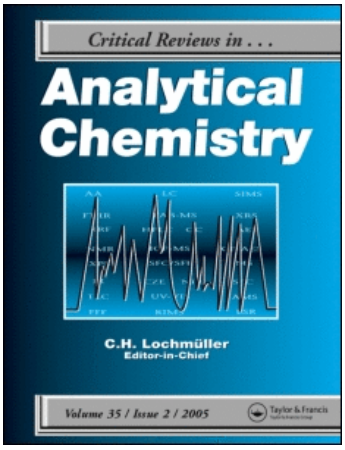

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Trace Determination of Mercury: A Review

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Trace Determination of Mercury: A Review

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ABSTRACT: Methods used for trace (sub-ppm) detection of mercury are reviewed. Included are spectrometric methods such as atomic absorption, fluorescence, emission, and mass spectrometry; electrochemical methods; and as radiometric methods as well as other common and novel techniques. Limits of detection are reported where given, and advantages and disadvantages are compared.

KEY WORDS: mercury.

I. INTRODUCTION

The contamination of the environment by mercury has been an important concern throughout the world for decades. Mercury, as a liquid with a high thermal conductivity, has many unique properties that make it useful in more than 3000 industrial applications, ranging from fungicides and bactericides in the agriculture industry to heat transfer agents and catalysts in the chemical industry. At the same time, mercury is a highly toxic compound that can cause kidney injury, central nervous system disorders, intellectual deterioration, and even death. The tragic effects of unrestricted industrial mercury dumping became undeniable in the mid-1950s, when more than 100 people in Minimata, Japan, died from eating fish contaminated by a methyl mercury discharge. After this disaster, industrialized nations around the world began prohibiting the dumping of mercury into waterways. This decrease of anthropogenic sources resulted in falling levels of mercury compounds in lakes and rivers that had been receiving these discharges.

Nevertheless, mercury contamination remains an important environmental problem in the 1990s. Mercury poisoning of both the environment and the human race is currently observed not only in unregulated areas such as the Brazilian Amazon[1,2] but also in the U.S. Great Lake region[3,4] and the Florida Everglades.[5,6] Sources range from unrestricted dumping to atmospheric deposition and agricultural runoff. Clearly, the problem of mercury is not going away, and thus the need for analytical techniques capable of detecting trace amounts of mercury is still of importance. Also, as environmental levels of mercury are reduced, increasingly sensitive techniques are required to monitor its distribution.

The goal of this article is to review the analytical techniques used for the detection of trace amounts of mercury in the last 20 years. In addition, landmark papers of some techniques are noted as well as similar reviews covering the years up to 1975. The

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best limit of detection for each method is given in Table 1. This article does not claim to include all publications on the topic; rather, it discusses several reports on different techniques used for trace mercury determination.

II. PREVIOUS REVIEWS

The early history of mercury detection was given by Woodson[7] in one of the first papers on the cold vapor atomic absorption detection of mercury and published in 1939. This short review was limited to the then-dominant colorimetric techniques and early optical methods. A 1975 review by Chilov[8] discussed techniques for determining mercury at the ppm level or less with 339 references, most of which were published after 1965. It covered sampling and sample storage as well as methods of analysis, with an emphasis on sensitivity and ease of application. This report acknowledged the replacement of colorimetry[9] by atomic absorption as the generally accepted technique, while noting that neutron activation allowed nondestructive analysis. An appendix listing the different techniques with their lower useful limits in different sample types was given. Another 1975 review by Ure[10] covered nonflame atomic absorption and fluorescence spectrometry determination of mercury. Nonflame methods here include pyrolysis, furnace techniques, combustion, and reduction-aeration (cold vapor) methods of sample introduction. However, while these nonflame methods were simple and sensitive, they experienced difficulties in giving accurate determinations in natural samples. Four hundred and forty-two references were given; in addition, they were cataloged by application.

In 1995, Morita et al.[11] reviewed atomic fluorescence spectrometry (AFS) methods for determining mercury. They noted that at that time, cold vapor (CV) AFS and CV atomic absorption spectrometry (AAS) were the most widely used methods for determining Hg. The review discussed the principles of AFS of Hg, the use of flow injection (FI) techniques, and applications of CV-AFS. Ninety-one references were given.

III. SPECTROSCOPIC METHODS

A. Sample Introduction

The most convenient and widely used method of sample introduction of mercury is the cold vapor technique, because mercury has a vapor pressure of 0.16 Pa at 20°C, corresponding to a concentration of ~14 mg m^{-3} in air. The cold vapor technique allows direct determination without an atomizer unit. Liquid samples can be analyzed by reducing the Hg ions in solution and aerating inert gas through the liquid to liberate all elemental Hg into the gas phase. Similarly, solid samples (soil, tissue, etc.) can be digested and the solution reduced and aerated.

Other flameless techniques still in use include furnace techniques, both with and without *in situ* preconcentration, which offer good detection limits despite suffering from matrix interference due to the high volatility of mercury that restricts the ashing temperature. At the same time, while mercury is one of the worst elements for detection by flame-AAS (due to its tendency to form stable molecules in the flame), some researchers continue to look for new ways to improve this method.

Preconcentration of mercury can be easily done using traps based on the amalgamation of Hg with noble metals such as silver, platinum, and especially gold.[12] Mercury vapor is caught in these traps and later released via heating for detection. This allows not only preconcentration but also the ventilation of interfering substances from the gas stream before measurement.

Speciation of different mercury compounds (Hg^0, Hg^+, Hg^{2+}, organomercurials, etc.) can also be carried out either on-line

TABLE 1
Best Reported LODs for Each Method

Method	Form of Hg	LOD (conc., abs.)	% RSD	LDR	Interferences
CV-AAS[24]	Hg^0	0.02 ppb, 0.1 ng	2%	0–30 ppb	N/A
CV-AAS, preconcentration[40]	Hg^0	0.042 pptr, 0.084 ng	10%	N/A	N/A
ETA-AAS, preconcentration[55]	Hg^0	0.1 pptr, 5 pg	2.7%	3 orders of magnitude	N/A
Speciation with AAS[60]	Hg^{2+}	0.4 pptr, 0.4 ng	18%	>3 orders of magnitude	1-octanol, butyltetrahydrofuran
	CH_3Hg^+	0.03 pptr, 0.03 ng	25%		
CV-AFS[72]	Hg^0	0.001 pptr, N/A	3%	N/A	N/A
CV-AFS,[78] preconcentration	Hg^0	0.1 pptr, 4.5 pg	5%	5 orders of magnitude	N/A
ETA-LEAFS[82]	Hg^0	1.4 pptr, 14 fg	3%	7 orders of magnitude	N/A
ICP-AFS[83] [a]	Hg^0	40 pptr, N/A	N/A	N/A	N/A
Speciation with AFS, preconcentration[84]	Hg^0	N/A, 0.3 pg	N/A	N/A	N/A
	$(CH_3)_2Hg$	N/A, 0.3 pg	N/A		
	$(C_2H_5)_2Hg$	N/A, 0.4 pg	N/A		
	CH_3HgCl	N/A, 2.0 pg	N/A		
	CH_3CH_2HgCl	N/A, 3.1 pg	N/A		
MIP-AES[90]	Hg^0	0.01 pptr, 0.5 pg	4.5%	>4 orders of magnitude	N/A
ICP-AES[99]	Hg^0	50 pptr, 5 ng	2.3%	N/A	Au, Pd, Pt, Sb
DCP-AES, preconcentration[100] [a]	Hg^0	50 pptr, 50 pg	1.6%	3 orders of magnitude	Se^{4+}, S^{2-}, I^-
Ring discharge AES, preconcentration[101] [a]	Hg^0	<0.5 pptr, N/A	1%	3 orders of magnitude	Matrix effects
Speciation with AES[104]	Hg^{2+}	0.28 ppb, 280 ng	N/A	N/A	humic substances
	CH_3Hg^+	0.04 ppb, 40 ng	N/A		
PAS[110]	Hg^{2+}	3 pptr	6%	>2 orders of magnitude	Ag^+, Au^{3+}, Cu^{2+}
METAL[112] [a]	Hg^0	3 ppq, N/A	N/A	8 orders of magnitude	N, O, NH_3, sample matrix
MIOR[113] [a]	Hg^0	N/A, 10 pg	N/A	N/A	N/A
XRFS, preconcentration[116]	Hg^0	60 pptr, 1.8 ng	N/A	N/A	N/A
MPIS[118]	Hg^0	0.22 ppb, 220 fg	N/A	N/A	N/A
LIBS[120] [a]	Hg^0	5 ppb, N/A	N/A	N/A	N/A
FANES[121] [a]	Hg^0	2 pptr, 20 pg	6%	3 orders of magnitude	N/A
ICP-MS[122]	Hg^0	0.08 pptr, 8 pg	2.7%	>3 orders of magnitude	N/A
Speciation with ICP-MS, preconcentration[128]	CH_3Hg^+	0.02 ppb, 1 pg	4%	>3 orders of magnitude	N/A
Enzyme inhibition spectrophotometry[136]	Hg^{2+}	0.1 pptr, N/A	7%	4 orders of magnitude	Bi^{3+}, Cd^{2+}

TABLE 1 (continued)
Best Reported LODs for Each Method

Method	Form of Hg	LOD (conc., abs.)	% RSD	LDR	Interferences
Enzyme inhibition fluorimetry[140]	Hg^{2+}	2 ppb, N/A	N/A	N/A	Ag^{+}
IDA, preconcentration[143 a]	Hg^{2+}	20 ppb, 0.2 μg	4.16%	N/A	MoO_4^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, Ce^{4+}, Sb^{3+}, Bi^{3+}, I^{-}
Au film sensor[144]	Hg^{0}	N/A, 0.05 ng	N/A	>3 orders of magnitude	H_2S
ASV[149]	Hg^{2+}	0.2 pptr	3.3%	0.3–2.4 pptr	N/A
PSA[155 a]	Hg^{2+}	0.5 ppb, N/A	2.5%	5–30 ppb	Rh^{3+}, Pb^{2+}
CSP[156 a]	Hg^{2+}	0.1 ppb, 1 ng	4%	3 orders of magnitude	Fe^{3+}, NO_x, CO_2
DPV[157 a]	$HgCl_4^{2-}$	2 pptr, N/A	N/A	3 orders of magnitude	Cu^{2+}, SO_4^{2-}
VSA[158 a]	Hg^{2+}	0.6 ppb, N/A	2.6%	2 orders of magnitude	N/A
Enzyme inhibition conductimetry[159 a]	Hg^{2+}	20 ppb, N/A	2.9%	N/A	Ag^{2+}
Electrochemical biosensor[160 a]	Hg^{2+} CH_3Hg^{+} $C_2H_5Hg^{+}$	1 ppb, N/A 2 ppb, N/A 2 ppb, N/A	≤4%	2–10 ppb	N/A

Note: All LODs in table are assumed to be defined as 3 σ.

[a] This is the only LOD given for this technique in the articles reviewed here.

with species detection or off-line with total mercury determination. The speciation of mercury compounds is important due to the varying levels of toxicity associated with the different forms that Hg can take. Of particular interest are methylmercury compounds, not only because they are highly toxic but also because mercury can be methylated in the environment (especially marine and freshwater sediments) and accumulated in the tissue of fish, continuing up the food chain.[13,14] When mercury in any form and from any source enters the environment, it can be converted into its toxic methyl derivative. The chemical pathways for the methylation of mercury in the environment have been reviewed.[15] Chromatographic techniques are most commonly used for speciation, including GC, HPLC, and ion chromatography.

