (ppt)	GF-AAS	Vol.-based subsampling	Welz, 1992
		Pb	River and seawater	64	4.5 (ppt)	ET-AAS	—	Sun, 1997
RP-C-18	Ion-pair sorbent extraction	Pb	Biological materials	36	3	FAAS	—	Tao, 1996

Polygosil-C18	Ion-pair adsorption	Co	Biological materials	—	3	FAAS	—	Liu, 1995
Alumina	Adsorption	Pb	Potable water	—	0.7	FAAS	—	Dadfarnia, 1994
		PT(IV)	Natural waters	—	10	FAAS	—	Cantarero, 1994
		S	High-purity iron samples	—	300	ICP-AES	—	Yamada, 1992
		Se(IV), SE(VI)	Natural waters	—	0.006	AAS	Hydride-generation	Larraya, 1994
		Co(II)	Tobacco, seawaters	—	0.44	FAAS	—	Trojanowicz, 1994
		Cr(III), Cr(VI)	Natural waters	25	1.0, 0.8	FAAS	Selective adsorption	Sperling, 1992
		Ag	Borehole water	—	4	FAAS	Na, Mg, Ca interfer.	Coetzee, 1990
		Cr	Riverwater	—	—	ICP-AES	Field sampling	Cox, 1992
		Se(IV), Se(VI)	Simulated Freshwater	—	0.07, 0.11 (ng)	HG-AAS	tech. Interlabor. study	Cobo-Fdez, 1995
Alumina	Adsorption	Pb	Potable water	—	0.7	FAAS	—	Dadfarnia, 1994
		Pt(IV)	Natural waters	—	10	FAAS	—	Cantarero, 1994
		S	High-purity iron samples	—	300	ICP-AES	—	Yamada, 1992
		Se(IV), Se(VI)	Natural waters	—	0.006	AAS	Hydride-generation	Larraya, 1994
		Co(II)	Tobacco, seawaters	—	0.44	FAAS	—	Trojanowicz, 1994
		Cr(III), Cr(VI)	Natural waters	25	1.0, 0.8	FAAS	Selective adsorption	Sperling, 1992
		Ag	Borehole water	—	4	FAAS	Na, Mg, Ca interfer.	Coetzee, 1990
		Cr	Riverwater	—	—	ICP-AES	Field sampling	Cox, 1992
		Se(IV), Se(VI)	Simulated freshwater	—	0.07, 0.11 (ng)	HG-AAS	tech. Interlabor. study	Cobo-Fdez, 1995
Amberlite-XAD	Adsorption	Al	Natural waters	—	10	ICP-AES	—	Fairman, 1995
XAD		Ni(II)	—	—	0.1	FAAS	Sorbent modified with Eriochrome blue black R	Olbrych, 1992

(*continued*)

Table 1. Continued

Material	*Retention Principle*	*Analyte*	*Sample*	*Prec. Factor*	*LOD**	*Detector*	*Other Aspects*	*Ref.*
		Cu	Natural water	—	—	FAAS	Sorbent modified with catechol violet	Naghmush, 1992
		Au	Mineral, ores, rocks	—	2	FAAS	—	Xu, 1991
Algae: *Selenstrum capricornutum Chlamydo-monus reinhartii*	Adsorption	Cu, Zn, Co, Hg, Cd, Pb	—	—	0.05, 0.2, 8, 30, 2, 2.5	FAAS	Algae immobilized on controlled pore glass	Elmahadi, 1991
		Cu(II), Zn(II)	Certified sediment Reference material	—	—	AAS		Elmahadi, 1994
Cyanobacteria (*Spirulina platensis*)	Adsorption	Cu(II), Pb, Fe(III), Cd, Zn	Dried sewage	—	—	AAS	Bacteria in activated controlled pore glass	Maquieira, 1994
		La(III), Ce(III), Nd(III)	High-purity Ce(III)	—	9, 0.21, 0.54	ICP-AES		Maquieira, 1996
Cysteine	Adsorption	Cu, Zn, Cd, Pb, Co, Hg	—	—	—	FAAS	Glutaraldehyde-immobilized cys. on controlled pore glass	Elmahadi, 1993
α-Amino pyridine resin	Adsorption	Au	Minerals, ores, rocks	—	0.065	GF-AAS	—	Di, 1995
		Pt, Pd, Ir	Certified samples	—	17, 9, 110	FAAS	Preconc. controlled by a computer	Di, 1995

Activated carbon fiber	Adsorption	Pd	Minerals, ores, rocks	—	0.3	FAAS	Two columns in parallel (preconc.) or in series (elut.)	Lin, 1995
Oxine-loaded activated carbon	Adsorption	Cu	Certified reference material	—	4.4	AAS	—	Murakami, 1992
Sulfhydryl cotton fiber	Adsorption	Ag	Tap waters	—	1	FAAS	—	Gómez-Gómez, 1995
Cellex T	Adsorption	Au(III)	Geochemical reference material	—	2.2	FAAS	—	Pyrzynska, 1994
Dowex 1X8	Adsorption	Se(IV), Se(VI)	Natural waters	—	—	HG-AAS	—	Ornemark, 1994
8531 fiber	Adsorption	Au	Ores, metallurgical samples	—	0.2	FAAS	Automatic preconcentration	Qi, 1992
Amberlyst/Mercaptoacetoxy cellulose	Adsorption	Au	Wastewaters	—	1.7, 0.8	ICP-AES	Comparison of two sorbents	Gómez, 1993
Thiol resin 190	Adsorption	Cd(II), Cu(II), Mn(II), Zn(II)	—	4–5	1.8–3.6	MPT-AES	Low-powered MW	Ye, 1996
Chloroxine	Adsorption	Cu(II), Zn(II), Cd(II), Co(II), Pb(II)	—	49–136	0.5, 0.2, 0.4, 0.6, 4	AAS	Reagent immobilized on controlled pore glass	Elmahadi, 1996
Poly(hydroxamic) acid resin	Adsorption	Cr(III)	Seawater	—	—	AAS	—	Shah, 1990
Silica gel	Adsorption	Pb(II)	Natural waters	100	4	FAAS	Sorbent coated with an ion pair	Rodríguez, 1994
Active carbon silica gel	Adsorption	Cu, Mn, Al, Fe, Cd	Serum	—	0.34–1.8	ICP-AES	8-hydroxyquinoline 5-sulfonic acid immobilized on the substrate	Peng, 1993

(*continued*)

Table 1. Continued

Material	*Retention Principle*	*Analyte*	*Sample*	*Prec. Factor*	*LOD**	*Detector*	*Other Aspects*	*Ref.*
Cellulose	Adsorption	Pb(II)	Natural waters	—	0.17	FAAS	Comparison of different sorbents; speciation of Pb	Naghmush, 1995
Resin CPPI	Chelation	Cu, Zn, Pb, Cd	Tap, rainwater	—	0.05, 0.08, 0.6, 0.1	ICP-AES	—	Yang, 1994
Iminodiacetic acidethylcellulose	Chelation	Cd, Co, Cu, Pb	Seawater, urine	2–4	—	ICP-AES	Computer-assisted system	Caroli, 1991
Oxine resins	Chelation	Cu	—	—	5	FAAS	Synthesis and characterization of different resins	Purohit, 1991
Tercopolymeric resins	Chelation	Zn, Cd	—	—	1	FAAS	Preparation and characterization of chelating resins	Purohit, 1991
Poly(amino-posphonic acid) resin	Chelation	Cr(III), Cr(VI)	Tap, mineral, river waters	—	0.2	FAAS	Chelation and speciation	Cespón-Romero, 1996
Muromac A-1 resin	Chelation	Cu, Mo	Seawater	—	0.009, 0.06	ET-AAS	Computer-controlled on-line preconcentration	Sung, 1997
Immobilized 8-hydroxyquinoline	Masking agent	Pb	Potable water	—	—	FAAS	—	Bysouth, 1990
Chelex 100	Ion exchange	Co	Glass	4	20	AAS	—	Valdés-Hevia, 1991
Dowex 1-X8	Anion exchange	Zn	Canned food	3.5	0.08	HG-AAS	—	Fang, 1992

		Mn	Geothermal fluids	—	0.2	AAS	Sulfur interference removal	Burguera, 1995
Dowex 50 W-X8	Cation exchange	Cu	River, tapwaters	25	1.5	FAAS	Fully automated system with a time-based injector	Burguera, 1995
Dowex 50-X8	Ion exchange	Sr	Marine organisms	—	—	ICP-AAS	Interference removal	Mazzucotelli, 1993
SCX	Cation exchange	Al	Tea leaves, beverages, natural water	—	75	FAAS	—	Salacinski, 1992
AG MP-1 macro-porous resin	Anion exchange	Al(III)	Dialysis fluids	—	1 (ppt)	FAAS	Matrix removal	Aceto, 1994
HEH(EHP)	Ion exchange	14 Rare earth metals, Y	Geological reference material	8–15	50–500	ICP-AES	Two micro-columns	Liang, 1995
732 resin	Cation exchange	B	Steels	—	5	ICP-AES	Fe ion matrix removal	Wang, 1996

Note: *Expressed in ppb, unless otherwise noted.

interest. C_{18}-bonded silica beads and, to a lesser extent, alumina, are the most commonly used adsorptive materials for preconcentration; the analytes are normally retained as chelates formed with different reagents and later eluted with a water-miscible or immiscible organic solvent, thus increasing the flexibility of this technique. Solid exchange materials used as packings for preconcentration minicolumns can be either commercially available ion-exchange resins or ion exchangers prepared in the laboratory from an adsorbent material that is activated and then bonded to a chelating molecule. The latter minicolumns can also be employed to retain excess reagent. 8-Hydroxyquinoline is the most frequently immobilized chelating agent used for preconcentration purposes. It is usually supported on silica and placed either in the transport zone or in the loop of the injection valve. Attempts are also being made at using sorbents for selectively retaining the target analytes in the presence of relatively high concentrations of coexisting metals, thus overcoming the typically low capacity of the column which restricts the amount of sample to be loaded (particularly when high concentrations of interferents compete with the analyte for the active sites on the sorbent).

Sorbent extraction can also be used either to selectively preconcentrate one oxidation state of elements occurring in more than one valency [thus providing a means for speciation and the differential determination of individual oxidation states as proposed by Welz (1992)], or to retain two oxidation states and selectively elute them with appropriate solutions as reported by Bryce et al. (1995).

One alternative to minicolumns is a membrane disc containing ion-exchange material, as used by Dolan et al. (1991) for the on-line preconcentration of iodine and iodate ions prior to conversion of the analytes into iodide for more effective nebulization; in this way, the sensitivity of the ICP-AES method is raised from 150 μg/mL to 0.75 ng/mL.

Liquid–solid preconcentration can also be carried out by sorption preconcentration on the inner walls of *knotted reactors*, which are normally made of PTFE. The analyte is preconcentrated as a chelate that is formed on-line in the FI system and later eluted by washing the reactor with an appropriate organic solvent. The ensuing method has been applied to the determination of Sb in water by ET-AAS (Yan et al., 1996), that of Cu in water and rice (Chen et al., 1994), and that of Cd in biological samples by FAAS (Fang et al., 1994). The limits of detection were in the nanogram-per-milliliter range in all instances.

Precipitation and Coprecipitation. This is a less frequently used liquid–solid preconcentration technique even though the in situ formation of a solid phase in an FI manifold and its retention on an appropriate filter provide high preconcentration factors. The technique was first coupled to FAAS in the late 1980s, but has scarcely been applied to other atomic spectrometric techniques.

Samples are injected into a reagent stream and the precipitate formed is retained on a stainless steel or nonmetallic filter. Most applications in this context focus on the indirect determination of nonmetals and organic compounds in different types

of samples including pharmaceuticals, beverages, and sweeteners (Esmadi et al., 1990, 1994; Laredo-Ortiz et al., 1993; Eisman et al., 1994; Yebra et al., 1995). Precipitation has also been used by Esmadi et al. (1995) for the sequential determination of mixtures of different analytes with improved selectivity.

In addition to conventional FI, reversed-FI manifolds have also been used in this context. The reagent is injected into a sample flow and positive peaks are produced by its excess after precipitation. When the detector coupled to a normal FI manifold saturates owing to the high reagent concentration required to obtain a precipitate, an additional water flow can be merged with the reagent to decrease its concentration, thus effecting post-filter dilution and solving the problem.

The volume of sample injected and the length of the reaction coil are of paramount importance to the analytical features of a method based on precipitation. Decreased filter efficiency occurs if the precipitate is too bulky (i.e. if a large sample volume is used). The reaction coil must be long enough to ensure quantitative reaction, but not too long in order to minimize dispersion.

Several FI modifications have been proposed in order to improve preconcentration processes. One involves using a closed-loop recirculating manifold that allows interferences to be removed (and selectivity to be increased) by precipitating and retaining interferents on a nylon fiber filter that is regenerated after each injection (Debrah and Tyson, 1992).

Difficulties experienced in on-line column systems with samples containing relatively large concentrations of transition metals are partially circumvented by on-line coprecipitation systems where different reagents are used to coprecipitate the analyte of interest. On-line manipulation of relatively large amounts of precipitate in a flow system is possible by using a knotted reactor as a filterless precipitate collector (Fang and Dong, 1992; Pei and Fang, 1994; Chen et al., 1995; Wei-Min et al., 1995; Nielsen et al., 1996; Zou et al., 1996). This device also allows the use of coprecipitation systems as a means for on-line preconcentration in atomic spectroscopy (Wang et al., 1995).

On-Line Partitioning

On-line partitioning between two liquid phases involves an immiscible solvent in most cases. On the other hand, membrane-based partitioning between miscible phases (i.e. dialysis) has only occasionally been used.

On-Line Liquid–Liquid Solvent Extraction. This is a useful FI application to atomic spectrometry. Most often a derivatization (complex or ion-pair formation) reaction is required prior to or simultaneously with the extraction step in order to facilitate extraction or improve the subsequent determination step. The sample and a chelating reagent are previously mixed and an organic solvent is then used to extract the complex in an extraction coil (alternatively, the chelating reagent is dissolved in the organic phase). In either case, the two phases are separated by a gravitational or, more usually, by a membrane-phase separator, and the organic

phase is directly introduced into the atomic detector for determination (Carbonell et al., 1992). An ion pair can also be formed instead of a complex in the aqueous phase that can subsequently be extracted into or formed in the organic phase (Santelli et al., 1991). In some cases, both the aqueous and the organic phases are of interest (e.g. in the continuous speciation and separation of two complexes formed in the two phases) (Menéndez-García et al., 1995). Supported liquid membranes have also been used for liquid–liquid extraction. They are formed by in situ coating of a thin layer of organic phase onto a polymeric support (Taylor et al., 1992).

