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Determination of Heavy Metals in Seawater by Atomic Absorption Spectrometry after Electrodeposition on Pyrolytic Graphite-Coated Tubes

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A tubular, pyrolytic graphite-coated furnace has been incorporated in a flow-through cell for the electrodeposition with mercury of heavy metals from seawater. After plating, the furnace is transferred to an atomic absorption (AA) spectrometer for atomization of the deposited metals. The flow assembly has been tested for the analysis of lead in seawater, comparing results with those obtained by anodic stripping voltammetry (ASV). The technique is applied to the determination in seawater of both labile and total cobalt and nickel. These metals are irreversibly deposited on graphite and have poor sensitivity using ASV but are readily measured by AA. Measurements are reproducible with a relative standard deviation of 15%. For 15- and 10-minute depositions, respectively, Co and Ni characteristic concentrations are 0.02 μg per liter.

Although a considerable effort has been devoted to studies of a wide range of spectral and chemical interferences affecting furnace atomization, the direct determination of trace metals in complex matrices, such as seawater, still presents considerable difficulties (1, 2). Attempts have been made to overcome very high levels of molecular absorption and light scattering by matrix components of seawater, using background correction (3, 4) or selective volatilization techniques (4). For the direct determination of metals in seawater, the latter has been successful only for elements having high atomization temperatures and which are present in detectably high concentrations, such as iron. Under optimum conditions, the detection limits for heavy metals in seawater by graphite furnace atomic absorption spectrometry are generally above 1 $\mu\text{g L}^{-1}$. Consequently, for many elements of importance in environmental studies, such as lead, copper, cobalt, nickel, and chromium, detection limits exceed their natural concentrations.

Many recent studies have reported the use of electrolytic preconcentration and separation of trace metals from seawater in order to eliminate matrix interferences and to lower the limits of detection. Following the initial attempts by Brandenberger and Bader (5), Fairless and Bard (6) published preliminary results on the electrodeposition of metals in the well of a carbon rod; however, the porosity and tendency of the carbon to crumble made it relatively undesirable. Subsequently, they examined the use of hanging mercury drop electrodes (7) but experienced difficulties in the reproducible positioning of the mercury drop in the graphite tube furnace. Jensen et al. (8) had greater success with mercury drop atomization from graphite boats.

The electrodeposition of heavy metals on wires of high melting point metals, such as tungsten or iridium, has been the subject of a number of investigations (9–12). Metals have

been atomized either in a flame or by electrical heating of the wire. The small electrode areas necessitate long deposition times and, in seawater, only cadmium has been satisfactorily determined at the natural levels using such techniques (13).

An alternative approach by Thomassen et al. (14) involved graphite electrodeposition, in which the graphite was subsequently ground and analyzed by furnace AA. An advantage of this technique is that more than one element can be determined using different aliquots of the powder; however, the possibility of sample contamination is increased. Considering the problems and limitations of previously described electrodeposition methods, we believed that these could be overcome by the use of controlled potential electrodeposition on a tubular pyrolytic graphite-coated furnace prior to AA analysis. Because of its relatively nonporous, smooth surface, pyrolytic graphite has found successful application as an electrode material in ASV methods (15), and pyrolytic graphite-coated furnaces have considerable advantages for furnace atomization (16).

Several authors have reported the use of tubular electrodes in flowing systems for ASV analysis (17–20). We have examined these systems and designed an assembly which allows ready removal and transfer of the cathode to the furnace assembly of an AA spectrometer.

In this paper we report the development of a graphite tube electrodeposition-atomization method and its application to the determination of heavy metals in seawater. Initial studies were confined to lead but other metals such as cadmium, copper, thallium, antimony, bismuth, indium, and zinc can also be readily analyzed. Although these metals can also be conveniently analyzed by ASV (21), there are a number of elements, notably cobalt, nickel, manganese, and chromium for which the ASV reduction is irreversible. Nevertheless, they are still suitable for subsequent determination by furnace AA. Results are now reported for the analysis of lead, cobalt, and nickel in seawater.