B. CV-AAS: No Preconcentration

The cold vapor (CV) technique was originally developed as an introduction method for atomic absorption spectrometry (AAS), although it was later used for other techniques (most notably AFS). For this reason, a review of the literature of the development of AAS of mercury is also the story of the development of the cold vapor technique.

The first instrument based on the absorption of UV (253.7 nm) light by mercury

vapor was proposed by Woodson in 1938 to detect Hg in flue gas from a mercury boiler.[7] It was reported to be small and portable, with a useful range of 1 ppm to 1 ppb.

The cold vapor atomic absorption procedure, as it is known today, is typically attributed to Hatch and Ott.[16] Reduction of dissolved solid samples occurred by tin (II) sulfate after which aeration occurred, carrying the vapor to a 25 mm × 15 cm glass tube with quartz windows. A detection limit of 1 ppb in solution was reported.

Five years later, Gilbert and Hume[17] reported an improvement on the technique, which involved a more efficient aeration technique, reducing analysis time and yielding an LOD (defined as 2 σ of the blank) of 0.4 ppb or 4 ng absolute. In addition to using tin (II) chloride as a reducing agent, it reported and referenced the use of oxidizing agents permanganate and persulfate to maintain Hg in the divalent, nonvolatile state, and UV irradiation and hot acid to destroy organic matrices and organomercurial compounds.

In 1996, Zhou et al.[18] compared four different acid mixtures for high-pressure microwave digestion methods for determining total Hg in sediments. After comparing HNO_3/H_2SO_4, $HNO_3/HClO_4$, HCL/HNO_3, and $HCl/HNO_3/HF$, aqua regia was chosen as it was time saving, less dangerous, and suitable for other trace metal analyses. Good recoveries (94 to 104%) were obtained from different soil and marine sediment matrices.

The advantages of using sodium borohydride as the reducing agent for Hg in solution was discussed by Toffaletti and Savory[19] and Rooney.[20] Rooney reported a 10-fold increase in signal when using $NaBH_4$ rather than $SnCl_2$, giving a detection limit of 20 ng absolute. However, he also noted that an $NaBH_4$ solution must be used within 1 h of preparation. Yamamoto et al.[21] found that while both reducing agents yielded similar calibration curves and limits of detection, the precision using $NaBH_4$ was 2.5%, while for $SnCl_2$ it was 4.9%. In 1988, Welz and Schubert-Jacobs[22] also compared the two reducing agents. They claimed $NaBH_4$ performed as well as or better than $SnCl_2$ as a reducing agent for Hg in addition to reducing most of the organic compounds in solution. Despite these results, most papers encountered in this review utilized the more robust $SnCl_2$, due to its longer shelf life and less violently reactive nature.

In 1996, Brindle and Zheng[23] compared different designs of gas-liquid separators for sequential injection CV-AAS, including two Perkin-Elmer designs, a spray chamber system, and a frit-based design. Their comparison was based on efficient stripping of the analyte from solution and a small dead volume to ensure minimal dilution of the analyte with the carrier gas. They determined the Perkin-Elmer FIAS Chemifold gas-liquid separator to be the best, with the frit-based nebulizer a close second, although it experienced memory effects for high concentrations of mercury.

A method for measuring a stationary rather than a transient signal of mercury vapor was reported by Tong.[24] An ordinary 4-cm UV-cell was used as both reducing and detection cell, as the mercury was reduced in solution and partitioned between the aqueous and gas phase in the stoppered cell. In this way, the sensitivity of the method was reported to be improved due to the minimum of dead volume as opposed to a flow-through system. A detection of 0.02 ppb or 0.1 ng absolute was achieved.

Methods for continuous flow monitoring of Hg were reported by Oda and Ingle[25] and Goto et al.[26] The Oda and Ingle technique involved a continuous sample introduction reduction vessel into which sample and reductant solutions were continuously fed and Hg was reduced and volatilized. An LOD of 0.03 ppb was reported, which was observed to improve to 0.003 ppb with discrete sampling. Goto et al. utilized a method of continuous flow digestion, reduction, and extraction in small-bore tubes at slow flow rates. A detection limit of 0.1 ppb was

obtained using a gas-liquid separator and 8 µl flow cell.

Mineralization processes for biological materials were compared for CV-AAS by Colina de Vargas and Romero.[27] Both a cold mineralization (acid digestion at −10°C for 1 week) method and high-pressure bomb digestion (at 130° for 2.5 h) were found to result in no Hg losses due to volatilization or adsorption. While the cold mineralization process took more time, it was recommended for processing large numbers of samples. The accuracy of the method was determined by comparison with a tuna certified reference material.

Yamada et al.[28] reported the use of a mixture of $SnCl_2$ and $NaBH_4$ in acidic solution to reduce the interference of I with the detection of Hg. Iodide has been found to interfere with the reduction of Hg in solution. This report attributed the interference to the formation of Hg complexes with I_3^-. In this way, 85% of Hg in the presence of I was recovered. This was noted to be of interest when measuring Hg in wastewater or sewage samples.

Saraswati et al.[29] combined flow injection analysis (FIA) with CV-AAS in order to miniaturize and automate the method. They noted the improvement in speed, precision, and sensitivity the addition of FIA can offer. After correcting the signal for matrix suppression by standard additions, an LOD of 0.08 ppb in a zinc ore matrix was obtained. Hanna and McIntosh[30] described the determination of total Hg in environmental samples with FI-CV-AAS after on-line microwave digestion. The method was fully automated with a limit of detection of 0.035 ppb or 0.18 ng absolute and an RSD of 1.1%. Because the entire analytical process occurred in a closed system, opportunities for contamination were greatly reduced.

Determination of total mercury in environmental and biological samples were carried out by Murphy et al.[31] using an FI method with microwave digestion. The use of FIA in this case allowed for the rapid analysis of between 20 and 30 samples per hour, with an LOD of 0.2 ppb or 0.1 ng absolute and a RSD of less than 10%.

C. CV-AAS: Preconcentration

Dumarey et al.[32] compared the use of activated charcoal, silver-coated sand, and gold-coated sand as mercury collectors. It was noted that sheets or grains of Ag or Au show considerable memory effects and poor reproducibility. In their comparison, activated charcoal was found to be unsuitable, as it had a high capacity for collecting interfering compounds and Hg desorption was incomplete at 600°C. When Ag-coated sand was used, desorption was fast and complete, but organomercurials were poorly absorbed. In addition, on prolonged use of the Ag coating, it was slowly converted to the sulfide, resulting in a slight decrease in response. Au-coated sand was the only collector to retain the total content of volatile Hg compounds and was unaffected by sulfur compounds. In 1985, Dumarey et al.[33] made a similar comparison. This time, they reported that activated charcoal and Ag-coated sand as absorbers suffered from poor quantitation and were dependent on sampling flow rate and duration, the nature of the mercury compounds, and interfering substances. It was reported that the Au-coated and amalgamation traps showed a quantitative collection for a sampling flow rate up to 5 l min^{-1} when heated to 800°C. Yoshida and Motojima[34] reported the use of Au-coated quartz wool as a mercury collector that was then heated to 650°C for rapid determination of Hg in air. They noted that the performance of the trap deteriorated after 10 uses. Most of the papers encountered in this review used Au-coated sand as the collector.

Another determination of Hg in air was reported by Fitzgerald and Gill.[35] In this method, a two-stage Au amalgamation for

atmospheric analysis of Hg was used. A field sampling technique was employed in which the major volatile Hg species in the near ground atmosphere were collected on Au-coated beads, and atmospheric particulates were collected on glass fiber filters. The two-stage Au amalgamation technique was reported to separate interfering substances from the Hg vapor before the Hg was released to the detector. With this method, good precision and a good detection limit was achievable with an inexpensive single beam instrument. An LOD (2 σ) of 0.06 ng absolute was reported with 4% RSD.

In 1974, Ólafsson[36] reported the use of amalgamation on Au foil strips coupled to CV-AAS to detect Hg in seawater. After collection, the trap was heated to 300°C. Interferences included I^- and Br^-. Freimann and Schmidt[37] reported the use of an Au-coated silica wool plug in a 50-mm column as an amalgamation trap for determination of Hg in seawater. A Teflon® sampling bottle was also used as the reaction vessel to reduce sample contamination. An LOD of 0.5 pptr or 50 pg absolute was reported with a 4% RSD. Welz et al.[38] reported a method for picotrace (<1 ng/l) determination of mercury. After studying various amalgamation methods, they determined a gold/platinum gauze (90% Au, 10% Pt) to work the best due to its excellent sensitivity and reproducibility and because it could be easily cleaned in hot HNO_3. They also reported that $SnCl_2$ was superior to $NaBH_4$ as a reducing agent when using amalgamation despite the higher, faster reducing power of $NaBH_4$ and its ability to decrease interferences such as I and Se. This was because the reduction reaction of $NaBH_4$ was a violent reaction, which could cause water droplets to be carried with the gas stream to the amalgamation trap, contaminating and deactivating it. At the same time, $NaBH_4$ was used for hydride generation of elements that were not normally volatile, allowing them to be carried with the gas stream and interfere with the detection of Hg. In addition, they recommended the use of PTFE tubing over silicone to avoid memory effects, He as the purge gas over Ar and N_2 due to its superior stripping efficiency, and $Mg(ClO_4)_2$ or H_2SO_4 over $CaCl_2$ as the desiccant to avoid capture of Hg. The method was reported to have good accuracy.

Temmerman et al.[39] reported a method for determining Hg in drinking water after Au-coated sand amalgamation. An absolute LOD of 0.6 pptr or 0.6 ng absolute with >10% RSD was reported. A method for measuring picomolar concentrations in seawater involving two-stage Au amalgamation was reported by Gill and Fitzgerald.[40] An LOD of 0.84 p*M* (0.042 pptr) or 0.084 ng absolute was determined. Welz et al.[41] used an on-line microwave digestion method to determine total Hg, including organics, in water and urine. It was noted that on-line sample pretreatment was of interest because of problems due to contamination, volatilization, and adsorption losses when the sample was transported. An LOD of 10 pptr or 0.1 ng absolute was reported for water samples using a flow injection method. Good agreement with certified values was obtained for urine samples. A similar study by Hanna et al.[42] compared on- and off-line oxidation of organomercury compounds in water and urine for total mercury detection. An on-line LOD of 0.23 ppb or 0.12 ng absolute with 1.4% RSD was reported, with simplified sample pretreatment and an elevated operating temperature. An automated FI-CV-AAS method using Au gauze amalgamation was used by McIntosh.[43] A detection limit of 2 ppb or 17 ng absolute was reported. Streško et al.[44] used a collection method utilizing the chelating ion exchanger Spheron Thiol for the preconcentration of mercury. This took advantage of the affinity of Hg for SH groups. An LOD of 0.05 pptr or 0.05 ng absolute of water was achieved with an RSD of 10%. Garcia et al.[45] compared different Hg chelate-forming reagents (diethyldithiocarbamate, pyrrolidin-1-dithioformate,

and diphenylthiocarbazone [dithizone]) for the preconcentration of ultratrace amounts of inorganic Hg and CH_3Hg^+. It was observed that the carbamate type reagents performed superiorly to dithizone for on-line concentration, and volumes of 100 ml could be preconcentrated with 100% efficiency for both inorganic mercury and methylmercury. Detection limits of 16 pptr or 0.4 ng absolute of mercury were achieved, and the method was applied successfully to seawater samples.