Flow injection and on-line liquid–liquid extraction feature a high throughput and reduce environmental contamination, operating time and manual effort. The liquid–liquid extraction of a metal from an aqueous phase into an organic phase allows the element to be removed from the matrix, thus avoiding interferences and achieving preconcentration providing both the volume of organic solvent is smaller than the original one and the partition coefficient is favorable enough. Other parameters affecting sensitivity are the extraction coil length, sampling and sample injection times, and flow rate of both the sample and carrier streams. Methylisobutyl ketone is the most frequently used organic extractant on account of its good burning properties which result in markedly increased sensitivity. Other individual and mixed solvents have also been used by Memon et al. (1993). The indirect determination of nonmetal elements and organic compounds can also be carried out after liquid–liquid extraction (Jiménez de Blas et al., 1990; Manzoori and Miyazaki, 1990). This technique has been used mainly in FI-AES; however, the number of reported applications compares unfavorably with other preconcentration modes, possibly because of inadequate stability in some on-line phase separators and of difficulties in using some organic solvents in conventional FI systems. Tao and Fang (1995) developed a system with organic solvent propulsion using PTFE tubing and a conical–cavity gravitational-phase separator of stainless steel and PTFE in order to overcome these problems.

Dialysis. This technique combined on-line with atomic detectors is one other very effective way of accomplishing liquid–liquid extraction and preconcentration; it avoids interferences from macromolecules and provides high enrichment factors and low limits of detection. There are very few reported FI applications of this type in atomic spectroscopy. Enrichment factors of 200 for cations with an 8 min dialysis time have been obtained with Donnan dialysis. These factors can be further improved by increasing the dialysis time, the final sample solution temperature, or the sample volume. Additionally, the tubing length must be optimized and the void volumes minimized (Kasthurishnan and Koropchak, 1993).

Serially arranged dialysers have been used for the sequential separation of different analytes in the same sample with the analytes being subsequently determined by the same (Lima et al., 1996) or different techniques (one being an atomic spectroscopy technique in most cases) (van Staden, 1990, 1991). Serial dialysis has

also been used with other preconcentration devices such as ion exchange columns [van Staden and Hattingh (1995)] and with other separation techniques for the sequential individual isolation of analytes [Benedine-Martelli et al. (1995)]. The results warrant more attention to dialysis as a powerful tool increasing the sensitivity of FI-AS couplings.

Various flow injection systems involving dialysis units and stream splitting have also been used to dilute samples, add reagents and introduce samples extracts into the detector in soil analyses by FES and AAS. An additional dialysis unit increases sensitivity, as demonstrated by Ferreira et al. (1995).

Gas–Liquid Separation

Despite the small number of species capable of yielding a gas by reaction, gas–liquid separation techniques based on vapor generation (VG) have gained extensive use in FI-AS (Huang, 1994; Matusiewicz and Sturgeon, 1996), particularly in FI-ICP-AES, where vapor generation considerably raises the analytical potential for multielemental determinations of volatile vapor-forming elements at the ultratrace level in environmental samples. These techniques include classic choices such as *hydride generation* (HG) and *cold vapor generation* (CV), and a new alternative: *pervaporation.*

HG-AAS. This is currently the most popular combination for the determination of trace amounts of As, Se, Bi, Sb, and other elements which form volatile covalent hydrides. On the other hand, CV-AAS is the most broadly applied approach to the determination of Hg in different types of samples, including biological fluids (Nixon et al., 1996) and environmental materials (Erber et al., 1994; McIntosh et al., 1994). The inception of commercially available FI-VG-AS equipment (at least three models of dedicated VG-AAS instruments currently exist) has allowed several research groups (particularly those of Tyson and of Tao and Fang) to diversify the uses of this system. Many of the newer applications use simple manifolds and time-based sampling techniques (Burguera et al., 1995); some employ autosamplers but no injection valves. These designs are prone to cross-contamination between successive samples, so the first measurement in each set of replicates must be discarded. This problem has been solved by Tao and Fang (1993) using either an injection valve in the time-based sampling manifold or an automated hydride sequestration system. FI-hydride sequestration has also been performed with volume-based sampling by loading the sample into a loop; however, the sensitivity obtained is generally inferior to that provided by time-based conditions. The need for a carrier gas (usually argon) to transport the hydrides into the detector is most often met by the hydrogen gas produced during reduction. High flow-rates can reduce the sequestration efficiency.

FI-HG-AAS has some advantages over alternative approaches, namely:

- over 90% reduction in sample and reagent consumption;

- at least double sample throughput;
- better precision (typically about 1% RSD); and
- one or two orders of magnitude higher tolerance to major interferents.

These advantages have fostered applications to all hydride-forming elements in different fields of interest, FI being the main operating mode for HG-AS procedures.

The nonequilibrium conditions of FI-VG-AS systems improve selectivity by kinetically discriminating the main hydride reaction from slower interfering reactions, and by reducing contact of the analyte with solid-phase interferents; however, the ability to control kinetic effects for increased selectivity (instead of sensitivity) through optimal FI parameters and reaction conditions has not yet been fully explored. Although kinetic discrimination can reduce interferences, tolerated levels may still be inadequate for some samples; interferences can also be removed by on-line separation (e.g. with ion-exchange microcolumns). Hydride-forming elements in different oxidation states often exhibit differential sensitivity in HG-AAS determinations with the lower oxidation states resulting in the higher sensitivities. Thus, previously reducing the analytes to their lower oxidation states is one way to improve sensitivity, as demonstrated by Cobo-Fernández et al. (1993). Individual oxidation states can also be determined by using appropriate FI manifolds in conjunction with either AAS (Ruede and Puchelt, 1994) or AES (Bryce et al., 1995). Organic Hg in saliva has been determined by on-line addition of $KMnO_4$ to convert organic Hg into inorganic Hg ions that are detected by cold-vapor AAS (Guo et al., 1996). The flow injection parameters to be optimized in a VG-AAS system are the reagent concentration, carrier gas-flow rate, reaction coil length, gas–liquid separator characteristics, and atomizer dimensions.

Coupling FI manifolds with small, dedicated atomic fluorescence (AF) detectors is one inexpensive way of developing methods based on HG-AF with excellent analytical features. Because they are used in speciation analyses, they are discussed in Section IV.

On-line preconcentration systems [e.g. ion exchange, sorbent minicolumns, liquid–liquid extraction or precipitation (García et al., 1994; Canada-Rudner et al., 1994)] have also been successfully used with FI-VG-AS; in some cases, the acid eluent used to flush retained analytes on the column provides the acid conditions for the vapor generation reaction. Columns packed with ion exchange resins have also been used on-line with these systems for matrix removal (Tyson et al., 1992) or integrated reaction–separation (Offley et al., 1992) in order to improve tolerance to interferences by virtue of the almost immediate separation of the hydrides from the reaction medium; they also provide better conditions for kinetic discrimination of the analytical reaction. One shortcoming of these approaches involving liquid–solid separation is a low throughput (about 15 samples/h) (Fang et al., 1996). A more powerful separation technique, ion exchange chromatography, has also been coupled with FI-HG-AAS for the determination of total As in urine (Jimenez de

Blas et al., 1994). Amalgam preconcentration has also been used in FI-CV-AAS for the determination of Hg; to this end, various gas–liquid separators have been designed and the influence of reagent flow rate, Ar purge flow rate, injection time, and postinjection purge time studied, and their efficiencies compared (Hanna et al., 1993). In situ preconcentration of vapor-forming analytes in a graphite furnace following the vapor-generation reaction is a relatively new technique for ultratrace analysis by AAS (Walcerz et al., 1994; Haug and Liao, 1995, 1996) or ETAAS (Tao and Fang, 1995); implementation of FI techniques in the in situ preconcentration system improves the performance of the system. A dehydration trap after the gas–liquid separator was used by Narasaki and Cao (1996) to dehydrate the hydride produced before it was swept into an electrically heated furnace.

The simultaneous determination of hydride- and non-hydride-forming elements by ICP-AES has also been accomplished by McIntosh and Slavin (1992), who split the sample solution into two streams, one being pumped directly into the nebulizer and the other mixed with HCl and $NaBH_4$ solution in the mixing tubes of the chemifold.

The reversed-FI mode has also been applied to cold-vapor AS. The sample solution is mixed with an $SnCl_2$ acid stream and, after passing by the mixing zone, through a reaction coil; the Hg formed is swept from the solution to a PTFE membrane in a permeation cell by means of a He stream and permeated Hg is passed to a quartz tube containing Au foil onto which the Hg is subsequently concentrated and released by resistive heating for its AES determination (De Andrade and Bueno, 1994).

Flow injection–electrochemical hydride generation (FI-EHG) is a new technique that circumvents some of the shortcomings of FI-HG systems based on the use of $NaBH_4$, namely the contamination introduced by impurities in $NaBH_4$; the high cost of this reagent, and the instability of its aqueous solutions, which entails daily preparation of fresh solutions; and the sensitivity of the process to concomitant ions. The FI-EHG approach was initially adapted to AAS detection. A thin-layer-type flow cell was designed to handle the small sample volumes typically used by FI techniques; Pt material was used as anode, with the cathode usually made of vitreous carbon material (Lin et al., 1992; Brockmann et al., 1993; Schaumloeffel and Neidhart, 1996). The technique was further combined with ICP-AES for multidemand simultaneous determination of hydride-forming elements. Compared to the $NaBH_4$ acid reaction system, the interference from coexisting transition elements was greatly reduced. Some interferences can be avoided by changing electrolytic conditions such as the electrode material, electrolytic current, or surface area of the electrodes. However, the interference from other elements is rather serious in some cases (Ding and Sturgeon, 1996). Thus, selenium considerably hinders hydride generation of other elements, probably as a result of the more positive reduction potential of the Se^{4+}/Se^0 system relative to the other hydride-forming elements. The products of Se^0 or SeH_4 can be adsorbed on the surface of the electrode, which prevents the formation of other hydrides.

Pervaporation. This separation technique has long been used in the industrial field in competition with gas diffusion and evaporation, but scarcely used in the analytical laboratory. The initial attempts of Prinzing et al. in 1990 at incorporating pervaporation into the analytical laboratory have so far been the only one taking full advantage of this membrane-based separation technique. Late in 1994 and early in 1995 our research group studied the efficiency of mass transfer in the pervaporation process and demonstrated the use of this technique for routine analysis as an alternative to gas diffusion in FI systems (Mattos et al., 1994, 1995). Pervaporation, which can be defined as integrated evaporation and gas diffusion, has one special advantage over gas diffusion: the sample never comes into contact with the membrane since the volatile analyte or its volatile reaction product evaporates from the sample matrix (a liquid or solid) to a space between the sample and membrane, and then diffuses through the membrane to a static or flowing acceptor solution. This makes pervaporation suitable for separating a number of volatile analytes or reaction products from liquid and solid matrices (Luque de Castro and Papaefstathiou, 1997). The pervaporation cell can be connected on-line to a dedicated atomic fluorescence detector, whether directly or via intervening a gas chromatograph (Bryce et al., 1996, 1997). In the latter, the pervaporator acts as an effective, advantageous alternative to headspace. Because the main goal of the FI-pervaporation-AD coupling is speciation analysis, its applications are discussed in Section IV.

Electrochemical/Sorption Cell. Some special preconcentration systems have been used in specific cases such as the preconcentration of Cr(III) and total Cr in waters using a flow-through electrochemical/sorption cell containing activated alumina with the electrodes off-circuited. The Cr(III) is subsequently eluted and determined by FAAS. The cell contains a porous glassy carbon electrode coated with Au, a layer of sorbent, and a serial counter electrode. Total Cr is determined after reducing Cr(VI) to Cr(III) by pumping water through the cell while a constant current of −5 to −10 mA is applied. A limit of detection of 0.5 ng/mL was thus achieved by Beinhrohr et al. (1996). *Near-melting point* FI improves FAAS LODs by virtue of the enrichment occurring at grain boundaries in a liquid phase. A continuous flow of solvent is used under nonequilibrium conditions to ensure highly efficient analyte removal. The sample is slowly heated beyond its melting point and the reactive solvent is brought into contact with it through a coarse sintered glass filter. The method was applied by Walter and Aleboyeh in 1996 to determine Cs impurities in Na by FAAS, with an LOD of 5 μg/Kg. One particular case of mercury preconcentration is an *amalgamation technique* which was used by McIntosh in 1993 to determine this element in environmental samples. Mercury was collected on a heated Au gauze and the released analyte being swept into a quartz cell located in the sample compartment of an FAAS by a carrier gas.

B. Improved Precision

Flow injection is a very reproducible means of both inserting a precise volume of sample and improving the detector performance by minimizing blockage at the interface (thus increasing the detector stability). The FI-ICP-AES coupling significantly improves precision through reduced buildup (more stable plasma) and improved torch stability (absence of air pockets). This assembly also affords a constant sample solution flow rate (by use of a pump to avoid problems posed by viscosity changes). The ability to use small sample volumes reduces loading of undesirable matrices on nebulizers and torches, particularly in samples with high salt content or organic solvent solutions. An injection volume as low as possible without increasing limits of detection should be chosen in order to minimize solid sample deposition on the torch injector tip. This avoids matrix deposition and increases the reproducibility for a particular measurement. It also ensures better long-term stability of the instrument. The FI technique enables determinations in samples with total dissolved solid concentrations 20–30 times higher than those handled by conventional solution aspiration.

Memory effects are also minimal in a FI-AS coupling because the carrier immediately follows each sample plug; this results in a continuous rinsing effect that dramatically reduces clogging of the interface by deposition of solids. The rinsing effect of the carrier decreases washout times and increases throughput as a result. Since the carrier is flowing continuously, plasmas that normally extinguish at the air–water interface will no longer do so. In addition, injection of the sample avoids its passage through the flexible tubing of peristaltic pumps, which can adsorb the analyte and result in diminished signals and memory effects that severely degrade precision; in addition, this ensures precise control of the flow-rate (Luque de Castro and Tena, 1995).

C. Manipulating Sensitivity

Atomic spectrometers are known to exhibit narrow linear response ranges. The solution is subjected to or preconcentration steps which can be done in the FI system. Solutions containing high analyte concentrations must be diluted to a variable degree depending on the sensitivity of the analyte concerned. Often, dilution is also needed to overcome matrix effects which can be suppressed by dilution as proposed by Arruda et al. in 1993 and 1994 for the determination of Se and Al in fruit juices using an automatic FI method involving dilution, addition of a chemical modifier, and delivery of the filtered sample to an autosampler prior to AAS detection. The FI technique avoids the need for prior manual dilution, thus simplifying handling of samples that are too concentrated or troublesome for direct aspiration, and affording dilution factors in the range 0–200 for samples and standards. This asset by itself justifies its coupling with atomic techniques in replacement of other, less flexible dilution systems. This goal can be achieved by

a short piece of wide-bore tubing or a delay coil, by merging streams or by zone sampling approaches involving unstirred or stirred chambers.