EXPERIMENTAL

Apparatus. Controlled potential electrodeposition was performed using a Princeton Applied Research Model 174 Polarographic Analyzer. ASV studies used the differential pulse mode, 25-mV pulse modulation, 0.5-s pulse repetition, and a scan rate of 5 mV s^{-1} .

Pyrolytic graphite-coated electrodes, 9 mm \times 3 mm i.d., supplied by Varian for use in their CRA-90 furnace unit were used in these studies, the exterior pyrolytic coating being machined away to improve electrical contacts. The injection hole in the side of the tube needed to be blanked using a polypropylene plug which was removed during AA analysis. These electrodes were later replaced by tubes without holes supplied by Ultra Carbon Corp., Bay City, Mich.

The flow-through cell assembly is illustrated in Figure 1. The electrode holder consisted of two recessed, glass-filled Teflon ends containing Teflon washers, into which the graphite tube closely

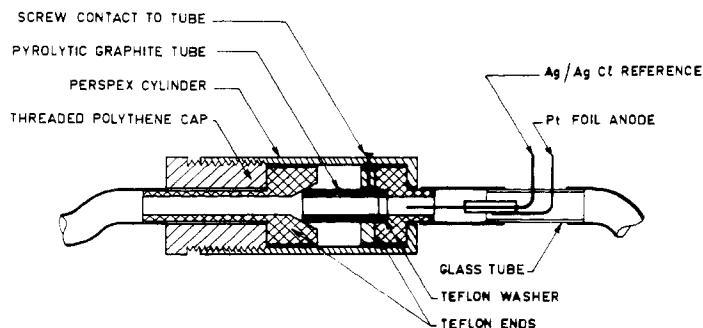


Figure 1. Flow-through cell

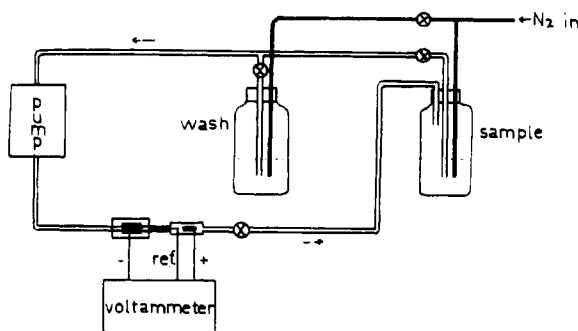


Figure 2. Diagram of flow system

fitted. Around the upper circumference of one end was a tight-fitting aluminum band holding a screw-contact to the electrode surface. The other end made a tapered connection with the electrode, to allow easy removal. Both ends were supported within a Perspex cylinder, opened on one side to permit withdrawal of the electrode. Pressure on both ends on the electrode was maintained by a polythene screw-fitting, on one end of the Perspex cylinder. A cylindrical platinum foil anode was positioned in a glass tube downstream of the cathode. A concentric Ag/AgCl reference electrode was inserted into one end of the cathode holder. Solution flow was variable from 7 to 140 mL min⁻¹ using a Watson Marlow Ltd. HR flow inducer.

Atomic absorption analyses were performed on a Varian Techtron model 90 CRA furnace mounted in a Varian Techtron AA-5 atomic absorption spectrometer. Hollow cathode lamps from the same manufacturer were used for all elements investigated and were operated at the recommended currents. The furnace power supply was used in the atomization mode only, programmed as follows: Pb, 600 °C s⁻¹ ramp to 1800 °C with 2-s hold; Co and Ni, 600 °C s⁻¹ ramp to 2500 °C with 2-s hold. The monitored wavelengths for Pb, Co, and Ni were 217.0, 240.7, and 232.0 nm, respectively. Peak heights were recorded with a Mace FBQ 100 chart recorder.

Reagents. Merck "Suprapur" grade mercury, ammonia, nitric acid, sodium acetate, and sodium chloride were used to prepare reagent solutions. Cobalt-60 tracer as chloride in dilute HCl was supplied by the Isotope Division, Australian Atomic Energy Commission.

Seawater samples were collected in high-density polythene bottles as described previously (22). Samples were filtered through a 0.45-μm membrane filter on the day of collection and the filtrate was stored at 4 °C prior to analysis.