In 1976, Matsunaga and Takahashi[46] reported the detection of organic Hg in sediments and aquatic organisms by extraction of the organomercurials with benzene, back extraction, oxidation with potassium permanganate and persulfate, and preconcentration of Hg using Au granule amalgamation. With this technique, they were able to detect nanogram levels. Determination of Hg in environmental standard reference materials using pyrolysis to release Hg vapors, which were preconcentrated using a two-stage Au absorber system for CV-AAS, was reported by Dumarey et al.[47] This method was reported to be rapid and simple and free from the contamination of wet digestion. A detection limit of 5 ppb, or 0.1 ng absolute, was reported. Vermeir et al.[48] reported a method of determining mercury in biological samples after high-pressure HNO_3 digestion in a Teflon® bomb. Detection occurred after a two-step Au-coated sand amalgamation. An absolute LOD of 12 pptr or 0.12 ng absolute was reported, along with results in excellent agreement with certified reference material values. Horvat et al.[49] described the use of Au amalgamation CV-AAS for the determination of total Hg in coal fly ash. Digestion was carried out with acid in sealed Pyrex tubes to prevent losses by volatilization. The results showed good agreement with the certified values and results obtained by neutron activation analysis. Brandvold et al.[50] reported a novel combustion method of determining Hg in solid samples. Gaseous mercury was evolved when a solid sample is heated above 500°C in the presence of oxygen. The evolved Hg was collected on Ag wool, and 95% recovery was observed for various sediment and ash standards. The LOD (2 σ) was observed to be 2 to 3 ng absolute.

Ombaba[51] reported the use of an amalgamation tube (MAT) containing Au sites to preconcentrate Hg from environmental and biological standard samples followed by CV-AAS. The samples were microwave digested under high pressure and reduced with $SnCl_2$. Good agreement was found with several certified reference material values at sub-ppm levels.

D. F-AAS

Ellis and Roberts[52] reported the use of a Au-coated dual 'bent' tube atom trap in order to improve the normally poor sensitivity encountered with flame AAS. Mercury was collected in the trap, thereby reducing its volatility. It was determined that low fuel flow, percentage obscuration and high tube height were important for maximum sensitivity, and a precision of 2.9% was achieved. A comparison with CV-AAS found the results to be in close agreement, although not as sensitive.

E. ETA-AAS

Trace levels of Hg were determined without preconcentration by Keller et al.[53] using electrothermal atomization (ETA)-AAS with uncoated graphite furnace cuvettes. A detection limit of 0.6 ppb or 0.03 ng absolute was reported. The method was applied to samples of drinking water and was found to report results in good agreement with U.S. Environmental Protection Agency reference standard values.

Hladký et al.[54] determined mercury concentrated in mineral acids (HCl, H_2SO_4, and H_3PO_4) using an Au-coated graphite furnace cuvette from which the absorbance was read after the release of the Hg from the amal-

gam. The amalgam prevented analyte loss and removed nonspecific absorption and water vapor from the matrix, detecting concentrations from 100 to 5 ppb with a 15% RSD. Lee et al.[55] reported the determination of Hg in environmental samples by a combination CV/Au-coated graphite furnace technique. A detection limit of 0.1 pptr or 5 pg absolute was determined with an RSD of 2.7%. Analytical results were obtained for natural waters, marine biota, and sediments. Siemer and Hageman[56] reported the determination of Hg in water using Au-coated graphite furnace atomizer tubes, which were then placed into either a carbon rod atomizer or a Woodriff furnace. A detection limit of 14 pptr was reported.

Baxter and Frech[57] reported the use of a Pt-lined graphite furnace for *in situ* preconcentration of Hg, which was produced after the reduction of water samples. An LOD (2 σ) of 2 pptr or 0.1 ng absolute was determined, and synthetic seawater samples were analyzed.

F. Speciation Coupled with AAS

Rapsomanikis and Craig[58] reported a method of gas chromatography (GC) separation of organomercury compounds with quartz furnace AAS detection. Because CH_3Hg^+ is co-eluted with $(CH_3)_2Hg$ or Hg^0, causing difficulties in speciation, they performed an ethylation of CH_3Hg^+ in aqueous ethanolic solutions with $NaB(C_2H_5)_4$ and detected the resultant compounds. An oven temperature of 100°C was used, and an absolute detection limit of 123 ppb or 167 pg absolute for CH_3HgCl was observed. Fischer et al.[59] then applied this derivation method to the determination of CH_3Hg^+ in fish after dissolution in an alkaline methanolic solution. The detection limit was observed to be 4 ppb or 4 pg of CH_3Hg^+ as $C_2H_5HgCH_3$ and 75 ppb or 75 pg absolute of Hg^{2+} as $(C_2H_5)_2Hg$.

A method described by Emteborg et al.[60] used a preconcentration step with a dithiocarbamate resin before GC separation. In addition, simultaneous use of two wavelengths (184.9 nm and 253.7 nm) for absorption and a 2.4-cm cuvette were used to improve the dynamic range and sensitivity, which resulted in LODs of 0.03 pptr or 0.03 ng absolute for CH_3Hg^+ and 0.4 pptr or 0.4 ng absolute for Hg^{2+}.

Ahmed et al.[61] used an anion exchange column to separate CH_3Hg^+ from Hg^{2+} in rain samples. The CH_3Hg^+ was then decomposed by UV irradiation. Different acids at different concentrations were compared for decomposition and percent recoveries. Sarzanini et al.[62] reported the use of cation exchange ion chromatography to separate Hg compounds after *in situ* cysteine complexation ($Hg(Cys)_2$, CH_3HgCys, and C_2H_5HgCys). Detection limits of 20 pptr or 2 ng absolute for Hg^{2+}, 100 pptr or 10 ng absolute for CH_3Hg^+, and 40 pptr or 4 ng absolute for $C_2H_5Hg^+$ were reported, and the method was applied to synthetic mixtures and natural samples.

Liquid chromatography (LC) was coupled with CV-AAS with a continuous flow reducing vessel by Fujita and Takabatake.[63] Tin(II) chloride was used to reduce Hg alkane thiolates; reduction of inorganic, methyl, and ethyl mercuric compounds was carried out with $NaBH_4$. The authors reported high sensitivity and selectivity. Aizpún et al.[64] reported a method of HPLC-CV-AAS for the speciation of inorganic Hg^{2+} and CH_3Hg^+ using vesicles of didodecyldimethylammonium bromide (DDAB) rather than an organic solvent as the mobile phase. The use of DDAB vesicles was reported to improve CV generation of Hg. Before separation, off-line preconcentration of the aqueous samples was carried out using C_{18} Sep-pack cartridges modified with 2-mercaptoethanol solutions. LODs of 0.1 to 0.2 ppb of Hg were achieved, and the method was applied to spiked seawater and human urine.

Baker's yeast cells (*Saccharomyces cerevisiae*) were used to separate CH_3Hg^+ and Hg^{2+} by Madrid et al.[65] with good recov-

eries. The percentage of CH_3Hg^+ fraction bound to the yeast cells did not depend on the experimental conditions tested, whereas the retention of Hg^{2+} depended on analyte concentration, biomass, and incubation time.

G. F-AFS

Atomic fluorescence spectrometry (AFS) was first used to determine Hg by Winefordner and Staab in 1964.[66] An LOD of 5 ppm in a H_2/O_2 flame and 1 ppm in an C_2H_2/O_2 flame were achieved. These LODs were compared with an LOD of 25 ppm, of which F-AAS was capable at the time.

H. CV-AFS: No Preconcentration

Although CV-AAS has been the most common method for the detection of mercury for decades, AFS is being used increasingly today. AFS is currently the U.S. Environmental Protection Agency preferred method for determining Hg in water (Method 1631). It has a larger linear dynamic range and an inherently high sensitivity capable of measuring lower detection limits. In addition, it suffers from fewer interferences than AAS.

Hutton and Preston[67] reported the use of a nondispersive AFS instrument using CV generation in order to improve the detection limit for Hg. It was noted that the instrument compared favorably with other CV systems but without complex instrumentation. An LOD of 0.04 ppb or 0.04 ng absolute was reported with a precision of 2 to 3%. A flow injection method was employed by Morita et al.[68] Mercury fluorescence was detected at both 184.9 and 253.7 nm, and an LOD of 0.12 ppb (8 pg absolute) was determined.

Swift and Campbell[69] reported the determination of Hg in environmental samples after microwave digestion. A detection limit of 1.3 pptr was achieved, and the method was applied to water and soil samples. Lamble and Hill[70] described the use of batch and on-line microwave digestion of slurried environmental samples for the determination of total Hg. An LOD of 13 pptr was reported with 1.5% RSD, as well as good agreement with certified reference material values of dogfish muscle and marine sediment.

Stockwell and Corns[71] discussed the detection of Hg using a Merlin fluorescence detector with which they achieved an LOD of 0.37 pptr in 50 ml. Janjić and Kiurski[72] used CV-AFS to detect Hg in river water samples and achieved an LOD of 0.001 pptr with an RSD of 3%.

Corns et al.[73] described a method of determining Hg in urine samples using an automated continuous flow CV-AFS system with bromine oxidation. An LOD of 1 pptr or 50 pg absolute was achieved. Bloxham et al.[74] reported the use of bromination digestion for determining Hg in filtered seawater. In a flow injection method, on-line oxidation of organomercurials was used. Detection limits of 25 pptr or 0.5 pg for HgCl and 23 pptr or 0.5 ng for CH_3HgCl were reported, as well as good agreement with certified values for lobster hepatopancreas.

I. CV-AFS: Preconcentration

In 1972, Muscat et al.[75] described a CV-AFS method for determining Hg using amalgamation with an Ag wire for preconcentration. An absolute LOD (2 σ) of 0.6 ng was observed with an RSD between 10 to 20%. Mercury concentrations in certified materials and natural sediments were determined. Ferrara et al.[76] reported the use of Au wool for preconcentration of Hg in seawater. A Hg radiofrequency electrodeless discharge lamp was used as an excitation source. A detection limit of 0.01 ng was achieved.

A method involving flow injection of Hg vapor to a Au wire absorber for preconcentration was described by Chan and Sadana.[77] The method was used to determine Hg in water samples, had a detection

limit of 2 pptr or 54 pg absolute, and 3% RSD was obtained. Cossa et al.[78] described a method of determining Hg in natural waters using preconcentration on Au-Pt gauze. The automated method analyzed eight samples per hour with a detection limit of 0.1 pptr or 4.5 pg absolute with 5% RSD. These same authors later reported a method of automated Hg determination in waters with the same LOD and precision.[79]

Poissant et al.[80] reported the first telemetry and remote sensing design for an atmospheric Hg analyzer based on CV-AFS with Au amalgamation preconcentration. This fully automated portable system permitted easy on-site monitoring, real-time data acquisition, and was usable in hazardous environments or in remote areas.