One of the more flexible and routinely applicable technique for on-line dilution is the *zone penetration* or sequential injection approach proposed by Gine et al. in 1985. Three or even five different analyte dilution levels can be obtained in a single injection without the need for complicated gradient evaluations. The zone-penetration technique is strongly dependent on the performance of the propulsion system and has been evaluated using a peristaltic pump, a reciprocating piston pump, and a sinusoidal syringe pump as propulsion system. The dilution efficiency with FAAS detection was examined by Fang in 1992; he found the peristaltic pump to perform equally to or better than that of the other types, which only surpassed it as regards long-term stability. The combination of microsampling dilution with zone penetration provides an efficient automated dilution system for FAAS that enables the direct determination of various metals at the gram-per-liter level and affords dilution factors up 27,000, as reported by Xu and Fang in 1994.

The *zone sampling* technique has also been used in a fully automated FI dilution system including a microcomputer for instrument control and data acquisition and processing. Two rotary valves select different portions of the injected sample plug that are then re-sampled toward the atomic detector. The system automatically chooses a suitable dilution factor for each sample and enables up to 10,000-fold dilution as shown by Garrido et al. (1996). One other application of this technique based on two computer-controlled dilutions of the sample plug was reported by Lapas et al. in 1996.

Variable-volume dilution chambers have also been used to expand the dynamic range of FAAS (Beinrohr et al., 1991). A plug of air displaces the diluted solution from the chamber and facilitates mixing prior to nebulization (López-García et al., 1992). *Variable-volume injectors* also simplify the on line dilution and analysis of samples by AAS and AES (de la Guardia et al., 1993). *Computer-controlled peristaltic pumps* have been used for dilution, the pump rate being raised when higher dilution is required. One approach to expanding the dynamic range is an FI dilution system based on dispersion of microliter-volume samples that comprises two computer-controlled peristaltic pumps (one for the sample solution and the other for the diluent). The use of variable dilution factors allows the linear working range to be altered (Fang et al., 1993). A T-piece can be placed before the nebulizer to ensure constant flow. The pump can be used with an electromagnetic rotary valve, also controlled by a computer, to obtain dilution rates up to 2000, as reported by López-García et al. in 1994. Wabner and Sears (1996) proposed serial dilution blocks to be applied in the analysis of undiluted urine samples by FAAS, thus expanding the nonlinear calibration graphs. A closed dissolution system connected to an FI manifold was used by Matousek et al. in 1996 to determine the real stoichiometry of small semiconductor crystals. They obtain similar or better precision, relative to conventional open dissolution and direct batch aspiration procedures.

One other approach to expanding the dynamic range in FAAS is the use of computer-controlled FI manifolds for metering sub-microliter volume samples into a slow moving carrier. After injection, the flow rate of carrier is increased and an additional channel is used to offset the difference between the flow delivered by the pump and the nebulizer uptake (López-García et al., 1995). These and other dilution systems were compared by the same authors in 1996, who found both flow injection and continuous-flow procedures to be suitable choices for implementation in automated and semiautomated dilution systems.

D. Calibration

The ability to implement on-line sample pretreatment procedures such as those of standard additions and the internal standard, which are both time- and sample-saving, make it a useful tool for sample handling.

The standard addition method has proved effective in overcoming matrix effects, one of the main sources of impaired precision and sensitivity for some samples. The FI manifold can be designed either to add the standard to the sample or to inject the standard into the sample (reversed-FI). In the latter mode, the standard addition method is implemented by continuously pumping the sample to the detector rather than the carrier solution; the baseline value is used to zero-in the detector and standard solutions are injected into the sample stream. The calibration curve can be constructed from injections of identical volumes of standards of variable concentration or different volumes of the same standard solution (a simple variable volume injector can be used with this purpose, as proposed by Burguera et al. in 1990). Alternatively, an FI dilution method can be employed prior to injection and calibration done by a series of standards prepared by serial dilution (this is the most widespread calibration procedure for routine applications). Merging the sample and standard before injection is one easy way to implement the standard addition method. The sample–standard mixed stream can also be merged with a third stream of internal standard.

Some FI manifolds designed in the last few years implement automatic standard calibration methods. Automated addition of internal standards for ICP-AES was reported by Milburn in 1996. The manifold comprised a sample pump controlled by a commercially available computer, and a separate peristaltic pump that delivered the internal standard at as low as possible flow rate. The sample and internal standard were mixed in a reaction coil prior to nebulization. One other system of this type involves microsampling of a single standard using computer-controlled stepper-motor-driven peristaltic pumps; it relies on the linear relationship between the reciprocal of the dispersion coefficient (or analyte concentration) and sample volume in FI systems with dispersion coefficients higher than approximately 30. The ensuing method was applied to the determination of Mg by FAAS (Fang et al., 1996).

One other approach is based on merging zones and gradient; the method uses a single standard solution and provides a series of addition levels per injection. The dual-channel flow manifold used is equipped with a sample injection loop in each channel to allow simultaneous injection into two water streams that are merged and passed through the detector for the transient signal to be monitored. Standard additions are performed by filling one loop with water and the other with sample solution, and recording the transient signal produced. Then, the loops are filled with standard and sample solutions and a second transient signal is recorded. About 150 measurements can be made along the tailing edge of each transient signal, providing about 150 addition levels per determination. All data are processed by a computer, and a mathematical model is used that takes into account changes in the sample matrix due to differences in dispersion associated with the different addition levels and corrects deviations related to the asymmetry of the merging zone process. The methodology was applied by Silva et al. (1996) to the AAS determination of Cu in spirits.

Combinations of the injector commutator and solenoid valves have provided a multipurpose FI system that performs programmable dilutions and standard additions. The sample zone is merged with an aliquot delivered from a trapped standard zone in a modified version of the zone sampling approach. This calibration procedure was applied by Freire dos Reis et al. (1992) to the analysis of plant digest samples by FI-ICP-AES.

Automatic calibrations by FI-FAAS for slurry atomization have also been reported. They usually involve a single- or dual-channel manifold that provides appropriate on-line dilution prior to measurement (Martínez-Ávila et al., 1993; Vinas et al., 1993; Bautista et al., 1994). One of these methods uses a standard analyte solution as carrier; a delivered equation allows calculation of the analyte concentration in the sample from the signal obtained by injection of the slurry and that for a standard solution (López-García et al., 1991).

A FI-hydride generator was designed and optimized by Marshall and van Staden in 1990 for automated standard additions in AAS. The system features rapid analysis, ease of automation, and simple in-line handling of interferences.

Chemometrics has been used to optimize a number of FI-AS applications such as the on-line dilution and determination of Cu by FAAS. A totally randomized factorial central composite design was employed for the exploration of the response as a function of the flow rate and length of the dispersion coil of the FI system. An empirical response function, taking into account the peak height and the response time, was employed by Matousek et al. in 1995 to evaluate the response. Response surfaces dependent on pH and the reagent concentration have also been reported for the determination of As(III) by FI-HG-AAS using several buffers. Wentzell et al. in 1994 obtained response surfaces using an automated continuous-flow apparatus under computer control and an experimental design based on continuous variations. In one other application, reported by Tsale et al. in 1996, a full 33-factorial design was used to optimize the reagent, $NaBH_4$, and acid concentra-

tions for the generation of hydrides that were trapped in an electrothermal atomizer coated with Ir/Zr in an automated FI-hydride generation system furnished with AAS detection.

Improved limits of detection for FI-FAAS were obtained by Sperling et al. (1992) using a manifold with two peristaltic pumps and a four-port injection valve, under computer control, for sequential injection. Dedicated data processing comprised summation and integration procedures applied to the signals collected.

E. Speciation Analysis in the FI-AD Couplings

Atomic detector can hardly distinguish among oxidation states of an element, coordination forms, or electron configurations. However, samples can be suitably processed in an intelligently designed FI manifold in order to facilitate speciation analyses with this type of detector. Some typical ways of manipulating samples for this purpose can be found in the FI-AD literature and are briefly discussed below.

The usual way of discriminating between two oxidation states of an element by FI-AD is sequential in nature and involves the formation of a volatile hydride of one of the states for its determination and the conversion of the non-hydride active form into the active one for the total determination of the two original forms. This procedure was used by Burguera and Burguera in 1993 for As speciation [as As(III)/As(V)] in waters based on the Fleitmann reaction, and by Borja et al. (1990) for Pb speciation (as tetraethylstannane and tetramethylstannane) in gasoline; an appropriate reductant and atomic absorptiometry were used in both cases. The same procedure and accelerated oxidation by effect of microwave radiation on sequential (Pitts and Worsfold, 1994) or simultaneous injections (Bryce et al., 1995) of two aliquots were used for the speciation analysis of selenium [as Se(IV)/Se(VI)] in liquid samples using AAS and AFS, respectively. The manifold used in the latter method is outlined in Figure 4a. One other method for selenium speciation is based on retention and selective elution of each oxidation state with an appropriate eluent prior to hydride generation for Se(IV) and microwave-assisted reduction to Se(IV) and subsequent hydride generation for Se(VI). The experimental set-up used is shown in Figure 4b.

Pervaporation is also suitable for speciation analysis, particularly of solid samples. The pervaporation module affords integrated leaching, derivatization (if required), and separation, thus miniaturizing the experimental set-up. Two different principles have been used in this context, namely: (a) the differential volatility of organic and inorganic mercury species, which are selectively pervaporated with the aid of focused microwaves and then determined by AFS (Bryce et al., 1996); and (b) a gas chromatograph acting as an interface between the pervaporator and an atomic fluorescence detector. Monomethyl, dimethyl, and diethyl forms of Hg were pervaporated from solid samples, chromatographied, and determined with excellent results with a very simple, automatable assembly by Bryce et al., 1997.

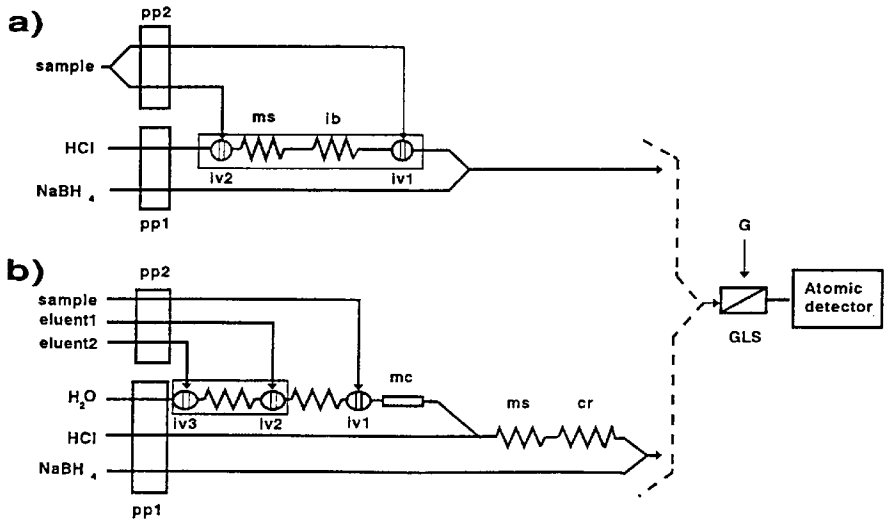

Figure 4. Speciation analysis. (a) Simultaneous injection of two aliquots and on-line treatment of one of them. (b) Sequential, selective elution of the two analyte forms. pp: peristaltic pump; iv: injection valve; ms: microwave source; ib: ice bath; mc: minicolumn; cr: cooling reactor; G: gas; GLS: gas-liquid separator.

Sorbent extraction also affords the differential determination of several oxidation states for an element, as noted in the Section III.A. The advantages of speciation by sorbent extraction include the ability to preconcentrate the analytes prior to their determination and to separate them from complex, potentially interfering matrices. Other oxidation states can be determined by difference following oxidation or reduction to the more reactive form (Welz, 1992).

Selective extraction of two different oxidation states can be accomplished by a continuous separation device. Extraction takes place in an appropriate coil and consecutive organic and aqueous segments containing each oxidation state are separated at a membrane-phase separator connected with the ICP-AES assembly (Menéndez-García et al., 1995).

F. Indirect Determinations

Indirect determinations of organic compounds can readily be carried out in an FI system, which broadens the scope of atomic spectroscopy. Several indirect methods are discussed in the previous sections. Drugs such as chloramphenicol and methadone were determined by Montoro et al. (1990) in pharmaceutical products and urine following on-line reduction on a Cd or Zn microcolumn and FAAS detection of the metal ions released. A high-pressure flow injection assembly has been used for the determination of glycine in pharmaceuticals by AAS using a packed-bed

reactor; the Cu-glycine complex formed being driven to the detector (Calatayud and García-Mateo, 1991). The oxidizing reagent MnO_2, incorporated into a polyester resin to form a packed-bed reactor, was used for the indirect determination of isoniazidin in tablets by monitoring the Mn(II) released (Lahuerta-Zamora et al., 1992).

Solid-phase reactors packed with different reagents have been used for the indirect determination of organic compounds. Lahuerta and Calatayud in 1995 reported a method for the FI-AAS determination of ondansetron in pharmaceuticals using PbO_2 entrapped by polymerization of unsaturated esters in a polyester resin and monitoring the Pb(II) released. This ion has also been monitored by FAAS following on-line oxidation of organic compounds in water using a solid-phase reactor prepared by in situ precipitation of PbO_2 on silica gel (Ruchti et al., 1992). Salicylic acid in pharmaceuticals can also be determined by reaction with copper carbonate entrapped in a polymeric material accommodated in a solid-phase reactor inserted in an FI manifold; the drug is quantified by monitoring the Cu(II) ions released (Rivas et al., 1995).

IV. TRENDS

The main directions for research into flow-injection atomic spectroscopy in the near future are expected to be as follows:

- On-line incorporation of new devices that enable direct treatment of solid samples and thus the entire analytical process to take place in the coupled assembly.
- Use of classic and new types of energy to accelerate sample pretreatment.
- Development of new packing materials for microcoulumns intended to improve existing preconcentration/separation methods and expand current applications of novel separation techniques such as pervaporation.
- Miniaturization of the experimental setup in order to save sample and reagents.
- Increased automation and hence decreased human intervention in these tasks.

REFERENCES

Aceto, M., Abollino, O., Sarzanini, C., Mentasti, E., Mariconti, F. *At. Spectrosc.* **1994**, *15*, 237.
Arruda, M.A.Z., Gallego, M., Valcárcel, M. *Anal. Chem.* **1993**, *65*, 3331.
Arruda, M.A.Z., Gallego, M., Valcárcel, M. *J. Anal. At. Spectrom.* **1994**, *9*, 657.
Atallah, R.H., Kalman, D.A. *Talanta* **1991**, *38*, 167.
Azeredo, L.C., Sturgeon, R.E., Curtius, A.J. Spectrochim. Acta **1993**, *48B*, 91.
Barnett, W.B., Porter, M.K., Kreitzberg, C. *At. Spectrosc.* **1994**, *15*, 156.
Bautista, M.A., Pérez-Sirvent, C., López-García, I., Hernández-Córdoba, M. *Fresenius J. Anal. Chem.* **1994**, *350*, 359.
Beinrohr, E., Manova, A., Dzurov, J. *Fresenius J. Anal. Chem.* **1996**, *355*, 528.
Beinrohr, E., Csemi, P., Tyson, J.F. *J. Anal. At. Spectrom.* **1991**, *6*, 307.