J. ETA-LEAFS

One of the advantages of AFS over AAS is that using more intense light sources can result in more sensitive measurements. Resto et al.[81] reported the use of electrothermal atomization two-step laser enhanced AFS (ETA-LEAFS) of Hg vapor in a graphite furnace. An excimer laser was used to pump two tunable dye lasers, set at 253.7 nm and 435.8 nm. A detection limit of 9 pptr or 90 fg absolute was achieved by measuring the atomic fluorescence at the 546.1 nm line. In addition, a linear dynamic range of seven orders of magnitude was reported. Pagano et al.[82] used this method to determine total mercury in microwave-digested soils and achieved a detection limit of 1.4 pptr or 14 fg absolute, which was the lowest reported absolute LOD for total Hg.

K. ICP-AFS

Lancione and Drew[83] used a commercial instrument with inductively coupled plasma atomic fluorescence spectrometry (ICP-AFS) and some modifications to determine Hg. Simultaneous element detection was possible with this instrument, and an LOD of 200 pptr was achieved. In the single element detection mode, the LOD was 40 pptr.

L. Speciation Coupled with AFS

Gas chromatography (GC) was coupled to CV-AFS by Bloom and Fitzgerald[84] for Hg determination after preconcentration from air on a Carbotrap column. The column temperature was ramped to 180°C over 20 min. The detection limits achieved were 0.3 pg for Hg and $(CH_3)_2Hg$, 0.4 pg for $(C_2H_5)_2Hg$, and 2.0 pg for CH_3HgCl. Saouter and Blattman[85] described a semiautomated analytical system for total Hg using GC-AFS with Au-coated sand preconcentration. LODs of 0.07 pptr (1.4 pg absolute) for aqueous and 1 ppb for tissue samples were reported. In addition, organic mercury was derivitized with $NaB(C_2H_5)_4$ before separation for detection limits of 0.05 pptr of CH_3Hg^+ for aqueous samples and 1.4 ppb for tissue samples. Gas chromatography was employed by Jones et al.[86] for total and organic Hg determinations in water, soil, and tissue samples. Water samples were brominated and preconcentrated onto sulfhydryl cotton fibers, and organic mercury was extracted into CH_2Cl_2 before being separated. Detection limits were 0.3 pptr or 0.6 ng absolute for inorganic Hg, 0.3 pptr or 0.6 ng for total Hg, and 0.02 pptr or 0.04 ng absolute for organic Hg, whereas in soil and tissue samples, the LOD for organic Hg was 0.2 pg absolute.

Jian and McLeod[87] carried out speciation on a column of sulfhydryl cotton for rapid sequential determination of Hg^{2+} and CH_3Hg^+ in natural water samples by FI-CV-AFS. The LOD was 6 pptr or 3 ng absolute.

M. MIP-AES

The advantages of microwave-induced plasma atomic emission spectrometry (MIP-

AES) include its high detection power, inherent multielement capability, large linear dynamic range, and high selectivity. A problem with interference is one disadvantage.

In 1994, Camuña-Aguilar et al.[88] compared three Ar and He MIPs for AES used specifically for excitation of Hg and its determination after on-line continuous CV generation. The He plasmas were found, by comparison of the analytical figures of merit, to be superior to the Ar plasmas for excitation of Hg. The best LOD for Hg, 10 pptr, was achieved with the He surfatron with a 1 mm i.d. fused silica tube as the plasma torch. In addition, a linear dynamic range of over three orders of magnitude was reported and an RSD of 4%, but the plasma was influenced by the entrance of molecular gases and water vapor. The application of these plasmas to seawater was studied.

An atmospheric pressure He MIP was used by Tanabe et al.[89] to determine Hg from solution. An LOD of 4 pptr or 8 pg absolute with 2% RSD was reported with a linear dynamic range of 2×10^5. Interferences were negligible except for Pt^{2+} and Pd^{2+}. Good agreement was reported with certified reference material values for bovine liver. Nojiri et al.[90] reported the determination of Hg in lake water with an atmospheric pressure He MIP using a Au-coated pumice amalgamation trap for preconcentration. An LOD of 0.01 pptr in 50 ml or 0.5 pg absolute was reported. Natarajan[91] reported the use of a low-power Ar MIP with amalgamation on Ag wool of Hg in solution. Determination of 50 pptr or 0.5 ng absolute is reported, and a detection limit of 0.1 ng was reported.

An atmospheric He MIP with an automated gas-handling system for GC-AES detection was reported by Quimby and Sullivan.[92] The system was optimized for microwave cavity, discharge tube, and gas flow system. Sensitivities for several elements were reported; the sensitivity for Hg was found to be 0.1 pg/s.

Tao and Miyazaki[93] reported the simultaneous determination of Hg with other elements subjected to hydride generation using a He MIP with a hydrogen separation membrane. The latter prevented byproducts of HG (H_2, CO_2, HCl, H_2O) from reaching the plasma that could be extinguished. A detection limit of 0.50 ppb for Hg was reported. Siemens et al.[94] reported the use of atmospheric pressure He and Ar MIPs for the continuous monitoring of Hg in flue gases. Both TM_{010} cavity (Beenakker resonator) and surfatron-type plasmas were tested. The detection limit of Hg in nitrogen was 8 $\mu g\ m^{-3}$ for the TM_{010} MIP and 10 $\mu g\ m^{-3}$ for the surfatron. The addition of main flue gas components such as H_2O vapor, O_2, and CO_2 were found to suppress Hg lines considerably.

N. ICP-AES

Nakahara and Wasa[95] reported a method using direct nebulization of the reductant solution for the determination of mercury with inductively coupled plasma atomic emission spectrometry (ICP-AES) in order to increase transport efficiency. Reducing agents $SnCl_2$, Na_2SO_3, NH_2OH, and $NaB(C_2H_5)_4$ were compared as reducing agents, and $SnCl_2$ was chosen because it gave the largest enhancing effect. An LOD of 1.3 ppb was reported with an RSD of 2.8%.

One problem associated with ICP-AES is its difficulty in determining trace elements in biological samples. In order to improve on this, Cañada Rudner et al.[96] reported a method of FI-ICP-AES with on-line preconcentration based on complexation of Hg with 1,5-*bis*(di-2-pyridyl)methylene thiocarbonohydrazide (DPTH) and its subsequent extraction into isobutyl methyl ketone (IBMK). Reduction and extraction from the organic phase occurred and Hg vapor was generated, followed by detection. An LOD of 2 ppb or 20 ng absolute was reported with 3.3% RSD, and few interference problems were encountered. These authors later reported a similar method[97] with which they obtained an LOD of 4 ppb or 40 ng absolute with 1% RSD.

Human hair, pig kidney, and dogfish muscle samples were analyzed with good agreement with certified values. Anderson et al.[98] reported a method for determining Hg in sediment and tissue samples using acid (HNO_3) digestion and heated permanganate oxidation, followed by $NaBH_4$ reduction and CV introduction into the plasma. The emission wavelength used was 194.2 nm, and a detection limit of 2 ppb or 20 ng absolute was reported. Excellent correlation with certified reference material values for environmental samples was achieved.

Jamoussi et al.[99] reported the use of ICP-AES to determine heavy metals in honey. Determination was carried out after high-pressure microwave digestion. A detection limit of 0.05 ppb or 5 ng absolute for Hg was reported, and the method was applied to honey samples from farms in north Tunisia. It was observed that concentrations of heavy metals lower than the safety levels established by the World Health Organization could be detected.

O. DCP-AES

A method for continuous flow CV determination of Hg by AES using reverse FI was reported by Carlos de Andrade and Bueno[100] using dc discharge He plasma atomic emission spectrometry (DCP-AES). The gas stream from the gas-liquid separator was used as the plasma medium. Preconcentration on Au foil was carried out, and a detection limit of 50 pptr or 50 pg absolute was achieved with an RSD of 1.6%. Good agreement was reported with certified reference material values for human hair.

P. Ring Discharge Plasma-AES

Wrembel[101] reported the use of ring discharge plasma AES with amalgamation preconcentration for determining Hg. The detection limit in pure water was found to be <0.5 pptr. The method was applied to synthetic and natural seawater samples.

Q. Speciation Coupled to AES

Gas chromatography (GC) was coupled with MIP-AES by Decadt et al.[102] for semiautomated headspace analysis of biological samples. This method was used to assess gas-liquid coefficients of CH_3Hg^+ halides dissolved in water or benzene. The highest vapor concentration was found to be for CH_3HgI. The method was applied to a series of biological samples with a detection limit of 1.5 ppb. The use of a headspace sampler lessened column degradation as opposed to direct on-column injection. Lansens et al.[103] used preconcentration of CH_3Hg^+ on a column of dithiocarbamate resin before converting it to the iodide and performing detection by headspace GC-MIP-AES.

Emteborg et al.[104] reported the preconcentration of CH_3Hg^+ and Hg^{2+} from humic-rich water on a dithiocarbamate resin. The Hg species were extracted and butylated before GC-injection and detection by MIP-AES. Good recoveries were reported with LODs of 0.04 ppb or 40 ng absolute for CH_3Hg^+ and 0.28 ppb or 280 ng absolute for Hg^{2+}. A purge-and-trap method of injection, which involved ethylation of the ionic species before cryogenic trapping and subsequent MIP-AES, was reported by Ceulmans and Adams.[105] LODs of 0.6 pptr or 6 pg absolute for CH_3Hg^+ and 2 pptr or 20 pg absolute for Hg^{2+} were found, and river and soil run-off samples were analyzed.

An alternating current He plasma detector was developed for GC detection by Costanzo and Barry.[106] A sensitivity of 20 pg/s for C_2H_5HgCl and 3.5 pg/s for CH_3HgCl with a linear dynamic range of three orders of magnitude was reported.

High-performance liquid chromatography (HPLC) was coupled with ICP-AES with post-column CV generation by Krull et al.[107] for Hg speciation. The ICP used had an all-glass chamber, which decreased the memory effects typically found with a polypropylene spray chamber. Detection limits (2 σ) were 37 ppb or 16 µg absolute for CH_3HgCl, 62 ppb or 31 µg absolute for CH_3CH_2HgCl, 35 ppb or 18 µg absolute for $HgCl_2$, and 62 ppb or 31 µg absolute for $(CH_3)_2Hg$. Costa-Fernández et al.[108] coupled HPLC with MIP-AES with CV generation. The vesicle-forming surfactant DDAB was employed as the HPLC mobile phase, increasing emission signals by 75%. Detection limits of 0.15 ppb for inorganic Hg and 0.35 ppb for CH_3Hg^+ were achieved, and the method was applied to natural water and human urine samples.

R. PAS

Patterson[109] reported the use of a differential photoacoustic mercury detector to determine Hg by photoacoustic spectroscopy (PAS). Gold foil within the two cells collected the Hg, and the difference between the two concentrations was measured as the differential between the photoacoustic signals detected by microphones. An LOD of <0.02 ng HG absolute was reported.

Chen et al.[110] reported the use of PAS to detect Hg^{2+} as Hg(II) dithizonate in the solid state. Mercury(II) was extracted to the organic phase as $Hg(HDz)_2$ that, under irradiation of strong visible light, underwent a reversible photochromic reaction that changed its absorption wavelength from 485 nm to 620 nm. This corresponded to an excited state of $Hg(HDz)_2$. This excited state was detected by PAS using a He-Ne laser. In this way, a detection limit of 3 pptr was achieved, with the absence of interferences because only $Hg(HDz)_2$ exhibited photochromism in the solid state. Chen and Lai[111] later reported the same measurement in organic solvents. They found a 1:1 v/v mixture of benzene and CCl_4 to be the optimum, with an LOD of 0.8 ppb.