Benedini-Martelli, P., Gomes-Neto, J.A., Zagatto, E.A.G., Boscolo-Brienza, S.M., Montenegro, M.C.B.S.M., Costa-Lima, J.L.F. *Anal. Chim. Acta* **1995**, *317*, 239.
Berndt, H., Mueller, A., Schaldach, G. *Fresenius J. Anal. Chem.* **1993**, *346*, 711.
Bordera, L., Hernandis, V., Canals, A. *Fresenius J. Anal. Chem.* **1996**, *355*, 112.
Borja, R., de la Guardia, M., Salvador, A., Burguera, J.L., Burguera, M. *Fresenius J. Anal. Chem.* **1990**, *338*, 9.
Brockmann, A., Nonn, C., Golloch, A. *J. Anal. At. Spectrom.* **1993**, *8*, 397.
Bryce, D.W., Izquierdo, A., Luque de Castro, M.D. *Anal. Chim. Acta* **1996**, *324*, 69.
Bryce, D.W., Izquierdo, A., Luque de Castro, M.D. *Anal. Chem.* **1997**, *69*, 844.
Bryce, D.W., Izquierdo, A., Luque de Castro, M.D. *J. Anal. At. Spectrom.* **1995**, *10*, 1059.
Burguera, J.L., Burguera, M., Rivas, C., de la Guardia, M., Salvador, A., Carbonell, V. *J. Flow Injection Anal.* **1990**, *7*, 11.
Burguera, M., Burguera, J.L., Brunetto, M.R., de la Guardia, M., Salvador, A. *Anal. Chim. Acta* **1992**, *261*, 105.
Burguera, J.L., Burguera, M., Carrero, P., Rivas, C., Gallignani, M., Brunetto, M.R. *Anal. Chim. Acta* **1995**, *308*, 349.
Burguera, J.L., Burguera, L., Rivas, C., Carrero, P., Gallignani, M., Brunetto, M.R. *J. Anal. At. Spectrom.* **1995**, *10*, 479.
Burguera, J.L., Burguera, M., Carrero, P., Marcano, J., Rivas, C., Brunetto, M.R. *J. Autom. Chem.* **1995**, *17*, 25.
Burguera, M., Burguera, J.L. *J. Anal. At. Spectrom.* **1993**, *8*, 229.
Burguera, J.L., Burguera, M. *J. Anal. At. Spectrom.* **1993**, *8*, 235.
Bysouth, S.R., Tyson, J.F., Stockwell, P.B. *Analyst* **1990**, *115*, 571.
Bysouth, S.R., Tyson, J.F. *Anal. Chim. Acta* **1992**, *258*, 55.
Cabrera, C., Madrid, Y., Cámara, C. *J. Anal. At. Spectrom.* **1994**, *9*, 1423.
Calatayud, J.M., García-Mateo, J.V. *Analyst* **1991**, *116*, 327.
Canada-Rudner, P., Cano-Ravon, J.M., García de Torres, A., Sánchez-Rojas, F. *Fresenius J. Anal. Chem.* **1995**, *352*, 615.
Cantarero, A., Gómez, M.M., Cámara, C., Palacios, M.A. *Anal. Chim. Acta* **1994**, *296*, 205.
Carbonell, V., Morales-Rubio, A., Salvador, A., de la Guardia, M., Burguera, J.L., Burguera, M. *J. Anal. At. Spectrom.* **1992**, *7*, 1085.
Carbonell, V., Salvador, A., de la Guardia, M. *Fresenius J. Anal. Chem.* **1992**, *342*, 529.
Caroli, S., Alimonti, A., Petrucci, F., Horvath, Z. *Anal. Chim. Acta* **1991**, *248*, 241.
Cespón-Romero, R.M., Yebra-Biurrun, M.C., Bermejo-Barrera, M.P. *Anal. Chim. Acta* **1996**, *327*, 37.
Chen, H.W., Xu, S.K., Fang, Z.L. *Anal. Chim. Acta* **1994**, *298*, 167.
Chen, H.W., Xu, S.K., Fang, Z.L. *J. Anal. At. Spectrom.* **1995**, *10*, 533.
Cobo-Fernández, M.G., Palacios, M.A., Cámara, C. *Anal. Chim. Acta* **1993**, *283*, 386.
Cobo-Fernández, M.G., Palacios, M.A., Cámara, C., Quevauviller, P. *Quim. Anal.* **1995**, *14*, 169.
Coetzee, P.P., Talijaard, I., de Beer, H. *Fresenius J. Anal. Chem.* **1990**, *336*, 201.
Cox, A.G., McLeod, C.W. *Mikrochim. Acta* **1992**, *109*, 161.
Dadfarnia, S., Green, I., McLeod, C.W. *Anal. Proc. (London)* **1994**, *31*, 61.
de Andrade, J.C., Bueno, M.I.M.S. *Spectrochim. Acta* **1994**, *49B*, 787.
de la Guardia, M., Morales-Rubio, A., Carbonell, V., Salvador, A., Burguera, J.L., Burguera, M. *Fresenius J. Anal. Chem.* **1993**, *345*, 579.
Debrah, E., Tyson, J.F., Hinds, M.W. *Talanta* **1992**, 39, 1525.
Di, P., Davey, D.E. *Talanta* **1995**, *42*, 685.
Di, P., Davey, D.E. *Talanta* **1995**, *42*, 1081.
Ding, W.W., Sturgeon, R.E. *J. Anal. At. Spectrom.* **1996**, *11*, 421.
Dolan, S.P., Sinex, S.A., Capar, S.G., Montaser, A., Clifford, R.H. *Anal. Chem.* **1991**, *63*, 2539.
Eisman, M., Gallego, M., Valcárcel, M. *J. Pharm. Biomed. Anal.* **1994**, *12*, 179.
Elmahadi, H.A.M., Greenway, G.M. *J. Anal. At. Spectrom.* **1991**, *6*, 643.

Elmahadi, H.A.M., Greenway, G.M. *Microchem. J.* **1996**, *53*, 188.
Elmahadi, H.A.M., Greenway, G.M. *J. Anal. At. Spectrom.* **1994**, *9*, 547.
Elmahadi, H.A.M., Greenway, G.M. *J. Anal. At. Spectrom.* **1993**, *8*, 1011.
Elsholz, O. *Fresenius J. Anal. Chem.* **1996**, *355*, 295.
Erber, D., Quick, L., Winter, F., Roth, J., Cammann, K. *Fresenius J. Anal. Chem.* **1994**, *349*, 502.
Esmadi, F.T., Kharoaf, M.A., Attiyat, A.S. *Talanta* **1990**, *37*, 1123.
Esmadi, F.T., Khasawneh, I.M., Kharoaf, M.A. *J. Flow Injection Anal.* **1995**, *12*, 35.
Esmadi, F.T., Attiyat, A.S. *Anal. Sci.* **1994**, *10*, 687.
Fairman, B., Sanz-Medel, A., Jones, P. *J. Anal. At. Spectrom.* **1995**, *10*, 281.
Fang, Z.L., Tao, G.H., Xu, S.K., Liu, X.Z., Wang, J. *Microchem. J.* **1996**, *53*, 42.
Fang, Z., Tao, G. *Fresenius J. Anal. Chem.* **1996**, *355*, 576.
Fang, Z.L., Hu, S.K., Tao, G.H. *J. Anal. At. Spectrom.* **1996**, *11*, 1.
Fang, Z.L., Xu, S.K., Bai, X.S. *Anal. Chim. Acta* **1996**, *326*, 49.
Fang, Z., Guo, T., Welz, B. *Talanta* **1991**, *38*, 613.
Fang, Z., Welz, B., Sperling, M. *Anal. Chem.* **1993**, *65*, 1682.
Fang, Z., Sun, L., Hansen, E.H., Olesen, J.E., Henriksen, L.M. *Talanta* **1992**, *39*, 383.
Fang, Z., Dong, L., Xu, S. *J. Anal. At. Spectrom.* **1992**, *7*, 293.
Fang, Z. *Flow-Injection Atomic-Absorption Spectrometry*, John Wiley: Chichester, W. Sussex, UK, 1995, p. 240.
Fang, Z., Dong, L. *J. Anal. At. Spectrom.* **1992**, *7*, 439.
Fang, Z.L., Sperling, M., Welz, B. *Anal. Chim. Acta* **1992**, *269*, 9.
Fang, Z.L., Xu, S.K., Dong, L.P., Li, W.Q. *Talanta* **1994**, *41*, 2165.
Fang, Z. *Spectrochim. Acta Rev.* **1991**, *14*, 235.
Ferreira, A.M.R., Rangel, A.O.S.S., Lima, J.L.F.C. *Commun. Soil Sci. Plant. Anal.* **1995**, *26*, 183.
Freire dos Reis, B., Fernanda-Gine, M., Jose-Krug, F., Bergamin-Filho, H. *J. Anal. At. Spectrom.* **1992**, *7*, 865.
Gallego, M., Valcárcel, M. *Mikrochim. Acta* **1991**, *III*, 163.
García, M.F., García, R.P., García, N.B., Sanz-Medel, A. *Talanta* **1994**, *41*, 1833.
Garrido, J.M.P.J., Lapa, R.A.S., Lima, J.L.F.C., Delerue-Matos, C., Santos, J.L.M. *J. Autom. Chem.* **1996**, *18*, 17.
Gine, M.F., Reis, B.F., Krug, F.J., Jacintho, A.O., Bergamin, H., filho, Zagatto, E.A.G. *ICP-Inf Newsl.* **1994**, *20*, 413.
Gluodenis, T.J., jun., Tyson, J.F. *J. Anal. At. Spectrom.* **1993**, *8*, 697.
Gluodenis, T.J., jun., Tyson, J.F. *J. Anal. At. Spectrom.* **1992**, *7*, 301.
Gómez, M.M., McLeod, C.W. *J. Anal. At. Spectrom.* **1993**, *8*, 461.
Gómez-Gómez, M.M., Hidalgo-García, M.M. *Analyst* **1995**, *120*, 1911.
Guo, T., Baasner, J., Gradl, M., Kistner, A. *Anal. Chim. Acta* **1996**, *320*, 171.
Guo, T., Baasner, J. *Talanta* **1993**, *40*, 1927.
Hanna, C.P., Haigh, P.E., Tyson, J.F., McIntosh, S. *J. Anal. At. Spectrom.* **1993**, *8*, 585.
Haswell, S.J., Barclay, D. *Analyst* **1992**, *117*, 117.
Haug, H.O., Liao, Y.P. *Spectrochim. Acta* **1995**, *50B*, 1311.
Haug, H.O. *Spectrochim. Acta* **1996**, *51B*, 1425.
Huang, B. *Can. J Appl. Spectrosc.* **1994**, *39*, 117.
Iyer, C.S.P., Rao, T.P., Kartikeyan, T., Damodaran, A.D. *At. Spectrosc.* **1994**, *15*, 234.
Jiménez de Blas, O., González, S.V., Rodríguez, R.S., Mémdez, J.H. *J. AOAC Int.* **1994**, *77*, 441.
Jiménez de Blas, O., Pereda de Paz, J.L., Hernández-Méndez, J. *J. Anal. At. Spectrom.* **1990**, *5*, 693.
Jiménez, M.S., Mir, J.M., Castillo, J.R. *J. Anal. At. Spectrom.* **1993**, *8*, 665.
Jin, Q., Zhang, H.Q., Liang, F., Yang, W.J., Jin, Q.H. *J. Anal. At. Spectrom.* **1996**, *11*, 331.
Jinno, K., Mae, H., Fujimoto, C. *J. High Resolut. Chromatogr.* **1990**, *13*, 13.
Karlberg, B., Pacey, G.E. *Flow Injection Analysis: A Practical Guide*; Elsevier: Amsterdam, 1989.
Kasthurikrishnan, N., Koropchak, J.A. *Anal. Chem.* **1993**, *65*, 857.