S. METAL

Dodge and Allen[112] reported the use of metastable energy transfer for atomic luminescence (METAL) to detect trace amounts of Hg. At pressures of ~1 Torr, an electrical or microwave discharge in flowing nitrogen produced a metastable-state molecule that interacted with Hg in a reaction cell to produce a chemiluminescent reaction. Metastable state N_2 molecule has been shown to excite the 253.7 nmHg emission. This type of detection was reported to give a detection limit of 10^7 atoms cm^{-3} (3 ppq), which is the lowest reported concentration LOD. The method also had a linear dynamic range of eight orders of magnitude.

T. MIOR

Magnetically induced optical rotation (MIOR) was reported by Stephens[113] for determining Hg in vapor. Its advantages included automatic correction of continuum background absorption and of source drift. A detection limit of 10 pg absolute was achieved, and the method was noted to have good selectivity and sensitivity.

U. XRFS

D'Silva and Fassel[114] reported a method of X-ray fluorescence spectroscopy (XRFS) of Hg vapors in Ar. Good reproducibility and ppb levels of determination were achieved. Biiat et al.[115] reported an energy-dispersive XRFS method for monitoring Hg contamination. Samples of plant effluents from a lead battery plant were made into

slurries and dried for analysis. The method was noted to be capable of yielding concentration profiles. A method of total reflection XRFS was reported by Holyńska et al.[116] for analyzing potable water after preconcentration with a mixture of carbamates. A detection limit of 60 pptr or 1.8 pg absolute was reported.

V. ^{199}Hg NMR

Methylmercury complexes were indirectly determined using ^{199}Hg nuclear magnetic resonance spectroscopy (NMR) by Robert and Rabenstein.[117] The heteronuclear multiple quantum coherence (HMQC) method that was applied provided a significant sensitivity enhancement for the spectra of $CH_3Hg(II)$. The method was applied to the study of the solution chemistry of $CH_3Hg(II)$-thiol ligand complexes.

W. MPIS

Laser ionization techniques are increasingly being studied as methods for ultratrace element analysis due to their high degree of sensitivity and selectivity. Disadvantages include their expense and sometimes complicated instrumentation.

Double resonance multiphoton ionization spectroscopy (MPIS) of mercury vapor was reported by Bushaw.[118] An LOD (2 σ) of 0.22 ppb or 220 fg absolute was reported. The method was used to detect mercury levels in the ambient laboratory air. Miziolek[119] used MPI and emission analysis (RIES) to detect Hg vapor as well as to direct ionization detection. A detection limit (2 σ) of 0.17 pptr was reported for ionization monitoring and 1.4 pptr for emission detection.

X. LIBS

Lazzari et al.[120] reported the use of time-resolved laser-induced breakdown spectroscopy (LIBS) for the detection of Hg in air. A limit of detection of 5 ppb was reported, as well as good accuracy. It is recommended for *in situ* continuous monitoring of industrial processes in factories or plants.

Y. FANES

Furnace atomic nonthermal excitation spectrometry (FANES) was used for determining Hg following reduction and *in situ* preconcentration in a Pt-gauze lined graphite tube by Baxter et al.[121] An absolute detection limit of 2 pptr or 20 pg absolute was reported. Three standard reference materials, citrus leaves, pine needles, and river sediment, were analyzed after microwave digestion and accurate results were obtained for sub-ppb levels.

Z. ICP-MS: No Preconcentration

Inductively coupled plasma ionization coupled with mass spectrometry (ICP-MS) has become a popular method for trace metal analysis since the 1980s due to its superior selectivity and detection limits. One disadvantage of detection of Hg is its high ionization potential (10.44 eV) and consequently poorer degree of ionization in the ICP. The method also suffers from matrix and memory effects.

Haraldsson et al.[122] used ICP-MS for determining Hg in natural waters after reduction to its elemental form. Sodium borohydride was used as the reductant rather than $SnCl_2$ to avoid contamination of the system with Sn. Determinations both with and without isotope dilution were carried out; the LOD for both was 0.08 pptr or 8 pg absolute with an RSD of 2.7%. Natural waters and reference sediment samples were analyzed. Direct injection nebulization (DIN) was used to determine mercury in drinking water by Powell et al.[123] DIN was compared with a conventional pneumatic nebulizer (PN) and

was found to have a comparable detection limit (40 pptr for PN, 30 pptr for DIN) with a drastic reduction in memory effects.

Hydride generation (HG)-ICP-MS was reported by Brown et al.[124] for determining Hg in biota. HG was compared with PN and was found to obviate memory effects to a great extent. An LOD of 100 pptr in urine is reported.

AA. ICP-MS: Preconcentration

Flow injection with preconcentration on Au-Pt gauze to detect Hg in water samples was reported by Debrah et al.[125] An LOD of 0.2 pptr or 5 pg absolute with 1% RSD is reported. The method was used to determine Hg in seawater and freshwater reference materials with good accuracy.

Smith[126] reported the use of isotope dilution ICP-MS for the determination of Hg in water and sediments. Preconcentration on Au foil was used. Samples were submitted to 1-h acid digestion and spiked with ^{201}Hg. An LOD of 0.2 pptr or 40 pg absolute was reported, and the method was used to analyze river water standards.

BB. Speciation Coupled with ICP-MS

GC-ICP-MS was used to determine that CH_3Hg^+ was the only significant organomercury compound in two marine biological standard reference materials by Beauchemin et al.[127] Analysis of the samples was done by extracting the CH_3HgCl from the material with toluene and back extracting into an aqueous medium of cysteine acetate. Isotope dilution and FIA were used in the sample introduction. Detection limits of 4.0 ppb or 1 ng absolute for ^{201}Hg and 2.2 ppb or 0.55 ng absolute of ^{202}Hg with FIA were determined with 7% RSD. Excellent agreement with certified values for dogfish muscle and lobster hepatopancreas was achieved. Hintelmann et al.[128] used GC-ICP-MS to measure methylation rates of mercury in sediments with enriched stable Hg isotopes combined with CH_3Hg^+ determination. Methylmercury was converted to $CH_3HgC_2H_5$ using $NaB(C_2H_5)_4$ and preconcentrated on a Tenax adsorber. A detection limit of 0.02 ppb or 1 pg absolute with 4% RSD was reported. Mercury methylation was investigated by spiking sediments with stable enriched Hg isotopes at *in situ* concentrations so as not to disturb the system. More than 3% of the added Hg was found to be methylated after an incubation period of 21 d.

Speciation by LC-ICP-MS was carried out by Bushee with post-column cold vapor generation.[129] The method was found to be linear over three to four orders of magnitude with detection limits (2 σ) of 0.6 ppb for (Note: $CH_3HgOOCH_3$), 1.2 ppb for $HgCl_2$, and 1.2 ppb for CH_3CH_2HgCl. Good agreement was obtained for a tuna certified reference material and for the detection of thimerosal in contact lens solution. Shum et al.[130] used a microbore column reversed-phase LC-ICP-MS with DIN to speciate Hg and Pb compounds. A detection limit of 7 pg absolute was achieved for Hg. It was reported that the urine samples analyzed did not contain sufficient organomercurials to be detected; however, good separations were obtained when these compounds were spiked into the sample.

Reversed-phase LC-ICP-MS with ultrasonic nebulization was reported by Huang and Jiang.[131] Detection limits were reported as 0.7 ppb or 0.14 ng absolute for CH_3HgCl, 0.4 ppb or 0.08 ng absolute for $HgCl_2$, and 0.8 ppb or 0.16 ng absolute for C_2H_5HgCl, and were compared with other LC coupled methods. Samples of contact lens solution, waste water, and fish were all analyzed, and the results were found to be in good agreement with certified values. Mercury species in seawater were determined by LC-ICP-MS by Bloxham et al. using a C_{18} column.[132] Detection limits in seawater of 0.25 ppb or 0.25 ng absolute CH_3HgCl and $HgCl_2$ and

0.75 ppb or 0.75 ng absolute C_2H_5HgCl were achieved. Using off-line preconcentration on a dithiocarbamate resin gave detection limits (2 σ) of 16 pptr or 16 ng absolute for CH_3HgCl and 17 pptr or 17 ng absolute for $HgCl_2$.

CC. Spectrophotometry

The determination of Hg^{2+} and $C_6H_5Hg^+$ using polyurethane foam (PUF) thin-layer spectrophotometry was reported by Abbas et al.[133] The PUF was loaded with dithizone to allow preconcentration of Hg^{2+} and $C_6H_5Hg^+$. The detection limit (2 σ) for Hg^{2+} was 5 ppb or 0.05 ng absolute and for $C_6H_5Hg^+$, 10 ppb or 0.1 ng absolute. Ag was found to interfere. A method involving the spectrophotometric determination of Hg as its dithizone complex in the presence of a neutral surfactant was reported by Singh et al.[134] The surfactant Triton X-100 allowed both the ligand and complex to be water soluble so the analysis could be carried out in aqueous media. An LOD of 1×10^{-6} *M* (200 ppb) or 20 ng absolute Hg^{2+} was reported, and the method was applied successfully to the analysis of a Hg-based pesticide. Ramesh[135] reported a method based on the spectrophotometric detection of an abstraction of CN^- from hexacyanoferrate(II) by Hg^{2+} in the presence of 4-(2′-thiazolylazo)resacetophenone oxime. The method allowed the determination of Hg down to 10 ppb or 1 ng absolute and was noted to be highly sensitive and accurate.

The determination of Hg based on its inhibitory effect on horseradish peroxidase that was immobilized on solid supports was reported by Shekhovtsova and Chernetskaya.[136] The inhibition of the enzyme increased in the presence of thiourea. Detection limits were reported as 0.1 to 10 pptr, depending on the specific indicator reaction. The reaction was complete in 15 min. A later report by Shekhovtsova et al.[137] determined Hg in natural water by this method in the presence of Fe, which is normally found in natural water. A detection limit of 10 pptr with 6% RSD was reported.

Trace amounts of Hg in wastewater were determined with *p*-azobenzenediazoaminoazobenzene sulfonic acid by Jiang et al.[138] The compound formed a red complex (528 nm) with Hg^{2+} in the presence of Triton X-100 and NH_3NH_4Cl. Spectrophotometric determination of the complex gave a detection limit of 6×10^{-8} *M* (12 ppb) or 0.5 ng absolute. The only interference was Cd, which could be masked with nitrilotriacetic acid.

DD. Fluorimetry

In 1973, Holzbecher and Ryan[139] reported the first observation of a Hg-complex induced fluorescence (at 440 nm) with an Hg-thiamine complex. In this way, Hg in solutions with low salt concentrations could be detected down to 10 ppb or 1 ng absolute with 3.2% RSD. Interferences included Fe^{2+} and Fe^{3+}. Fluorimetry was used by Narinesingh et al.[140] in a screening method for trace Hg analysis using FI; the method was based on the inhibitory effect Hg has on the enzyme urease. Urease catalyzes the conversion of urea to carbon dioxide; by fluorimetrically monitoring ammonia using *o*-phthaladehyde as the fluorophore, the activity of the enzyme could be determined and Hg concentrations could be detected down to an LOD of 2 ppb. This screening method could be used to determine other heavy metals as well.

IV. RADIOCHEMICAL METHODS

A. RNAA

Radiometric methods of analysis are suitable for trace metal analysis because they are simple, sensitive, and rapid. At the same time, they are virtually blank-free by nature.