Krekler, S., Frenzel, W., Schulze, G. *Anal. Chim. Acta* **1994**, *296*, 115.
Lahuerta-Zamora, L., Martínez-Calatayud, J. *Anal. Chim. Acta* **1995**, *300*, 143.
Lahuerta-Zamora, L., García-Mateo, J.V., Martínez-Calatayud, J. *Anal. Chim. Acta* **1992**, *265*, 81.
Lapa, R.A.S., Lima, J.L.F.C., Santos, J.L.M. *Food. Chem.* **1996**, *55*, 397.
Laredo-Ortiz, S., García-Mateo, J., Martínez-Calatayud, J. *Microchem. J.* **1993**, *48*, 112.
Larraya, A., Cobo-Fernández, M.G., Palacio, M.A. *Fresenius J. Anal. Chem.* **1994**, *350*, 667.
Li, Z., McIntosh, S., Slavin, W. *Anal. Proc. (London)* **1992**, *29*, 438.
Liang, Y.Z., Yin, N.W. *At. Spectrosc.* **1995**, *16*, 243.
Lima, R., Leandro, K.C., Santelli, R.E. *Talanta* **1996**, *43*, 977.
Lima, J.L.F.C., Rangel, A.O.S.S., Souto, M.R.S. *Anal. Sci.* **1996**, *12*, 81.
Lin, Y., Wang, X., Yuan, D., Yang, P., Huang, B., Zhuang, Z. *J. Anal. At. Spectrom.* **1992**, *7*, 287.
Lin, S.L., Zheng, C.S., Yun, G.Z. *Talanta* **1995**, *42*, 921.
Liu, W.Z., Fang, Z.L. *Anal. Chim. Acta* **1995**, *316*, 329.
Lofty, D. *Lab. Equip. Dig.* **1992**, *30*, 13.
López-García, I., Arroyo-Cortez, J., Hernández-Córdoba, M. *J. Anal. At. Spectrom.* **1992**, *7*, 1291.
López-García, I., Viñas, P., Campillo, N., Hernández-Córdoba, M. *Anal. Chim. Acta* **1995**, *308*, 85.
López-García, I., Ortiz-Sobejano, F., Hernández-Córdoba, M. *Analyst* **1991**, *116*, 831.
López-García, I., Viñas, P., Hernández-Córdoba, M. *J. Anal. At. Spectrom.* **1994**, *9*, 1167.
López-García, I., Viñas, P., Campillo, N., Hernández-Córdoba, M. *Fresenius J. Anal. Chem.* **1996**, *355*, 57.
López-Gonzalvez, M.A., Milagros-Gómez, M., Cámara, C., Palacios, M.A. *Mikrochim. Acta* **1995**, *120*, 301.
Luque de Castro, M.D., Papaefstathiou, I. *Trends Anal. Chem.* **1998**, *17*, 41.
Luque de Castro, M.D., Tena, M.T. *Talanta* **1993**, *40*, 21.
Luque de Castro, M.D., Tena, M.T. *Talanta* **1995**, *42*, 151.
Luque de Castro, M.D. *Trends in Anal. Chem.* **1992**, *11*, 149.
Ma, R., Adams, F. *Anal. Chim. Acta* **1995**, *317*, 215.
Ma, R., Van-Mol, W., Adams, F. *At. Spectrosc.* **1996**, *17*, 176.
Madrid, Y., Wu, M., Jin, Q.H., Hieftje, G.M. *Anal. Chim. Acta* **1993**, *277*, 1.
Manzoori, J.L., Miyazaki, A. *Anal. Chem.* **1990**, *62*, 2457.
Maquieira, A., Elmahadi, H., Puchades, R. *J. Anal. At. Spectrom.* **1996**, *11*, 99.
Maquieira, A., Elmahadi, H.A.M., Puchades, R. *Anal. Chem.* **1994**, *66*, 3632.
Marshall, G.D., Van-Staden, J.F. *J. Anal. At. Spectrom.* **1990**, *5*, 575.
Martínez-Avila, R., Carbonell, V., Salvador, A., de la Guardia, M. *Talanta* **1993**, *40*, 107.
Matousek de Abel de la Cruz, A., Burguera, J.L., Burguera, M., Wasim, S., Rivas, C. *Fresenius J. Anal. Chem.* **1996**, *354*, 184.
Matousek de Abel de la Cruz, A., Burguera, J.L., Burguera, M., Rivas, C. *Talanta* **1995**, *42*, 701.
Mattos, I.L., Luque de Castro, M.D., Valcárcel, M. *Talanta* **1995**, *42*, 755.
Mattos, I.L., Luque de Castro, M.D. *Anal. Chim. Acta* **1994**, *298*, 159.
Matusiewicz, H., Sturgeon, R.E. *Spectrochim. Acta* **1996**, *51B*, 377.
Mazzucotelli, A., Rivaro, P. *Ann. Chim.* **1993**, *83*, 105.
McIntosh, S. *At. Spectrosc.* **1993**, *14*, 47.
McIntosh, S., Baasner, J., Grosser, Z.A., Hanna, C. *At. Spectrosc.* **1994**, *15*, 161.
Memon, M.A., Wang, X.R., Huang, B.L. *At. Spectrosc.* **1993**, *14*, 99.
Menéndez-García, A., Pérez-Rodríguez, M.C., Sánchez-Uria, J.E., Sanz-Medel, A. *Fresenius J. Anal. Chem.* **1995**, *353*, 128.
Mentasti, E. *Ann. Chim. (Rome)* **1995**, *85*, 443.
Milburn, J.W. *At. Spectrosc.* **1996**, *17*, 9.
Montero, R., Gallego, M., Valcárcel, M. *Talanta* **1990**, *37*, 1129.
Montero, R., Gallego, M., Valcárcel, M. *Anal. Chim. Acta* **1990**, *234*, 433.
Murakami, K., Okamoto, Y., Kumamaru, T. *J. Flow Injection Anal.* **1992**, *9*, 195.

Naghmush, A.M., Trojanowicz, M., Olbrych-Sleszynska, E. *J. Anal. At. Spectrom.* **1992**, *7*, 323.
Naghmush, A.M., Pryzynska, K., Trojanowicz, M. *Talanta* **1995**, *42*, 851.
Narasaki, H., Cao, J.I. *Microchem. J.* **1996**, *53*, 18.
Nielsen, S., Sloth, J.J., Hansen, E.H. *Analyst* **1996**, *121*, 31.
Nixon, D.E., Mussmann, G.V., Moyer, T.P. *J. Anal. Toxicol.* **1996**, *20*, 17.
Offley, S.G., Seare, N.J., Tyson, J.F., Kibble, H.A.B. *Anal. Proc.* **1991**, *28*, 18.
Olbrych-Sleszynska, E., Brajter, K., Matuszewski, W. *Talanta* **1992**, *39*, 779.
Ornemark, U., Olin, A. *Talanta* **1994**, *41*, 67.
Pei, S., Fang, Z.L. *Anal. Chim. Acta* **1994**, *294*, 185.
Peng, X., Jiang, Z., Zen, Y. *Anal. Chim. Acta* **1993**, *283*, 887.
Pitts, L., Worsfold, P.J., Hill, S.J. *Analyst* **1994**, *119*, 2785.
Prinzing, U., Ogbomo, I., Lehn, C., Schmidt, H.L. *Sensors Actuators* **1990**, *B1*, 542.
Purohit, R., Devi, S. *Talanta* **1991**, *38*, 753.
Purohit, R., Devi, S. *Analyst* **1991**, *116*, 825.
Pyrzynska, K. *J. Anal. At. Spectrom.* **1994**, *9*, 801.
Qi, W.Y., Wu, X., Zhou, C., Wu, H.Z., Gao, Y.Q. *Anal. Chim. Acta* **1992**, *270*, 205.
Rivas, G.A., Martínez-Calatayud, J. *Talanta* **1995**, *42*, 1285.
Rodríguez, D., Fernández, P., Pérez-Conde, C., Gutierrez, A. *Fresenius J. Anal. Chem.* **1994**, 442.
Ruchti, B., Schramm, C., Kubitschko, S., Neidhart, B. *Fresenius J. Anal. Chem.* **1992**, *342*, 822.
Ruede, T.R., Puchelt, H. *Fresenius J. Anal. Chem.* **1994**, *350*, 44.
Ruzicka, J., Hansen, E.H. *Flow Injection Analysis*; Wiley: New York, 1988.
Salacinski, H.J., Riby, P.G., Haswell, S.J. *Anal. Chim. Acta* **1992**, *269*, 1.
Santelli, R., Gallego, M., Valcárcel, M. *Talanta* **1991**, *38*, 1241.
Schaumloeffel, D., Neidhart, B. *Fresenius J. Anal. Chem.* **1996**, *354*, 866.
Scheneider, C.A., Schulze, H., Baasner, J., McIntosh, S., Hanna, C. *Am. Lab.* **1994**, *26*, 20.
Shah, A., Devi, S. *Anal. Chim. Acta* **1990**, *236*, 469.
Silva, E.C., Araujo, M.C.U., Honorato, R.S., Costa-Lima, J.L.F., Zagatto, E.A.G., Boscolo-Brienza, S.M. *Anal. Chim. Acta* **1996**, *319*, 153.
Sneddon, J. *Advances in Atomic Spectroscopy*; JAI Press: Stamford, CT, 1992, Vol. 1, p. 238.
Sperling, M., Yin, X., Welz, B. *J. Anal. At. Spectrom.* **1991**, *6*, 295.
Sperling, M., Yin, X., Welz, B. *Spectrochim. Acta* **1991**, *46B*, 1789.
Sperling, M., Yin, X., Welz, B. *J. Anal. At. Spectrom.* **1991**, *6*, 615.
Sperling, M., Yin, X., Welz, B. *Analyst* **1992**, *117*, 629.
Sperling, M., Xu, S., Welz, B. *Anal. Chem.* **1992**, *64*, 3101.
Sperling, M., Koscielniak, P., Welz, B. *Anal. Chim. Acta* **1992**, *261*, 115.
Sun, X.S., Welz, B., Sperling, M. *Fenxi Kexue Xuebao* **1997**, *13*, 34.
Sung, Y.H., Liu, Z.S., Huang, S.D. *J. Anal. At. Spectrom.* **1997**, *12*, 841.
Tao, G.H., Fang, Z.L. *J. Anal. At. Spectrom.* **1993**, *8*, 577.
Tao, G.H., Fang, Z.L. *At. Spectrosc.* **1996**, *17*, 22.
Tao, G.H., Fang, Z.L. *Spectrochim. Acta* **1995**, *50*, 1747.
Tao, G., Fang, Z. *Talanta* **1995**, *42*, 375.
Taylor, M.J.C., Barnes, D.E., Marshall, G.D. *Anal. Chim. Acta* **1992**, *265*, 71.
Torres, P., Ballesteros, E., Luque de Castro, M.D. *Anal. Chim. Acta* **1995**, *308*, 371.
Trojanowicz, M., Olbrych-Sleszynska, E. *Chem. Anal. (Warsaw)* **1992**, *37*, 111.
Trojanowicz, M., Pyrzynska, K. *Anal. Chim. Acta* **1994**, *287*, 247.
Tsalev, D.L., Dulivo, A., Lampugnani, L., Di Marco, M., Zamboni, R. *J. Anal. At. Spectrom.* **1996**, *11*, 989.
Tyson, J.F. *Anal. Chim. Acta* **1990**, *234*, 3.
Tyson, J.F., Bysouth, S.R., Grzeszczyk, E.A., Debrah, E. *Anal. Chim. Acta* **1992**, *261*, 75.
Tyson, J.F., Offley, S.G., Seare, N.J., Kibble, H.A.B., Fellows, C. *J. Anal. At. Spectrom.* **1992**, *7*, 315.
Tyson, J.F. *Spectrochim. Acta Rev.* **1991**, *14*, 169.

Valcárcel, M., Luque de Castro, M.D. *Fresenius J. Anal. Chem.* **1990**, *337*, 662.
Valcárcel, M., Luque de Castro, M.D. *Flow Injection Analysis: Principles and Applications*; Ellis Horwood: Chichester, 1987.
Valcárcel, M., Luque de Castro, M.D. *Non-Chromatographic Continuous Separation Techniques*; Royal Soc. Chem.: Cambridge, 1991.
Valdés-Hevia y Temprano, M.C., Pérez-Parajón, J., Díaz-Garcia, M.E., Sanz-Medel, A. *Analyst* **1991**, *116*, 1141.
Van-Staden, J.F., Van-Rensburg, A. *Analyst* **1990**, *115*, 605.
Van-Staden, J.F., Van-Rensburg, A. *Fresenius J. Anal. Chem.* **1990**, *337*, 393.
Van-Staden, J.F., Hattingh, C.J. *Anal. Chim. Acta* **1995**, *308*, 214.
Van-Staden, J.F. *Talanta* **1991**, *38*, 1033.
Viñas, P., Campillo, N., López-García, I., Hernández-Córdoba, M. *Anal. Chim. Acta* **1993**, *283*, 393.
Wabner, C.L., Sears, D.C. *At. Spectrosc.* **1996**, *17*, 119.
Walcerz, M., Garbos, S., Bulska, E., Hulanicki, A. *Fresenius J. Anal. Chem.* **1994**, *350*, 662.
Walter, S., Aleboyeh, A. *Fresenius J. Anal. Chem.* **1996**, *355*, 687.
Wang, H.N., Chen, Y., Wang, J. *Microchem. J.* **1996**, *53*, 88.
Wang, X., Zhuang, Z., Yang, P., Huang, B. *Microchem. J.* **1995**, *51*, 88.
Wei-Min, R., Hansen, E.H. *Chem. Anal. (Warsaw)* **1995**, *40*, 361.
Welz, B. *Microchem. J.* **1992**, *45*, 163.
Welz, B., Tsalev, D.L., Sperling, M. *Anal. Chim. Acta* **1992**, *261*, 91.
Welz, B., Sperling, M., Fang. *Fresenius J. Anal. Chem.* **1990**, *337*, 135.
Welz, B., Yin, X., Sperling, M. *Anal. Chim. Acta* **1992**, *261*, 477.
Wentzell, P.D., Sundin, N.G., Hogeboom, C. *Analyst* **1994**, *119*, 1403.
Wu, M., Ensman, R., Hieftje, G.M. *Appl. Spectrosc.* **1994**, *48*, 448.
Xu, S.K., Fang, Z.L. *Microchem. J.* **1994**, *50*, 145.
Xu, S., Sun, L., Fang, Z. *Anal. Chim. Acta* **1991**, *245*, 7.
Xu, S.K., Sperling, M., Welz, B. *Fresenius J. Anal. Chem.* **1992**, *344*, 535.
Xu, S., Fang, Z. *Microchem. J.* **1995**, *51*, 360.
Yamada, K., McLeod, C.W., Kujirai, O., Okochi, H. *J. Anal. At. Spectrom.* **1992**, *7*, 661.
Yan, X.P., Mol, V.M., Adams, F. *Analyst* **1996**, *121*, 1061.
Yang, C.L., Zhuang, Z.X., Wang, X.R., Qin, S.D., Yang, P.Y. *At. Spectrosc.* **1994**, *15*, 135.
Ye, D.M., Zhang, H.Q., Jin, Q.H. *Talanta* **1996**, *43*, 535.
Yebra, M.C., Gallego, M., Valcárcel, M. *Anal. Chim. Acta* **1993**, *276*, 385.
Yebra, M.C., Gallego, M., Valcárcel, M. *Anal. Chim. Acta* **1995**, *308*, 275.
Yebra, M.C., Gallego, M., Valcárcel, M. *Anal. Chim. Acta* **1995**, *308*, 357.
Yuan, D., Wang, X., Yang, P., Huang, B. *Anal. Chim. Acta* **1991**, *243*, 65.
Zagatto, E.A.G., Gine, M.F., Fernandes, E.A.N., Reis, B.F., Krug, F.J. *Anal. Chim. Acta* **1985**, *173*, 289.
Zou, H.F., Xu, S.K., Fang, Z.L. *At. Spectrosc.* **1996**, *17*, 112.

DETERMINATION OF MERCURY BY ATOMIC SPECTROSCOPY:
APPLICATION TO FISH

Joseph Sneddon and Mary Gay Heagler

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ABSTRACT

The use of various atomic spectroscopic techniques including cold-vapor atomic absorption spectrometry, cold-vapor atomic fluorescence spectrometry, electrothermal atomization atomic absorption spectrometry, inductively coupled plasma–mass spectroscopy, and inductively coupled plasma–atomic emission spectrometry for the determination of mercury is described. A short overview of the history, current uses, and toxicity, is described. The application of these various atomic spectroscopic techniques to the determination of mercury in fish is thoroughly detailed.

I. INTRODUCTION

The known and well-documented toxicity of various forms of mercury has required its determination in a wide variety of environmental matrices including air, soils, rocks, plants, waters, and fish. The low concentrations to be determined require an analytical technique which is capable of accurate and precise determination in these complex matrices. Atomic spectroscopic methods have been developed and widely used and accepted for mercury determination. This chapter describes the use of atomic spectroscopic methods for the determination of mercury, in particular its application to fish.