Kučera and Soukal[141] reported a method of radiochemical neutron activation analysis (RNAA) of several metals, including Hg, in biological reference materials. The samples were decomposed with HNO_3 in Teflon® bombs heated to 150°C. Mercury was extracted from the sample using extraction by 0.01 *M* $Ni(DDC)_2$ in chloroform. Very good agreement of results with certified values was achieved, even at sub-ppb levels.

B. NAA

Shetty et al.[142] reported the determination of Hg in biological and environmental samples by neutron activation analysis (NAA). Mercury was separated from the samples after digestion in H_2SO_4 by ion extraction chromatography on a Chelex 100 anion exchange column. The Hg was selectively separated as $Hg(SO_4)_2^{2-}$, which was assumed to be the dominant form of Hg in the solution. The method was applied to orchard leaves and tuna fish certified reference materials, with good accuracy in the ppb range.

C. IDA

Substoichiometric isotope dilution analysis (IDA) for the determination of Hg was reported by Sandhya and Subramanian.[143] After preconcentration with a dithizone complex onto microcrystalline naphthalene, both labeled and inactive Hg were extracted into a CCl_4 solution containing α-Thiopicolin-*o*-anisylamide, a good ligand for Hg due to its affinity for S. The solution was analyzed with a scintillation detector. A detection limit of 20 ppb or 200 ng absolute with 4.16% RSD was reported.

V. ELECTROCHEMICAL METHODS

A. Gold Film Sensors

In 1972, McNerny et al.[144] reported a method for detecting Hg via its amalgamation on thin films of Au. The method depended on the significant increase in resistance that Au undergoes after the adsorption of Hg. They reported the change in resistance to be linear in nanogram amounts and noted an LOD of 0.05 ng of Hg. Crenshaw et al.[145] reported the use of Au film detectors for detecting Hg to locate the fault of an active volcano in Nicaragua. They had previously determined that Hg and Rn levels at known faults were 75% higher than normal. Ping and Dasgupta[146] determined total Hg in water using a Au film sensor following Fenton's reagent ($Fe(II) + H_2O_2$) digestion. Inorganic Hg is reduced to its elemental form and liberated to a conductimetric Au film. A detection limit of 10 pptr or 500 pg Hg absolute is reported.

B. ISE

An ion-selective electrode (ISE) array can allow for simultaneous and accurate detection when many interfering ions may be present. A composite graphite ion-selective electrode array was used for the detection of Hg and other relevant ions in aquatic systems by Shatkin et al.[147] The mercury ISE was responsive to changing halide concentrations, which were interpreted as Hg halide speciation in solution. Also included was an array of halide-detecting electrodes, which are a necessary first step toward developing an ion-selective microelectrode array. The electrodes have an easily renewable surface of 13 mm^2.

C. ASV

Traces of Hg were determined by Gao et al.[148] with a ferrocenoylpolythia crown ether-Nafion-modified glassy carbon electrode. Mercury was accumulated on the electrode surface by the complexing effect of the modifier during the electrochemical deposition then determined by anodic stripping

voltammetry (ASV). A detection limit of 1×10^{-9} *M* (0.2 ppb) with 3.8% RSD was achieved with 5-min preconcentration. The procedure was applied to Hg in hair, water, and urine samples. Turyan and Mandler[149] used a glass carbon electrode spin coated with 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane for very selective determination of Hg with no preconcentration by square wave ASV. The LOD was reported as $<10^{-12}$ *M* (0.2 pptr) with 3.3% RSD, and the method was used to determine the concentration of Hg in seawater as 1.01×10^{-11} *M*. Good selectivity was reported, with negligible interference from Zn, Cu, Pb, Mn, of Ag. Zen and Chung[150] used a poly(4-vinylpyridine)/gold film electrode to determine trace mercury in real samples by square-wave ASV. Mercury was preconcentrated by the ion exchange effect of the PVP as well as by amalgamation with Au. The electrode was resistant to interfering ions, especially Cu^{2+}, and could be easily renewed. A detection limit of 0.1 ppb with preconcentration was reported, and the method was applied to various water samples.

Mercury sorbed onto a rotating disk electrode was determined by differential pulse (DP)-ASV by Scholz et al.[151] Detection limits of 30 ng absolute in solution (with 6% RSD) and 1.7 pptr in air with a preconcentration time of 10 min were achieved. A glassy carbon rod coated with 2-mercaptobenzimidazole was used by Sousa and Bertazzoli[152] to determine Hg after preconcentration by DP-ASV. A detection limit of 0.1 ppm with 5% RSD was reported, as well as good discrimination against interference from Cu^{2+}. An Au-coated carbon electrode was used to determine Hg in water and biological samples via DP-ASV by Lo and Lee.[153] The Hg was preconcentrated by extraction with diethyldithiocarbamate and back extraction with Au^{3+}. Reliability and accuracy of this novel method were confirmed from the analysis of NBS biological standard reference materials.

The electrochemical quartz crystal microbalance was used as an ASV detector for trace mercury analysis by Andersen et al.[154] This method involved either the deposition of the ions from solution to an electrode on the crystal and measuring the resulting frequency changes or stripping the electrode quickly while measuring the frequency in order to eliminate the drift in crystal frequency during the long deposition time. A detection limit of 1 ppb was obtained.

D. PSA

Wang and Tian[155] used screen-printed carbon-strip electrodes coated with a thin Au film for potentiometric stripping analysis (PSA). For 4-min deposition, an LOD of 0.5 ppb was obtained with 2.5% RSD. The applicability of the method to the determination of alkyl mercury and selenium was also demonstrated. Interferences included Rh^{3+} and Pd^{2+}.

E. CSP

The use of a large surface porous electrode plated with a thin layer of Au was reported by Beinrohr et al.[156] for trace detection of Hg in a flow system by current stripping chronopotentiometry (CSP). Because complete electrochemical yields were achieved at both the deposition and dissolution steps, the Hg concentration in the sample solution could be calculated from Faraday's Law. A detection limit of 0.1 ppb or 0.01 ng absolute with 4% RSD was reported. Interferences included Fe^{3+}, NO_x, and CO_2.

F. DPV

Differential pulse voltammetry (DPV) was used by Ugo et al.[157] with glassy carbon electrodes modified with Tosflex®, a

polycationic polymer. In this way, they detected $HgCl_4^{2-}$, the prevailing inorganic Hg(II) species in seawater and other chlorine media. A detection limit of 10^{-11} *M* (2 pptr) was reported, and an analytical procedure for the determination of Hg in coastal waters samples was proposed and experimentally tested.

G. VSA

Khan et al.[158] described the use of a graphite tube modified with 2-mercaptobenzothiazole for carrying out voltammetric stripping analysis (VSA) of Hg^{2+}. Mercury was preconcentrated for 2 min on the electrode before being stripped. The fabricated electrode possessed good stability and had an extended lifetime. An LOD of 3.0×10^{-9} *M* (0.6 ppb) was reported with 2.6% RSD. Good agreement was found with a certified aqueous sample.

H. Conductimetry

Liu et al.[159] reported the use of a novel technique for measuring trace Hg based on its inhibitory effect on urease. Mercury(II) inhibits the urease-catalyzed urea hydrolysis by binding with SH groups of urease. The inhibited enzymatic reaction was monitored by a SAW device with a pair of parallel electrodes. A change in electrolyte conductivity in the solution resulted in a frequency response of the standing acoustic wave (SAW)/impedance enzyme transducer that corresponded to Hg^{2+} concentration. A LOD of 20 ppb or 2 ng absolute was reported with an RSD of 2.9%. The method was used successfully for the determination of trace amounts of mercury in waste water.

I. Electrochemical Biosensor

The use of an electrochemical enzyme glucose probe for the determination of Hg^{2+}, CH_3Hg^+, and $C_2H_5Hg^+$ was reported by Amine et al.[160] Mercury and its compounds inhibited the enzyme invertase that, in the presence of its substrate, sucrose, produced glucose. The decrease in glucose production caused by the inhibition of the enzyme was correlated to the concentration of mercury in solution. The three species of mercury were directly detected in solution with LODs of 1 ppb or 0.4 ng absolute for Hg^{2+} and 2 ppb or 0.8 ng absolute for CH_3Hg^+ and $C_2H_5Hg^+$.

VI. CONCLUSIONS

It is clear from the papers reviewed here that CV-AAS remains the most popular method for the trace detection of mercury. At the same time, CV-AFS is becoming more visible due to its simpler instrumentation and ultralow detection limits, as evidenced by its approval by the U.S. Environmental Protection Agency.

Detection limits for Hg using plasma AES and ICP-MS are limited by the high ionization potential of Hg, which cannot be efficiently reached in most plasmas. Exceptions are the He MIP and ring discharge plasma, which combined with AES offers LODs comparable to those using CV-AAS and CV-AFS. An advantage of these methods is their simultaneous multielement capabilities.

Laser ionization and fluorescence techniques clearly offer superior absolute detection limits, but only comparable concentration limits while using expensive, often complicated equipment.

Additional advantages of spectrometric methods include their amenability to automation and coupling with chromatographic methods for speciation. The use of chromatography to separate and speciate different inorganic and organic forms of Hg is of importance due to the varying toxicity of the different forms, especially in environmental samples. Ultralow level detection of CH_3Hg^+ species is especially important due to its high toxicity.

Electrochemical methods offer simplicity and inexpensive instrumentation but are not generally capable (with some exceptions) of speciating and detecting the sub-ppb levels at which Hg is still critical. Radiometric methods offer nondestructive analysis with high sensitivity and fewer reagents, but are not widely used due to the equipment and instrumentation required.

Lowering detection limits without loss of analyte or contamination will continue to be the main difficulties to overcome in the detection of Hg as research continues in the direction of analyzing real samples, such as sediments or biological tissues. In addition, the speciation of different Hg compounds will continue to be critical, as it becomes more clear the toxicity levels of the various forms.

In 1991, it was reported that as sampling techniques improved over just a few years, the estimates of Hg concentrations in one lake dropped by a factor of 500.[161] As external contamination of real samples decreases, it becomes increasingly clear the minimal concentrations and amounts of Hg that can pose an environmental and health threat. Improvements in sample handling and preparation along with increasingly sensitive techniques will be needed to face these challenges in trace analysis of Hg.

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APPENDIX 1

Glossary of acronyms used in this review.

AAS, atomic absorption spectrometry; **AES**, atomic emission spectrometry; **AFS**, atomic fluorescence spectrometry; **ASV**, anodic stripping voltammetry; **CSP**, current stripping chropotentiometry; **CV**, cold vapor (as in CV-AAS); **DCP**, DC discharge plasma (as in DCP-AES); **DIN**, direct injection nebulization (as in DIN-ICP-MS); **DP**, differential pulse (as in DP-ASV); **DPV**, differential pulse voltammetry; **ETA**, electrothermal atomization (as in ETA-LEAFS); **F**, flame (as in F-AFS); **FANES**, furnace atomic nonthermal excitation spectrometry; **FI**, flow injection (as in FI-ICP-MS); **FIA**, flow injection analysis; **GC**, gas chromatography; **HG**, hydride generation (as in HG-MIP-AES); **HPLC**, high-performance liquid chromatography; **ICP**, inductively coupled plasma (as in ICP-MS); **IDA**, isotope dilution analysis; **ISE**, ion-selective electrode; **LC**, liquid chromatography; **LDR**, linear dynamic range; defined as the range of concentrations (beginning at the LOD) for which the signal is linear with concentration; **LEAFS**, laser-enhanced atomic fluorescence spectroscopy; **LIBS**, laser-induced breakdown spectroscopy; **LOD**, limit of detection, defined as 3 × standard deviation of the blank signal (3 σ), unless otherwise noted; **METAL**, metastable energy transfer for atomic luminescence; **MIOR**, magnetically induced optical rotation; **MIP**, microwave-induced plasma (as in MIP-AES); **MPIS**, multiphoton ionization spectroscopy; **MS**, mass spectrometry; **NAA**, neutron activation analysis; **NMR**, nuclear magnetic resonance (spectroscopy); **PAS**, photoacoustic spectroscopy; **PN**, pneumatic nebulization (as in PN-ICP-MS); **PSA**, potentiometric stripping analysis; **RIES**, resonance ionization emission spectroscopy; **RNAA**, radiochemical neutron activation analysis; **RSD**, relative standard deviation (between identical samples); indicates the precision of the method; **SAW**, standing acoustic wave; **VSA**, voltammetric stripping analy-

sis; **XRFS**, X-ray fluorescence spectroscopy.