The interaction of energy with matter produce three closely related, yet separate phenomena; namely atomic absorption, atomic emission, and atomic fluorescence spectrometry. A closely related technique is that of plasma source–mass spectrometry, in particular inductively coupled plasma–mass spectrometry (ICP-MS). These techniques are collectively known as atomic spectroscopy or spectrochemical analysis techniques. They are widely used for the trace and ultratrace determination of metals in many samples. A detailed description of these techniques as they apply to mercury (or any other metal) determination is beyond the scope of this chapter. There are numerous books (Robinson, 1996; Ingle and Crouch, 1988; Lajunen, 1992; Sneddon, 1990; Haswell, 1992; Butcher and Sneddon, 1997; Montaser and Golightly, 1992) which detail the theory, instrumentation, method development, and applications of atomic spectroscopy. The reader is referred to these texts for detailed information on these areas of atomic spectroscopy.

II. HISTORICAL AND CURRENT USES OF MERCURY

A. Mercury in the Environment

Mercury is the only metal that is present in its elemental state as a liquid at room temperature. As a result, mercury has a tendency to vaporize easily, to have a strong affinity to form ligands, and to be easily absorbed onto surfaces. These characteristics cause mercury to be found in rocks, soils, air, and waters; in general mercury is widely distributed throughout the environment (Faust and Aly, 1981).

Mercury is introduced to the environment (and the mercury biogeochemical cycle) as a result of emissions from natural and anthropogenic sources. Natural sources of mercury include the volatilization of mercury from mercury-containing ore deposits, soil surfaces, and the release of mercury from volcanic eruptions. Anthropogenic sources of mercury include emissions from the burning of wood and fossil fuels, emission from chlor-alkali plants, and the use of mercury as a fungicide in agriculture and paints (Porcella, 1994).

Once mercury is released into the environment, the biogeochemical cycling of mercury leads to the accumulation of mercury in organisms in general and aquatic organisms in particular. The behavior and accumulation of mercury in the environment and in organisms is complex since extremely small concentrations or quantities of mercury in the atmosphere and water are the result of chemically and biologically mediated reactions (Fitzgerald, 1995).

The mercury cycle begins with the emission of mercury into the atmosphere from either natural or anthropogenic sources, with anthropogenic sources exceeding natural sources (Fitzgerald, 1995). Once emitted into the atmosphere, mercury deposition will occur on either a local or global scale. Local atmospheric deposition is mostly particulate mercury from flue emissions and soluble, reactive mercury (Hg(II)), while global deposition is predominantly elemental mercury (Hg^0) (Fitzgerald, 1995). The residence time in the atmosphere for Hg^0 can be as long as 3 years as compared to a few days for Hg(II) (WHO, 1991). Mercury in the atmosphere will be deposited either on land or into water, the largest component being oceanic deposition. Deposition on the land is the ultimate sink for mercury since the mercury is slowly mobilized and then enters the aquatic environment (Fitzgerald, 1995). Once in the aquatic environment, elemental mercury may be given off to the atmosphere or may undergo biological/chemical reactions within the aquatic environment.

Within the aquatic environment, mercury will exist as Hg^0, Hg(II), or in methylated forms. Fitzgerald (1995) has hypothesized that in the aquatic environment, the chemical and biological processes compete with each other for the reactant mercury (Hg(II)). Some of the mercury will be "removed" from the system by being incorporated into the sediments in the form of particulate mercury. However, in the sediments the inorganic forms of mercury may be converted into methylated forms through microbial action. Methylation generally occurs in the first few centimeters of the sediment but will vary depending on the sediment/water characteristics (Gilmore, 1995). The methylated mercury can remain tied up in the sediments or may be released into the water column. Once the mercury has been methylated, it is more available to be accumulated by aquatic organisms. However, all forms of mercury may be accumulated by aquatic organisms.

Mercury is accumulated in the tissues of aquatic organisms since the rate of accumulation tends to be greater than the rate of depuration. Most of the mercury that fish accumulate is a result of their diet rather than through direct contact with mercury. Mercury in the aquatic ecosystem will biomagnify: the concentration of

mercury will increase with each trophic level of the food chain/web. Plankton and zooplankton will accumulate mercury directly from the water and will in turn be food for small fish. The small fish will then be eaten by larger fish until the fish at the top of the food chain will have the highest mercury concentrations. For example, Becker and Bigham (1995) measured the methylmercury concentrations in the aquatic food web of a lake. The water had a methylmercury concentration of 0.0003 μg/kg. The first trophic level of the food web contained benthic macroinvertabrates and phytoplankton with measured methylmercury concentrations of 25 and 32 μg/kg, respectively. The second trophic level of the food web included zooplankton (260 μg/kg), plankivores (680 μg/kg), and benthivores (480 μg/kg): these organisms were feeding on the organism in the first trophic level. The third trophic level consists of piscivores (organisms which feed on fish) and had the highest concentration of methylmercury (1100 μg/kg).

B. Mercury Toxicity

There are three forms of mercury (elemental, inorganic, and organic) present in the environment and each one has its own toxic effects. The toxic effects of mercury are attributed to the cationic form of mercury, while the solubility, biotransformation, and the distribution of mercury in different tissues is a result of the valence state and anionic component of mercury (Berlin, 1986). Long-term exposure to elemental mercury, in its vapor form, results in neurasthenia as well as tremors; an enlarged thyroid gland; an erratic pulse rate; tremors in the fingers, eyelids, and lips progressing to tremors throughout the entire body; changes in personality and behavior; loss of memory; and hallucinations (Goyer, 1996).

The threshold limit value (TLV) for elemental mercury is 0.05 mg/m^3 in air and the LD_{50} for mammals is 1.5 mg/kg of bodyweight.

The toxicity of inorganic mercury varies depending on the inorganic compound. Mercuric compounds generally causes abdominal cramps, bloody diarrhea, kidney failure, and death (Goyer, 1996). Workers that have been exposed to inorganic mercury as mercuric chloride will develop proteinuria, which will reverse when the exposure has ceased (Goyer, 1996). Mercurous compounds are less toxic than mercuric compounds.

The most notable usage of mercurous mercury has been in the form of calomel, which has been used as a teething powder for children and is responsible for acrodynia (pink disease) in children (Goyer, 1996). Pink disease is thought to be a hypersensitivity response in the skin as a result of contact with mercury. The symptoms include the child developing a fever, the development of a pink rash, and the swelling of the spleen, lymph nodes, and the fingers (Goyer, 1996).

Meythlmercury, the most toxic form of mercury, is a potent neurotoxin in adults. Most of what is known and understood about methylmercury toxicity has been learned by a study of the epidemic poisoning in Japan and Iraq. In adults, symptoms of methylmercury poisoning include a numbness and tingling around the mouth,

lips, fingertips, and toes; a lack of muscle control resulting in an awkward, stumbling walk; difficulty in swallowing and in speaking; an inability to concentrate and a general feeling of weakness and fatigue; a loss of vision and hearing; muscle tremors; and finally death (Goyer, 1996). Bakir et al. (1973) described the epidemic of methylmercury poisoning in Iraq in 1972. The researchers determined the threshold concentration (the concentration at which symptoms of mercury poisoning are detectable) by measuring methylmercury concentrations in the blood of patients hospitalized with symptoms of mercury poisoning. Bakir et al. (1973) indicated that the onset of paresthesia occurred at a threshold body burden of approximately 25 mg of methylmercury while the thresholds for axtia, dysarthria, deafness, and death were 55, 90, 170, and 200 mg of mercury as methylmercury.

The exposure of pregnant woman to mercury is also of great concern since all forms of mercury have the ability to cross the placenta and affect the developing fetus (Goyer, 1996). In the developing fetus, high concentrations of mercury result in changes in the structure and synthesis of the DNA and RNA in the developing brain (Goyer, 1996), which can lead to mental retardation with cerebral palsy. Bakir et al. (1973) found that during the Iraq mercury poisoning epidemic, the methylmercury concentrations in the blood of newborn babies was greater than or equal to the mercury concentration of the mother. In addition, methylmercury will be present in the mother's milk, further contaminating the child while nursing (Goyer, 1996: Bakir et al., 1973).

C. Fish Collection, Preservation, and Preparation

Fish collected for mercury determination can be collected through a variety of techniques such as hook and line, electroshocking, and trapping. Once collected, the fish should be placed in a plastic bag (if size permits) and stored on ice for 24 hours (Heagler et al., 1996). Once the fish reaches the laboratory, the fish should be frozen either before or after dissecting tissue samples. If the samples are dissected prior to freezing, the samples should be collected in duplicate (Csuros, 1994). Any instruments used for dissecting the fish should be stainless steel and rinsed with deionized water prior to use.

Prior to analysis, the fish needs to be digested and researchers have investigated and used several different methods to digest fish tissue. Researchers have used a nitric acid/sulfuric acid combination to digest tissues samples prior to mercury analysis. If the fatty tissue remains in the digest after digestion, perchloric acid or hydrogen peroxide are used to further digest the tissue. Modifications of the digestion procedure of Hatch and Ott (1968) and of Kivalo et al. (1974) are commonly used. Hatch and Ott (1968) gently heated the sample in a round bottom flask after the addition of nitric and sulfuric acids. Kivalo et al. (1974) added nitric and sulfuric acids to the tissue sample and then refluxed the sample using Allihan condensors. Both methods produce digests that can be analyzed by atomic spectroscopic methods. Recently Tinggi and Craven (1996) have shown that microwave

digestion procedures can be as effective as traditional digestion techniques. The microwave techniques allow greater numbers of samples to be processed in less time with less contamination.

Results are reported on a wet basis. To report on a dry-weight basis, a subset of the tissue to be analyzed can be oven dried and a wet-to-dry weight ratio calculated (Heagler et al. 1993). The ratio can then be used to report the mercury concentration in terms of dry weight.

D. Mercury in Fish

Mercury has been determined in a wide variety of environmental samples including natural waters, seawaters (Bermejo-Barrera et al., 1997), sediments (Woller et al., 1997), and air (Karanassios et al., 1994). This section will report only on the determination of mercury in fish.

Methylmercury, the most toxic form of mercury, has been found to occur in both freshwater and saltwater fish. This is a public health concern because methylmercury is a potent neurotoxin in adults. The major source of methlymercury exposure for the general public is from the consumption of contaminated fish (Goyer, 1996). In order to protect the public from mercury-contaminated fish, "action levels" have been established. If the mercury concentration in fish exceeds the action level, then action is taken to protect the public either by notifying the public about restricting their consumption of certain types of fish, closing waters to fishing, or by restricting the sale of fish.

In the United States, two federal agencies have established action levels to protect the public from mercury-contaminated fish: the Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA).

The EPA has set an action level of 0.5 μg/g for mercury and is attempting to protect subsistence fisherman, sports fisherman, and the general public from mercury-contaminated fish. If the EPA measures mercury concentrations in fish above the action level, fish advisories will be issued and the public notified. The advisories can range from advising people to limit their consumption of fish to advising them not to eat a certain species of fish. In addition, young children and pregnant and nursing women are often advised to prohibit consumption of contaminated fish.

The FDA has set an action level of 1.0 μg/g mercury as an action level for commercial fish (fish commercially bought through interstate commerce). If the mercury concentrations of the fish exceed the action level, the FDA can prohibit the sale of the fish.

A literature survey of mercury concentrations in fish was undertaken and shown in Table 1. Mercury concentrations were measured in fish from waters with known or suspected mercury contamination. If the mercury concentrations of the fish and shellfish listed in Table 1 are compared to the mercury action levels, 24 of the fish exceed the FDA action level of 1.0 μg/g and 11 exceed the EPA action levels of 0.5

Table 1. Mercury Concentrations in Fish and Seafood

Species	*Tissue Type*	*Mercury Concentration*	*Analytical Method*[a]	*Reference*
Rainbow trout (*Salmo gairdneri*)	Lateral muscle	1.1–1.4 μg/g	CVAAS	Phyllips and Buhler, 1980
Cod *Gadus morhua* L.)	Tissue	0.08 mg/g	Hydride generation and AAS	Staveland et al., 1993
Flounder (*Platichthys flesus* L.)	Tissue	0.15 mg/g		
Northern pike (*Esox lucius*)	Muscle	0.33–1.21 μg/g wet wt	CVAAS	Smith et al., 1975
Large lake trout (*Salvelinus namaycush*)	Muscle	0.12–1.21 μg/g wet wt		
Yellow walleye (*Stizostedion v. vitreum*)	Muscle	0.78 μg/g wet wt		
Brook trout (*Salvelinus fontinalis*)	Muscle	0.12–0.57 μg/g wet wt		
Lake whitefish (*Coregonus clupeaformis*)	Muscle	0.06–0.22 μg/g wet wt		
Gray mullet (*Mugil cephalus*)	Muscle	$\bar{x} \pm$ SD 0.03 ± 0.12 μg/g	CVAAS	Reimer and Reimer, 1975
Shrimp (*Penaeus aztecus*)		0.06 ± 0.12 μg/g		
Shrimp (*Penaeus stylirostris*)		0.09 ± 0.12 μg/g		
Shrimp (*Penaeus californiensis*)		0.12 ± 0.10 μg/g		
Oyster (*Crassostrea virginica*)		0.09 ± 0.01 μg/g		
Mollusc (*Codakia orbicularis*)		0.09 ± 0.06 μg/g		
Pacific blue marlin (*Makaira nigricans*)	Muscle	Total Hg: $\bar{x}$ = 2.06 μg/g Organic Hg: $\bar{x}$ = 0.36 μg/g	AAS with a Manning vapor chamber	Shultz et al., 1976
Large-mouth bass (*Micropterus salmoides*)	Muscle	0.34–4.49 μg/g wet wt.	AAS	Abernathy and Cumbie, 1976
15 freshwater species of fish (alewife, brown bullhead, carp, freshwater drum, gizzard shad, golden shiner, lake whitefish, largemouth bass, longnose sucker, pumkinseed, rainbow smelt, rock bass, white bass, white sucker, and yellow perch)	Muscle	0.01–0.67 μg/g wet wt.	CVAAS	Brown and Chow, 1976

Table 1. (Continued)

Species	*Tissue Type*	*Mercury Concentration*	*Analytical Method*[a]	*Reference*
53 species of marine fish and molluscs (included *Aristeomorpha foliacea, Arnoglossus* sp., *Eledon* sp., *Etmopterus spinax, Solea vulgaris, Sphurema sphurema,* etc.)		Trace–2.50 μg/g	Flameless AAS	Caviglia and Cugurra, 1978
Crab (*Callinectes sapidus*)	Tissue from leg and abdominal areas	0.005 μg/g wet wt	Neutron activation	Guthrie et al., 1979
Oyster (*Crassostrea virginica*)	Meat	0.07 μg/g wet wt		
Clam (*Rangia cuneata*)	Meat	0.11 μg/g wet wt		
Cybium comersonii	Edible parts	0.07–0.56 μg/g	Flameless AAS	Parvaneh, 1979
Cybium guttatum		0.08–0.20 μg/g		
Lutjanus coccineus		0.08–0.48 μg/g		
Psettodes erimei		0.04–0.30 μg/g		
Euthynnus offinis (canned tuna fish)		0.20–0.44 μg/g		
Epinephenlus chlostigma (Val)	All fish were deboned and then homogenized	0.003–0.14 μg/g wet wt.	CVAAS	Babji et al., 1979
Plotosus anguillaris (Bloch)		0.04–0.12 μg/g wet wt.		
Sciaena russeli (Curvier)		0.05–0.12 μg/g wet wt.		
Sillago sihama (Forskal)		0.05–0.12 μg/g wet wt.		
Tachysurus maculatus (Thun)		0.02–0.15 μg/g wet wt.		
Upeneus sulphureus (Curvier)		0.05–0.12 μg/g wet wt.		
Shrimp (*Macrobrachium lanchesteri*)	Whole shrimp	neutron activation: 0.001–0.02 μg/g flameless AAS: 0.006–0.12 μg/g	Neutron activation and flameless AAS	Suckcharoen, 1980
Lake trout (*Salvelinus fontinalis*)	Muscle	0.10–1.11 μg/g wet wt.	Flameless AAS	Akielaszek and Haines, 1981
Brook trout (*Salvelinus fontinalis*)	Muscle	0.08–0.58 μg/g wet wt.		