REFERENCES

1. **Barbosa, A. C.; Boischio, A. A.; East, G. A.; Ferrari, I.; Goncalves, A.; Silva, P. R. M.; da Cruz, T. M. E.** *Water, Air, Soil Pollut.* 1995, 80, 109–21.
2. **Homewood, B.** *New Sci.* 1991, Nov. 9, 18.
3. **Glass, G. E.; Sorensen, J. A.; Schmidt, K. W.; Rapp, G. R.** *Environ. Sci. Technol.* 1990, 24, 1059–69.
4. **Glass, G. E.; Sorensen, J. A.; Schmidt, K. W.; Rapp, G. R.; Yap, D.; Fraser, D.** *Water, Air, Soil Pollut.* 1995, 80, 235–44.
5. **Fleming, L. E.; Watkins, S.; Kaderman, R.; Levin, B.; Ayyar, D. R.; Bizzio, M.; Stephens, D.; Bean, J. A.** *Water, Air, Soil Pollut.* 1995, 80, 41–8.
6. **Rood, B. E.; Gottgens, J. F.; Delfino, J. J.; Earle, C. D.; Crisman, T. L.** *Water, Air, Soil Pollut.* 1995, 80, 981–90.
7. **Woodson, T. T.** *Rev. Sci. Instrum.* 1939, 10, 308–11.
8. **Chilov, S. Talanta,** 1975, 22, 205–32.
9. Analytical Methods Committee, Society for Analytical Chemistry. *Analyst* 1965, 90, 515–30.
10. **Ure, A. M.** *Anal.Chim. Acta* 1975, 76, 1–26.
11. **Morita, H.; Tanaka, H.; Smimomura, S.** *Spectrochim. Acta Part B* 1995, 50, 69–84.
12. **Muscat, V. I.; Vickers, T. J.; Andren, A.** *Anal. Chem.* 1972, 44, 218–21.
13. **Jensen, S.; Jernelov, A.** *Nature* 1968, 223, 753–4.
14. **Wood, J. M.; Kennedy, F. S.; Rosen, C. G.** *Nature* 1968, 220, 173–4.
15. **Rapsomanikis, S.; Weber, J. H.,** in *Organometallic Compounds in the Environment;* P. J. Craig, Ed.; Longmans: Harlow, 1986; p. 279.
16. **Hatch, W. R.; Ott, W. L.** *Anal. Chem.* 1968, 40, 2085–7.
17. **Gilbert, T. R.; Hume, D. N.** *Anal. Chim. Acta* 1973, 65, 461–5.
18. **Zhou, C. Y.; Wong, M. K.; Koh, L. L.; Wee, Y. C.** *Anal. Sci.* 1996, 12, 471–6.
19. **Toffaletti, J.; Savory, J.** *Anal. Chem.* 1975, 47, 2091–5.
20. **Rooney, R. C.** *Analyst* 1976, 101, 678–82.
21. **Yamamoto, Y.; Kumamaru, T.; Shiraki, A.** *Fresenius Z. Anal. Chem.* 1978, 292, 273–7.
22. **Welz, B.; Schubert-Jacobs, M.** *Fresenius Z. Anal. Chem.* 1988, 331, 324–9.
23. **Brindle, I. D.; Zheng, S.** *Spectrochim. Acta Part B* 1996, 51, 1777–80.
24. **Tong, S.** *Anal. Chem.* 1978, 50, 412–4.
25. **Oda, C. E.; Ingle, J. D. Jr.** *Anal. Chem.* 1981, 53, 2030–3.
26. **Goto, M.; Shibakawa, T.; Arita, T.; Ishii, D.** *Anal. Chim. Acta* 1982, 140, 179–85.
27. **Colina de Vargas, M.; Romero, R. A.** *At. Spectrosc.* 1989, 10, 160–4.
28. **Yamada, E.; Yamada, T.; Sato, M.** *Anal. Sci.* 1992, 8, 863–8.
29. **Saraswati, R.; Beck, C. M.; Epstein, M. S.** *Talanta* 1993, 40, 1477–80.
30. **Hanna, C. P.; McIntosh, S. A.** *At. Spectrosc.* 1995, 16, 106–14.
31. **Murphy, J.; Jones, P.; Hill, S. J.** *Spectrochim. Acta Part B* 1996, 51, 1867–73.
32. **Dumarey, R.; Heindryckx, R.; Dams, R.; Hoste, J.** *Anal. Chim. Acta* 1979, 107, 159–67.
33. **Dumarey, R.; Dams, R.; Hoste, J.** *Anal. Chem.* 1985, 57, 2638–43.
34. **Yoshida, Z.; Motojima, K.** *Anal. Chim. Acta* 1979, 106, 405–10.
35. **Fitzgerald, W. F.; Gill, G. A.** *Anal. Chem.* 1979, 51, 1714–20.
36. **Ólafsson, J.** *Anal. Chim. Acta* 1974, 68, 207–11.
37. **Freimann, P.; Schmidt, D.** *Fresenius Z. Anal. Chem.* 1982, 313, 200–2.

38. **Welz, B.; Melcher, M.; Sinemus, H. S.; Maier, D.** *At. Spectrosc.* 1984, 5, 37–42.

39. **Temmerman, E.; Dumarey, R.; Dams, R.** *Anal. Lett.* 1985, 18, 203–16.

40. **Gill, G. A.; Fitzgerald, W. F.** *Mar. Chem.* 1987, 20, 227–43.

41. **Welz, B.; Tsalev, D.; Sperling, M.** *Anal. Chim. Acta* 1992, 261, 91–103.

42. **Hanna, C. P.; Tyson, J. F., McIntosh, S.** *Anal. Chem.* 1993, 65, 653–6.

43. **McIntosh, S.** *At. Spectrosc.* 1993, 14, 47–9.

44. **Streško, V.; Polakovičová, J.; Kubová, J.** *J. Anal. At. Spectr.* 1994, 9, 1173–5.

45. **Garcia, M. F.; Garcia, R. P.; Garcia, N. B.; Sanz-Medel, A.** *Talanta* 1994, 41, 1833–9.

46. **Matsunaga, K.; Takahashi, S.** *Anal. Chim. Acta* 1976, 87, 487–9.

47. **Dumarey, R.; Heindryckx, R.; Dams, R.** *Anal. Chim. Acta* 1980, 118, 381–3.

48. **Vermeir, G.; Vandecasteele, C.; Temmerman, E.; Dams, R.; Versieck, J.** *Mikrochim. Acta* 1988, 111, 305–13.

49. **Horvat, M.; Lupšina, V.; Pihlar, B.** *Anal. Chim. Acta* 1991, 243, 71–9.

50. **Brandvold, D. K.; Martinez, P.; Matlock, C.** *Anal. Instr.* 1993, 21, 63–7.

51. **Ombaba, J. M.** *Microchem. J.* 1996, 53, 195–200.

52. **Ellis, L. A.; Roberts, D. J.** *J. Anal. At. Spectr.* 1996, 11, 1063–6.

53. **Keller, B. J.; Peden, M. E.; Rattonetti, A.** *Anal. Chem.* 1984, 56, 2617–8.

54. **Hladký, Z.; Říšova, J.; Fišera, M.** *J. Anal. At. Spectr.* 1990, 5, 691–2.

55. **Lee, S. H.; Jung, K. H.; Lee, D. S.** *Talanta* 1989, 36, 999–1003.

56. **Siemer, D. D.; Hageman, L.** *Anal. Chem.* 1980, 52, 105–8.

57. **Baxter, D. C.; Frech, W.** *Anal. Chim. Acta* 1989, 225, 175–83.

58. **Rapsomanikis, S.; Craig, P. J.** *Anal. Chim. Acta* 1991, 248, 563–7.

59. **Fischer, R.; Rapsomanikis, S.; Andreae, M. O.** *Anal. Chem.* 1993, 65, 763–6.

60. **Emteborg, H.; Sinemus, H. W.; Radziuk, B.; Baxter, D. C.; Frech, W.** *Spectrochim. Acta. Part B* 1996, 51, 829–37.

61. **Ahmed, R.; May, K.; Stoeppler, M.** *Fresenius Z. Anal. Chem.* 1987, 326, 510–6.

62. **Sarzanini, C.; Sacchero, G.; Aceto, M.; Abollino, O.; Mentasti, E.** *Anal. Chim. Acta* 1994, 284, 661–7.

63. **Fujita, M.; Takabatake, E.** *Anal. Chem.* 1983, 55, 454–7.

64. **Aizpun, B.; Fernández, M. L.; Blanco, E.; Sanz-Medel, A.** *J. Anal. At. Spectr.* 1994, 9, 1279–84.

65. **Madrid, Y.; Cabrera, C.; Perez-Corona, T.; Cámara, C.** *Anal. Chem.* 1995, 67, 750–4.

66. **Winefordner, J. D.; Staab, R. A.** *Anal. Chem.* 1964, 36, 165–8.

67. **Hutton, R. C.; Preston, B.** *Analyst* 1980, 105, 981–4.

68. **Morita, H.; Kimoto, T.; Shimomura, S.** *Anal. Lett.* 1983, 16, 1187–95.

69. **Swift, R. P.; Campbell, J. E.** *Spectroscopy* 1993, 8, 38–47.

70. **Lamble, K. J.; Hill, S. J.** *J. Anal. At. Spectr.* 1996, 11, 1099–103.

71. **Stockwell, P. B.; Corns, W. T.** *Analyst* 1994, 119, 1641–5.

72. **Janjic, J.; Kiurski, J.** *Water Res.* 1994, 28, 233–5.

73. **Corns, W. T.; Stockwell, P. B.; Jameel, M.** *Analyst* 1994, 119, 2481–4.

74. **Bloxham, M. J.; Hill, S. J.; Worsfold, P. J.** *J. Anal. At. Spectr.* 1996, 11, 511–4.

75. **Muscat, V. I.; Vickers, T. J.; Andren, A.** *Anal. Chem.* 1972, 44, 218–21.

76. **Ferrara, R.; Seritti, A.; Barghigiani, C.; Petrosino, A.** *Anal. Chim. Acta* 1980, 117, 391–5.

77. **Chan, C. C. Y.; Sadana, R. S.** *Anal. Chim. Acta* 1993, 282, 109–15.