Table 1. (Continued)

Species	*Tissue Type*	*Mercury Concentration*	*Analytical Method*[a]	*Reference*
Lake whitefish (*Coregonus clupeaformis*)	Muscle	0.30–2.17 μg/g wet wt.		
Burbot (*Lota lota*)	Muscle	0.35–1.29 μg/g wet wt.		
Rainbow smelt (*Osmerus mordax*)	Muscle	0.28–0.59 μg/g wet wt.		
Whiting (*Merluccius bilearis*)	Muscle (frozen)	0.4 ± 0.1 μg/g wet wt	CVAAS	Klusek and Heit, 1982
Mussel (*Mytilus edulis*)		0.11 ± 0.06 μg/g wet wt		
Oyster (*Crassostrea virginica*)	Whole body	0.0746 μg/g wet wt.	CVAAS	Lytle and Lytle, 1982
Lobsters (*Homarus americanus*)	Claw and tail muscle	0.08–0.50 μg/g	CVAAS	Roberts et al., 1982
Sacramento blackfish (*Orthodon microlepidotus*)	Muscle	0.80–1.92 μg/g wet wt.	CVAAS	Cooper, 1983
Carp (*Cyprinus carpio*)	Muscle	0.71–2.34 μg/g wet wt.		
Brown bullhead (*Ictalurus nebulosus*)	Muscle	0.95–1.09 μg/g wet wt.		
Yellow perch (*Perca flavescens*)	Muscle	0.23–2.83 μg/g wet wt.		
White catfish (*Ictalurus catus*)	Muscle	0.69–2.34 μg/g wet wt.		
Tahoe sucker (*Catostomus tahoensis*)	Muscle	0.65–1.64 μg/g wet wt.		
Channel catfish (*Ictalurus punctatus*)	Muscle	1.01–2.36 μg/g wet wt.		
White crappie (*Pomoxis annularis*)	Muscle	0.15–3.42 μg/g wet wt.		
White bass (*Morone chrysops*)	Muscle	0.97–3.95 μg/g wet wt.		
Crayfish (*Pacifastacus* sp.)	Tail muscle	0.57–5.72 μg/g wet wt.		
Green mussel (*Mytilus viridis*)	Whole body	0.011–0.848 μg/g wet wt.	Flameless AAS	Hutagalung, 1989
Walleye (*Stizostedion vitreum vitreum*)	Muscle	0.19–0.999 μg/g wet wt.	CVAAS	Gerstenberger et al., 1992
Oyster (*Saccostrea cucullata*)	Whole body	0.010–0.73 μg/g wet wt.	Flameless AAS	Peerzada et al., 1993
Oyster (*Saccostrea echinata*)	Whole body	0.016–0.125 μg/g wet wt.		
Cisco (*Coregonus albula*)	Muscle	0.21 ± 0.08 μg/g wet wt.	CVAAS	Frøslie et al., 1985
Brown trout (*Salmo trutta*)	Muscle	1.29 ± 0.44 μg/g wet wt.		
Smelt (*Omerus eperlanus*)	Muscle	0.3 ± 0.03 μg/g wet wt.		

Table 1. (Continued)

Species	*Tissue Type*	*Mercury Concentration*	*Analytical Method*[a]	*Reference*
Burbot (*Lota lota*)	Muscle	1.07 ± 0.53 μg/g wet wt.		
Pike (*Esox lucius*)	Muscle	1.12 ± 0.54 μg/g wet wt.		
Perch (*Perca fluviatilis*)	Muscle	0.50 ± 0.61 μg/g wet wt.		
Tilapa (*Tilapa mossambica*)	Muscle	0.01–0.14 ug/g dry wt.	CVAAS	Gutiérrez-Galindo, 1988
Freshwater clam (*Corbicula fluminea*)	Whole body	0.01–0.32 ug/g dry wt.		
Redfish (*Sebastes marinus* and *Sebastes mentella*)	Muscle	0.077 μg/g total Hg dry wt. 0.041 μg/g MeHg dry wt.	CVAAS	Joiris et al., 1994
Capelin (*Mallotus villosus*)	Muscle	0.073 μg/g total Hg dry wt. 0.027 μg/g MeHg dry wt.		
Haddock (*Melanogrammus aeglefinus*)	Muscle	0.067 μg/g total Hg dry wt. 0.041 μg/g MeHg dry wt.		
Mosquitofish (*Gambusia affinis*)	Whole body	0.226–0.786 μg/g wet wt.	CVAAS	Heagler et al., 1993
Blue crab (*Callinectes sapidus*)	Claw muscle	<0.01–5.07 μg/g wet wt.	CVAAS	Heagler, unpublished data, 1997
	Body muscle	<0.01–0.76 μg/g wet wt.		

Note: [a]CVAAS = cold-vapor atomic adsorption spectroscopy.

μg/g. The highest mercury concentrations were found in crayfish [*Pacifastucus sp.*; 0.57–5.72 μg/g) by Cooper (1983)] and in large-mouth bass [*Micropterus salmoides*; 0.34–4.49 μg/g) by Abernathy and Cumbie (1976)]. The lowest mercury concentrations were found in crabs [*Callinectes sapidus*: 0.005 μg/g by Guthrie et al. (1979)] and in shrimp [*Macrobrachium lonchesteri*: 0.001–0.210 μg/g by Suckcharoen (1980)].

As the survey included fish collected from mercury-contaminated waters as well as noncontaminated waters, a wide range of mercury concentrations in the fish was expected. The range of concentrations was greatest in the bass species, ranging from 0.34 to 3.95 μg/g. The least amount of variation occurred in oysters (*Crassostrea virginica*) with a concentration range of 0.07 to 0.09 μg/g.

III. ATOMIC SPECTROSCOPY TECHNIQUES FOR DETERMINING MERCURY

The direct determination of mercury by conventional flame atomic absorption, emission, or fluorescence spectrometry lacks the sensitivity, typically around 10–100 parts per million (ppm), for many applications including fish. Elemental mercury exhibits an appreciable vapor pressure, even at room temperature and the vapor is monoatomic. This results in a flame being unnecessary for mercury, provided the mercury in the sample matrix can be converted into its elemental form. This is the basis of the most widely used atomic spectroscopic techniques, namely the cold-vapor methods.

Flame atomic absorption spectrometry (FAAS), when combined with a dual "bent" tube atom trap for collection of mercury, resulted in a sensitivity of 0.0598 mg/L for 2 min collection and 0.0326 mg/L for 5 min collection (Ellis and Roberts, 1996). A number of tube coatings were investigated, and instrumental parameters of fuel flow tube height above the burner and percent obscuration of the tube by the light source were optimized to achieve the best sensitivity.

The use of flow injection analysis (FIA) combined with various atomic spectroscopic techniques for determining metals, including mercury, has increased dramatically in the last decade. A detailed description of FIA has been described elsewhere (Tyson, 1992). The basic principle involves the transport of a discrete volume of sample in a closed conduit by a continuously flowing carrier stream.

This section describes recent (within the last 3 to 5 years) applications of atomic spectroscopy to the determination of mercury.

A. Cold-Vapor Atomic Absorption Spectrometry

Cold-vapor atomic absorption spectrometry (CVAAS) is frequently used to determine mercury because of simplicity, high sensitivity, and modest-to-low cost. The technique was first proposed in the late 1960s (Hatch and Ott, 1968). It takes advantage of the fact that mercury is unique among elements in that it possesses a high vapor pressure at room temperature and readily exists as a monoatomic vapor. This means that no atomizer is required and a sample can be reduced, usually by stannous chloride and hydrochloric acid, and the elemental vapor swept by a carrier gas (argon, nitrogen, or air) into the path of the mercury hollow cathode lamp. While there are many examples of laboratory-constructed systems, the most commonly employed system used involves an electric pump which circulates the mercury vapor, and the AAS measurements are made using a quartz open-ended cell in this light path. The detection limit for a 50 mL sample is in the sub-ppb (parts per billion) concentration levels.

Most major manufacturers of AAS instrumentation and AAS accessories will produce a cold-vapor accessory or complete AAS system dedicated to mercury determination. Current systems can be computer-controlled, linked to sample preparation systems, and give improved detection limits with reduced sample

volumes. A typical example is the M-6000A Automated Mercury Analyzer from CETAC Technologies (Omaha, Nebraska). This is a double-beam cold-vapor atomic absorption spectrometer with (claimed) detection limits to less than 1 part per trillion (ppt). The system is controlled by a Windows™ based software package and can be fully automated (dilutions, calibration curves, repeats, etc.) using a CETAC ASX-500 autosampler. Sensitivity can be controlled and adjusted by changing the gas flow rate, e.g. high sensitivity of 1 ppt can be achieved using a low-gas flow rate of 30–40 mL/min, whereas a high-gas flow rate of 300–350 mL/min will provide increased throughput of samples at a reduced sensitivity.

An investigation of collectors filled with gold/platinum wire were found to be more efficient than those packed with gold or silver wire for the collection of mercury in natural gases prior to thermal desorption and determination by CVAAS. Precision for field measurements was found to be between 8 and 15% relative standard deviation and detection limit of 30 ng/m^3 for a 10 L sample (Frech et al., 1995).

A method utilizing an off-line microwave digestion stage followed by FIA and detection by CVAAS was developed to determine total mercury in biological and environmental samples (Murphy et al., 1996). A detection limit of 0.2 ng/g was found and the method applied to river sediments and canned tuna fish, giving results in the range 0.1–3.0 mg/kg.

A study of interference effects from Cd, Cu, Ni, and Pb as well as As(III), As(IV), and Se(IV) in a continuous-flow mercury cold vapor AAS alleviated by generating the mercury cold vapor in micellar media was investigated (Madrid et al., 1994). These authors found that the use of HCl/tetradecyltrimethylammonium bromide reduced or minimized interferences from the transition metals, whereas citric acid reduced interferences from the hydride-forming metals.

Mixtures of HNO_3–H_2SO_4–H_2O_2 and HNO_3–H_2SO_4–HCl were used to microwave-digest marine biological samples with mercury recoveries ranging from 91 to 108% for subsequent determination by CVAAS (Tinggi and Craven, 1996). The results were verified using certified standards.

B. Cold-Vapor Atomic Fluorescence Spectrometry

Cold-vapor atomic fluorescence spectrometry (CVAFS) shows improved detection limits over CVAAS. A commercial CV-AFS dedicated to mercury determination is available (PS Analytical, Kent, UK).

An excellent review is available (Morita et al., 1995) describing the use AFS for the determination of mercury, a description of the loss and increase in mercury through its transfer between gas and solution phases, potential interferences in the determination, preconcentration techniques, methods for total and selective determination, various types of automated and semiautomated procedures, and availability and concentration of various reference and certified materials.

An FI-AFS method incorporating an on-line bromide–bromination oxidation step to determine mercury in filtered seawater samples is described (Bloxham et al., 1996).

Detection limits for mercury (II) chloride and methylmercury were 25 and 23 ng/L, respectively. Good agreement with certified samples were obtained.

C. Electrothermal Atomization Atomic Absorption Spectrometry

Electrothermal atomization atomic absorption spectrometry (ETAAS) or graphite furnace atomic absorption spectrometry (GFAAS) is a highly sensitive technique for metal determination, typically 10–100× lower detection limits than conventional flame AAS.

Total and inorganic mercury in natural waters were trapped by cold-vapor generation-trapping and atomization in a graphite furnace by selective reduction with $NaBH_4$ and $SnCl_2$ (Bermejo-Barrera et al., 1997). Ir-, W-, and Zr-coated tubes were investigated with Ir-coated tubes giving a characteristic mass of 300 and 240 pg for total and inorganic mercury, respectively, and detection limits of 90 and 60 ng/L, respectively, for a 1500 microliter solution.

Au, Rh, Ir, Pd, and Rh were investigated as chemical modifiers for mercury determination by ETAAS (Bulska et al., 1996). Using a Au/Rh mixture and Pd alone, thermally reduced on the graphite tube and electrodeposited, Pd gave the best analytical performance with a characteristic mass of 110 pg for mercury.

D. Inductively Coupled Plasma–Mass Spectroscopy

Inductively coupled plasma–mass spectroscopy (ICP-MS) is a highly sensitive technique for the determination of metals. In this case the ICP is used as the ion source for mass spectroscopy when determining mercury (or other elements). A detailed description of the technique is described elsewhere (Fisher and Ebdon, 1997). An ICP-MS consists of the ion source, an interface system, which consists of a sampling cone, a differentially pumped zone, a skimming zone, ion lenses, a quadruple mass spectrometer, and a detector. Its advantages include a 2 to 3 orders of magnitude improvement in sensitivity compared to conventional inductively coupled plasma–atomic emission spectrometry, inherent multielement coverage, and the measurement of elemental isotopic ratios. Disadvantages include increased cost and complexity of instrumentation and the potential of spectral interferences from molecular species.

The determination of total mercury in sediments by microwave-assisted digestion flow-injection–ICP-MS was performed (Woller et al, 1997). Standard additions and internal standardization was used for calibration and correction of the system. The method was validated using certified reference materials. Detection limits of 10 ng/g for solution and 1 ng/g for dry sediment samples were obtained.

The accurate and precise determination of total mercury in biological and environmental samples by isotope dilution ICP-MS was obtained (Yoshinga and Morita, 1997). Precision at 20 ppb level was < 0.5%. Accuracy was assessed using certified human hair and sediments.