78. **Cossa, D.; Sanjuan, J.; Cloud, J.; Stockwell, P. B.; Corns, W. T.** *J. Anal. At. Spectr.* 1995, 10, 287–91.

79. **Cossa, D.; Sanjuan, J.; Cloud, J.; Stockwell, P. B.; Corns, W. T.** *Water, Air, Soil Pollut.* 1995, 80, 1279–84.

80. **Poissant, L.; Harvey, B.; Casimir, A.** *Env. Technol.* 1996, 17, 891–6.

81. **Resto, W.; Badini, R. G.; Smith, B. W.; Stevenson, C. L.; Winefordner, J. D.** *Spectrochim. Acta. Part B* 1993, 48, 627–32.

82. **Pagano, S. T.; Smith, B. W.; Winefordner, J. D.** *Talanta* 1994, 41, 2073–8.

83. **Lancione, R. L.; Drew, D. M.** *Spectrochim. Acta. Part B* 1985, 40, 107–13.

84. **Bloom, N.; Fitzgerald, W. F.** *Anal. Chim. Acta* 1988, 208, 151–61.

85. **Saouter, E.; Blattmann, B.** *Anal. Chem.* 1994, 66, 2031–7.

86. **Jones, R. D.; Jacobson, M. E.; Jaffe, R.; West-Thomas, J.; Arfstrom, C.; Alli, A.** *Water, Air, Soil Pollut.* 1995, 80, 1285–94.

87. **Jian, W.; McLeod, C. W.** *Talanta* 1992, 39, 1537–42.

88. **Camuña-Aguilar, J. F.; Pereiro-Garcia, R.; Sánchez-Uría, J. E.; Sanz-Medel, A.** *Spectrochim. Acta. Part B* 1994, 49, 475–84.

89. **Tanabe, K.; Chiba, K.; Haraguchi, H.; Fuwa, K.** *Anal. Chem.* 1981, 53, 1450–3.

90. **Nojiri, Y.; Otsuki, A.; Fuwa, K.** *Anal. Chem.* 1986, 58, 544–7.

91. **Natarajan, S.** *At. Spectrosc.* 1988, 9, 59–62.

92. **Quimby, B. D.; Sullivan, J. J.** *Anal. Chem.* 1990, 62, 1027–34.

93. **Tao, H.; Miyazaki, A.** *Anal. Sci.* 1991, 7, 55–9.

94. **Siemens, V.; Harju, T.; Laitinen, T.; Larjava, K.; Broekaert, J. A. C.** *Fresenius J. Anal. Chem.* 1995, 351, 11–8.

95. **Nakahara, T.; Wasa, T.** *Bull. Chem. Soc. Jpn.* 1992, 65, 1165–7.

96. **Cañada Rudner, P.; Garcia de Torres, A.; Cano Pavón, J. M.** *J. Anal. At. Spectr.* 1993, 8, 705–9.

97. **Cañada Rudner, P.; Cano Pavón, J. M.; Garcia de Torres, A.; Sanchez Rojas, F.** *Fresenius J. Anal. Chem.* 1995, 352, 615–7.

98. **Anderson, K. A.; Isaacs, B.; Tracy, M.; Möller, G. J.** AOAC Int. 1994, 77, 473–9.

99. **Jamoussi, B.; Zafaouf, M.; Hassine, B. B.** *Int. J. Environ. Anal. Chem.* 1995, 61, 249–56.

100. **Carlos de Andrade, J.; Bueno, M. I. M. S.** *Spectrochim. Acta. Part B* 1994, 49, 787–95.

101. **Wrembel, H. Z.** *Spectrochim. Acta. Part B* 1986, 41, 247–56.

102. **Decadt, G.; Baeyens, W.; Bradley, D.; Goeyens, L.** *Anal. Chem.* 1985, 57, 2788–91.

103. **Lansens, P.; Meulman, C.; Leermakers, M.; Baeyens, W.** *Anal. Chim. Acta* 1990, 234, 417–24.

104. **Emteborg, H.; Baxter, D. C.; Sharp, M.; Frech, W.** *Analyst* 1995, 120, 69–77.

105. **Ceulemans, M.; Adams, F. C.** *J. Anal. At. Spectr.* 1996, 11, 201–6.

106. **Costanzo, R. B.; Barry, E. F.** *Anal. Chem.* 1988, 60, 826–9.

107. **Krull, I. S.; Bushee, D. S.; Schleicher, R. G.; Smith, S. B. Jr.** *Analyst* 1986, 111, 345–9.

108. **Costa-Fernández, J. M.; Lunzer, F.; Pereiro-García, R.; Sanz-Medel, A.** *J. Anal. At. Spectr.* 1995, 10, 1019–25.

109. **Patterson, J. E.** *Anal. Chim. Acta* 1984, 164, 119–26.

110. **Chen, N.; Guo, R.; Lai, E. P. C.** *Anal. Chem.* 1988, 60, 2435–9.

111. **Chen, N.; Lai, E. P. C.** *Talanta* 1989, 36, 479–83.

112. **Dodge, W. B. III; Allen, R. O.** *Anal. Chem.* 1981, 53, 1279–86.

113. **Stephens, R.** *Anal. Chim. Acta* 1978, 98, 291–8.

114. **D'Silva, A.; Fassel, V. A.** *Anal. Chem.* 1972, 44, 2115–6.

115. **Biiat, C. K.; Bhat, C. L.; Lodha, G. S.; Koul, D. K.** *Environ. Monit. Assess.* 1996, 41, 77–86.

116. **Holynska, B.; Ostachowica, B.; Wegrzynek, D.** *Spectrochim. Acta. Part B* 1996, 51, 769–73.

117. **Robert, J. M.; Rabenstein, D. L.** *Anal. Chem.* 1991, 63, 2674–9.

118. **Bushaw, B. A.** *Anal. Chem.* 1985, 57, 2397–9.

119. **Miziolek, A. W.** *Anal. Chem.* 1981, 53, 118–20.

120. **Lazzari, C.; De Rosa, M.; Rastelli, S.; Ciucci, A.; Palleschi, V.; Salvetti, A.** *Laser Part. Beams* 1994, 12, 525–30.

121. **Baxter, D. C.; Nichol, R.; Littlejohn, D.** *Spectrochim. Acta. Part B* 1992, 47, 1155–63.

122. **Haraldsson, C.; Westerlund, S.; Öhman, P.** *Anal. Chim. Acta* 1989, 221, 77–84.

123. **Powell, M. J.; Quan, E. S. K.; Boomer, D. W.; Wiederin, D. R.** *Anal. Chem.* 1992, 64, 2253–7.

124. **Brown, R.; Gray, D. J.; Tye, D.** *Water, Air, Soil Pollut.* 1995, 80, 1237–45.

125. **Debrah, E.; Denoyer, E. R.; Tyson, J. F.** *J. Anal. At. Spectr.* 1996, 11, 127–32.

126. **Smith, R. G.** *Anal. Chem.* 1993, 65, 2485–8.

127. **Beauchemin, D.; Siu, K. W. M.; Berman, S. S.** *Anal. Chem.* 1988, 60, 2587–90.

128. **Hintelmann, H.; Evans, R. D.; Villeneuve, J. V.** *J. Anal. At. Spectr.* 1995, 10, 619–24.

129. **Bushee, D. S.** *Analyst* 1988, 113, 1167–70.

130. **Shum, S. C. K.; Pang, H.; Houk, R. S.** *Anal. Chem.* 1992, 64, 2444–50.

131. **Huang, C.; Jiang, S.** *J. Anal. At. Spectr.* 1993, 8, 681–6.

132. **Bioxham, M. J.; Gachanja, A.; Hill, S. J.; Worsfold, P. J.** *J. Anal. At. Spectr.* 1996, 11, 145–8.

133. **Abbas, M. N.; EL-Assy, N. B.; Abdel-Moniem, SH.** *Anal. Lett.* 1989, 22, 2575–85.

134. **Singh, H. B.; Kumar, B.; Sharma, R. L.; Katyal, M.** *Analyst* 1989, 114, 853–5.

135. **Ramesh, A.** *Analyst* 1993, 118, 945–6.

136. **Shekhovtsova, T. N.; Chernetskaya, S. V.** *Anal. Lett.* 1994, 27, 2883–98.

137. **Shekhovtsova, T. N.; Chernetskaya, S. V.; Dolmanova, I. F.** J. Anal. Chem. 1995, 50, 280–2.

138. **Jiang, W.; Zhu, Y.; Jin, G.; Wu, G.** *Anal. Lett.* 1996, 29, 2221–6.

139. **Holzbecher, J.; Ryan, D. E.** *Anal. Chim. Acta* 1973, 64, 333–6.

140. **Narinesingh, D.; Mungal, R.; Ngo, T. T.** *Anal. Chim. Acta* 1994, 292, 185–90.

141. **Kučera, J.; Soukal, L.** *J. Radioanal. Nucl. Chem.* 1993, 168, 185–99.

142. **Shetty, P.; Moosavi-Movahedi, A. A.; Rengan, K.** *J. Radioanal. Nucl. Chem.* 1994, 182, 205–11.

143. **Sandhya, D.; Subramanian, M. S.** *Radiochim. Acta* 1994, 65, 105–9.

144. **McNerny, J. J.; Busceck, P. R.; Hanson, R. C.** *Science* 1972, 178, 611–2.

145. **Crenshaw, W. B.; Williams, S. N.; Stoiber, R. E.** *Nature* 1982, 300, 345–6.

146. **Ping, L.; Dasgupta, P. K.** *Anal. Chem.* 1989, 61, 1230–5.

147. **Shatkin, J. A.; Brown, H. S.; Licht, S.** *Anal. Chem.* 1995, 67, 1147–51.

148. **Gao, Z.; Li, P.; Zhao, Z.** *Microchem. J.* 1991, 43, 121–32.

149. **Turyan, I.; Mandler, D.** *Nature* 1993, 362, 703–4.

150. **Zen, J.; Chung, M.** *Anal. Chem.* 1995, 67, 3571–7.

151. **Scholz, F.; Nitschke, L.; Henrion, G.** *Anal. Chim. Acta* 1987, 199, 167–71.

152. **Sousa, M. de F. B.; Bertazzoli, R.** *Anal. Chem.* 1996, 68, 1258–61.

153. **Lo, J.; Lee, J.** *Anal. Chem.* 1994, 66, 1242–8.

154. **Andersen, N. P. R.; Holst-Hansen, P.; Britz, D.** *Anal. Chim. Acta* 1996, 329, 253–6.

155. **Wang, J.; Tian, B.** *Anal. Chim. Acta* 1993, 274, 1–6.

156. **Beinrohr, E.; Čakrt, M.; Dzurov, J.; Kottaš, P.; Kozáková, E.** *Fresenius J. Anal. Chem.* 1996, 365, 253–8.

157. **Ugo, P.; Moretto, L. M.; Mazzocchin, G. A.** *Anal. Chim. Acta* 1995, 305, 74–82.

158. **Khan, M. R.; Khoo, S. B.** *Anal. Chem.* 1996, 68, 3290–4.

159. **Liu, D.; Yin, A.; Chen, K.; Ge, K.; Nie, L.; Yao, S.** *Anal. Lett.* 1995, 28, 1323–37.

160. **Amine, A.; Cremisini, C.; Palleschi, G.** *Mikrochim. Acta* 1995, 121, 183–90.

161. **Douglas, J.** *EPRI J.* 1991, Dec. 4–11.