Trace concentrations of mercury in water samples were determined by a method involving a preconcentration where the mercury vapor, generated by tin(II) chloride as the reductant, was trapped by amalgamation on a gold–platinum gauze, and released by controlled heating for ICP-MS detection (Debrah et al., 1996). A flow-injection sample introduction system with time-based injection was used and the sensitivity was proportional to the mass of mercury in sample. A detection limit of 200 pg/L for a 25 mL sample was obtained with a precision of 1% at 1 μg/L.

E. Inductively Coupled Plasma–Atomic Emission Spectrometry

Inductively coupled plasma–atomic emission spectrometry (ICP-AES) is a widely used and accepted technique for the determination of metal. In the traditional mode of operation, the technique has a comparable detection limit for mercury as FAAS.

A method for the determination of mercury vapor in ambient air using an electrically heated, gold wire loop for collection, torch vapor sample introduction, and ICP-AES with a photodiode array detector (PDA) has been described (Karanassios et al., 1994).

F. Other

Mercury was determined using furnace atomic nonthermal excitation spectrometry (FANES) (Dittrich et al., 1994). For microvolumes, the use of Ir and Pd as chemical modifiers for the stabilization of mercury during thermal pretreatment gave absolute detection limits of 4 pg (with Ir) and 12 pg (with Pd). Combining FANES with CV and an amalgam attachment gave a detection limit of 22 ng/L.

The speciation of mercury in natural waters was achieved using gas chromatography of derivatized mercury species on a widebore capillary column, with the separated mercury species being pyrolized on-line at 800 °C for detection by AAS (Emteborg et al., 1996). Detection limits using a 1 L sample were 0.03 ng/L for methylmercury and 0.4 ng/L for inorganic mercury.

Using an argon and helium microwave-induced plasmas (MIP), sustained in a Beenakker cavity (with capillary tube and tangential flow torches), a surfatron and microwave plasma torch have been compared in terms of their discharges properties and ability to excite mercury atoms (Camuna-Aguilar et al., 1994). An on-line continuous CV system, using $SnCl_2$/HCl as chemical reducing agent, was used for sample introduction. A detection limit of 10 pg/mL, a linear dynamic range of more than 3 orders of magnitude and precision of ±4% was achieved using the He surfatron.

The on-line Hg^{2+} reduction using reverse FIA and CV coupled to a dc discharge plasma chamber for atomic emission spectrometric determination of mercury was investigated (de Andrade and Bueno, 1994). A linear calibration up to 50 ng/mL was achieved with an injection (analyses) frequency of 120/h.

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REFERENCES

Abernathy, R., Cumbie, P.M. *Bull. Environm. Contam. Toxicol.* **1976**, *17*, 595.
Akielaszek, J.J., Haines, T.A. *Bull. Environm. Contam. Toxicol.* **1981**, *27*, 201.
Anderson, R.V. *Bull. Environm. Contam. Toxicol.* **1977**, *18*, 492.
Babji, A.S., Embong, M.S., Woon, W.W. *Bull. Environm. Contam. Toxicol.* **1979**, *23*, 830.
Berlin, M. In *Handbook on the Toxicology of Metals*, 2nd edn.; Friberg, L., Nordberg, G.F., Nordman, C. Eds.; Elsevier: Amsterdam, The Netherlands, 1986.
Bermejo-Barrera, P., Moreda-Pineiro, J., Moreda-Pineiro, A., Bermejo-Barrera, A. *J. Anal. Atom. Spectrom.* **1997**, *12*, 317.
Bloom, N.S. *Can. J. Fish. Aquatic. Sci.* **1992**, *49*, 1010.
Bloxham, M.J., Hill, S.J., Worsfold, P.J. *J. Anal. Atom. Spectrom.* **1996**, *11*, 511.
Bianchini, A., Giles, R. *Bull. Environm. Contam. Toxicol.* **1996**, *57*, 91.
Becker, D.S., Bigham, G.N. *Distribution of Mercury in the Aquatic Food Web of Onondaga Lake, New York, in Mercury as a Global Pollutant*; Kluwer Academic: Dordrecht, The Netherlands, 1995.
Berlin, M. In *Handbook on the Toxicology of Metals*, 2nd edn.; Friberg, L., Nordberg, G.F., Nordman, C. Eds.; Elsevier: Amsterdam, The Netherlands, 1986.
Brown, J.R., Chow, L.Y. *Bull. Environm. Contam. Toxicol.* **1976**, *17*, 190.
Bulska, E., Kandler, W. Hulanicki, A. *Spectrochimica Acta* **1996**, *51B*, 1263.
Butcher, D.J., Sneddon, J. *Practical Guide to Graphite Furnace Atomic Absorption Spectrometry*; John Wiley: New York, 1997.
Camuan-Aguilar, J.F., Pereiro-Garcia, R., Sanchez-Uria, J.E. *Spectrochimica Acta* **1994**, *49B*, 475.
Cappon, C.J., Crispin Smith, J. *Bull. Environm. Contam. Toxicol.* **1976**, *18*, 600.
Caviglia, A., Cugurra, F. *Bull. Environm. Contam. Toxicol.* **1978**, *19*, 528.
Chandra, M.G.P. *Bull. Environm. Contam. Toxicol.* **1996**, *56*, 319.
Cooper, J.J. *Bull. Environm. Contam. Toxicol.* **1983**, *31*, 9.
Crecelius, E.A. *Bull. Environm. Contam. Toxicol.* **1977**, *18*, 227.
Csuros, M. *Environmental Sampling and Analysis for Technicians*; Lewis Publishers: Boca Raton, FL, 1994.
Cugurra, F., Maura, G. *Bull. Environm. Contam. Toxicol.* **1976**, *15*, 568.
de Andrade, J.C., Bueno, M.I.M.S. *Spectrochimica Acta* **1994**, *49B*, 787.
Debrah, E., Denoyer, E.R., Tyson, J.F. *J. Anal. Atom. Spectrom.* **1996**, *11*, 127.
Dittrich, K., Franz, T., Wennrich, R. *Spectrochimica Acta* **1994**, *49B*, 1695.
Ellis, L.A., Roberts, D.J. *J. Anal. Atom. Spectrom.* **1996**, *11*, 1063.
Emteborg, H., Sinemus, H.-W., Radziuk, B., Baxter, D.C., Frech, W. *Spectrochimica Acta* **1996**, *51B*, 829.
Faust, S.M., Aly, O.M. *Chemistry of Natural Waters*; Ann Arbor Science: Ann Arbor, MI, 1981.
Fisher, A.S., Ebdon, L. In *Advances in Atomic Spectroscopy*; Sneddon, J., Ed.; JAI Press: Stamford, CT, 1997, Vol. 3, Chap. 1.
Fitzgerald, W.F. In *National Forum on Mercury in Fish Proceedings*: USEPA 823-R-95-002, 1995.
Frech, W., Baxter, D.C., Dyvik, G., Dybdahl, B. *J. Anal. Atom. Spectrom.* **1995**, *10*, 769.
Froslie, A., Norheim, G., Sandlund, O.T. *Bull. Environm. Contam. Toxicol.* **1985**, *34*, 572.
Gerstenberger, S.L., Pratt-Shelley, J., Beattie, M.S., Dellinger, J.A. *Bull. Environm. Contam. Toxicol.* **1993**, *50*, 612.
Gilmore, C.C. In *National Forum on Mercury in Fish*; Proceedings USEPA 823-R-95-002, 1995.

Goyer, R.A. In *Casarett and Doull's Toxicology: The Basic Science of Poisons*; ed. Klaassen, C.D., Ed.; McGraw-Hill: New York, 1996.

Greig, R.A., Wenzloff, D.R., MacKenzie Jr., C.L., Merrill, A.S., Zdanowicz, V.S. *Bull. Environm. Contam. Toxicol.* **1979**, *22*, 326.

Guthrie, R.K., Davis, E.M., Cherry, D.S., Murray, H.E. *Bull. Environm. Contam. Toxicol.* **1979**, *21*, 53.

Gutierrez-Gahndo, E., Numoz, G.F., Flores, A.A. *Bull. Environm. Contam. Toxicol.* **1988**, *41*, 201.

Hall, E.T. *J. of AOAC* **1974**, *57*, 1068.

Haswell, S.J. (Ed.). *Atomic Absorption: Theory, Design, and Applications*; Elsevier Science: Amsterdam, 1991.

Hatch, W.R., Ott, W.L. *Anal. Chem.* **1968**, *40*, 2085.

Heagler, M.G., Newman, M.C., Mulvey, M., Dixon, P.M. *Bull. Environm. Contam. Toxicol.* **1993**, *12*, 285.

Heagler, M.G. Lindow, A.G., Beck, J.N., Jackson, C.S., and Sneddon, J. *Microchem. J.* **1996**, *53*, 472.

Heagler, M.G. Unpublished data, 1997.

Hintelmann, H., Hempel, M., Wilken, R.D. *Environ. Sci. & Technol.* **1995**, *29*, 1845.

Hurley, J.P., Benoit, J.M., Babiarz, C.L., Shafer, M.M., Andren, A.W., Sullivan, J.R., Hammond, R., Webb, D.A. *Environ. Sci. & Technol.* **1995**, *29*, 1867.

Hutagalung, H. *Bull. Environm. Contam. Toxicol.* **1989**, *42*, 814.

Ingle, J.D., Jr. Crouch, S.R. *Spectrochemical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1988.

Jackson, T.A. *Can J. Fish. Aquatic. Sci.* **1991**, *48*, 2449.

Johnson, T.A., Bodaly, R.A., Mathias, J.A. *Can. J. Fish. Aquat. Sc.* **1991**, *48*, 1468.

Johnson, G.D., McIntosh, A.W., Atchison, G.J. *Bull. Environm. Contam. Toxicol.* **1978**, *19*, 733.

Joiris, C.R., Ali, I.B., Holsbeek, L., Bossicart, M., Tapia, *G. Bull. Environm. Contam. Toxicol.* **1995**, *55*, 674.

Karanassios, V., Bateman, K.P., Spiers, G.A. *Spectrochimica Acta* **1994**, *49B*, 867.

Kim, E.Y., Murakami, T., Saeki, K., Tatsukawa, R. *Arch. Environ. Contamin. Toxicol.* **1996**, *30*, 259.

Klusek, C.S., Heit, M. *Bull. Environm. Contam. Toxicol.* **1982**, *28*, 202.

Koli, A.K., Canty, W.T. *Bull. Environm. Contam. Toxicol.* **1978**, *20*, 537.

Lajunen, L.H.J. *Spectrochemical Analysis by Atomic Absorption and Emission*; Royal Society of Chemistry: London, 1992.

Lorenzo, R.A., Carro, A., Rubi, E., Casais, C., Cela, R. *J. of AOAC International* **1993**, *76*, 608.

Lindberg, S.E., Kim, K.-H., Meyers, T.L., Owens, J.G. *Environ. Sci. & Technol.* **1995**, *29*, 126.

Lytle, T.F., Lytle, J.S. *Bull. Environm. Contam. Toxicol.* **1982**, *29*, 50.

Madrid, Y., Gutierrez, J.F., Camara, C. *Spectrochimica Act* **1994**, *49B*, 163.

Matilainen, T., Verta, M. Can. *J. Fish. Aquatic. Sci.* **1995**, *52*, 1597.

Montaser, A., Golightly, D.W. (Eds.). *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd edn.; VCH: New York, 1991

Morita, H., Tanaka, H., Shimomura, S. *Spectrochimica Acta* **1995**, *50B*, 69.

Mueller, C.S., Ramelow, G.R., Beck, J.N. *Bull. Environm. Contamin. Toxicol.* **1989**, *42*, 71.

Murphy, J., Jones, P., Hill, S.J. *Spectrochimica Acta* **1996**, *51B*, 1867.

Parvaneh, V. *Bull. Environm. Contam. Toxicol.* **1979**, *23*, 357.

Peerzado, N., Watson, D., Guinea, M. *Bull. Environm. Contam. Toxicol.* **1993**, *50*, 158.

Phyllips, G.R., Buhler, D.R. *Arch. Environ. Contam. Toxicol.* **1980**, *9*, 99.

Porcella, D.B. In *Mercury Pollution: Integration and Synthesis*; Watras, C.J. Huckabee, J.W. Eds.; Lewis Publishers: Boca Raton, FL, 1994.

Ray, S. *Bull. Environm. Contam. Toxicol.* **1978**, *19*, 631.

Reimer, A.A., Reimer, R.D. *Bull. Environm. Contam. Toxicol.* **1975**, *14*, 105.

Roberts, A.E., Hill, D.R., Tofft, E.C., Jr. *Bull. Environm. Contam. Toxicol.* **1982**, *29*, 711.

Robinson, J.W. *Atomic Spectroscopy*, 2nd edn.; Marcel Dekker: New York, 1996.

Saeki, K., Fujimoto, M., Kolinjim, D., Tatsukawa, R. *Arch. Environ. Contam. Toxicol.* **1996**, *30*, 412.

Shultz, C.D., Crear, D., Pearson, J.E., Rivers, J.B., Hylin, J.W. *Bull. Environm. Contam. Toxicol.* **1976**, *15*, 230.

Somers, K.M., Jackson, D.A. *Can. J. Fish. Aquatic. Sci.* **1993**, *50*, 2388.

Southworth, G.R., Peterson, M.J., Adams, S.M., Blaylock, B.G. *Bull. Environ. Contam. Toxicol.* **1994**, *53*, 211.

Smith, E.C., Berkes, F., Spence, J.A. *Bull. Environm. Contam. Toxicol.* **1975**, *13*, 673.

Staveland, G., Marthinsen, G., Norheim, G., Julshamn, K. *Arch. Environ. Contamin. Toxicol.* **1993**, *24*, 187.

Suckcharoen, S. *Bull. Environm. Contam. Toxicol.* **1980**, *24*, 511.

Tinggi, U., Craven, G. *Microchem. J.* **1996**, *54*, 168.

Tyson, J.F. In *Advances in Atomic Spectroscopy*; Sneddon, J., Ed.; JAI Press: Stamford, CT, 1992, Vol. 1, Chap. 5.

Uchino, E., Kosuga, T., Konishi, S., Nishimura, M. *Environ. Sci. & Technol.* **1987**, *21*, 920.

Wang, W., Driscoll, C.T. *Environ. Sci. & Technol.* **1995**, *29*, 2261.

WHO. *Environmental Health Criteria 118: Inorganic Mercury.* World Health Organization: Geneva, Switzerland, 1991.

Woller, A., Garraud, H., Martin, F., Donard, O.F.X., Fodor, P. *J. Anal. Atom. Spectrom.* **1997**, *12*, 53.

Yoshinaga, J., Morita, M. *J. Anal. Atom. Spectrom.* **1997**, *12*, 417.

Yess, N.J. *J. of AOAC International.* **1993**, *76*, 36.

Zilliouxy E.J., Porcella, D.B., Benoit, J.M. *Environm. Toxicol. and Chemistry* **1993**, *12*, 2245.

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Advances in Atomic Spectroscopy

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