Procedure. An analysis is performed as follows: To the solution for analysis (50 mL) in a 100-mL polythene bottle, 0.3 mL of 2 M acetate buffer pH 4.6, and 0.5 mL of 1.5 × 10⁻² M Hg(NO₃)₂ is added. The bottle is connected to the flow system (Figure 2) and deaerated with nitrogen for 5 min. In a second bottle, a wash solution of acidified 0.5 M ammonium nitrate solution is simultaneously deaerated. Sample flow through the electrode system is initiated ensuring absence of gas bubbles. The prescribed control voltage is applied for the desired time. At the end of this interval, the stopcock is opened to permit flow of the wash solution while the sample flow is closed. After 10 s, the pump is stopped and the electrode assembly isolated. Holding the assembly in a vertical position, the upper Teflon end is removed;

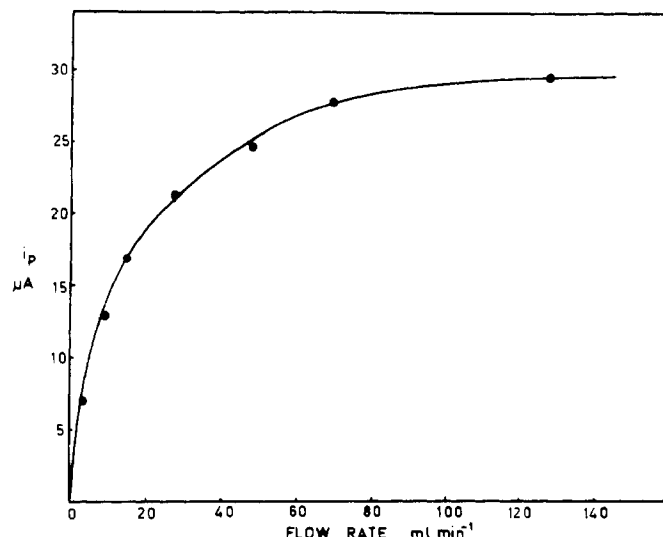


Figure 3. Effect of flow rate on peak current for 4.1 μg L⁻¹ Pb. 0.5M NaCl, 0.012 M acetate (pH 4.6), 1.5 × 10⁻⁴ M Hg(NO₃)₂, 5-min deposition at -0.85 V vs. Ag/AgCl

then, with the voltage still applied, the lower stopcock is opened to drain the electrode. The voltage is switched off and the graphite tube removed using plastic-coated tweezers. The ends of the tube are wiped with a filter paper; then, holding the tube with Teflon-tipped tweezers so as to seal the ends, the outside is washed with distilled water and touched dry with a filter paper. The tube is dried for 5 min under an infrared lamp, then stored in a plastic pill pack prior to AA analysis.

RESULTS AND DISCUSSION

Evaluation of Flow-Through Cell. A series of preliminary experiments were performed to evaluate and optimize conditions for the operation of the flow-through cell. The analysis of lead in 0.5 M NaCl buffered to pH 4.6 was examined with monitoring initially by ASV and later by AA as well. The effect of solution flow rate on ASV peak current is shown in Figure 3. A flow rate of 120 mL min⁻¹ was chosen for these studies. Lieberman and Zirino (19) have shown that under these conditions solution flow is no longer laminar.

Since ASV peak current is a nonlinear inverse function of solution resistance (23), careful consideration of anode and reference electrode design was necessary to minimize this resistance. In early studies, the use of platinum and silver wire coils located downstream of the cathode, gave cell resistances in 0.5 M NaCl in excess of 1000 Ω. An acceptable resistance of 500 Ω was obtained using a cylindrical platinum foil anode of larger area, situated as close as possible to the cathode.

Film Stability. Since even small amounts of NaCl remaining in the graphite electrode after deposition were sufficient to cause spectral interference in the AA determination, an electrode washing stage was necessary. Both in the presence and absence of an applied voltage, the deposited film was unstable to washing by distilled water; however, with the deposition voltage applied, a 10-s wash with either dilute HNO₃ or acidified 0.5 M ammonium nitrate, was shown to be satisfactory. The introduction of air or gas bubbles into the electrode assembly during the washing cycle resulted in interruptions to the applied voltage and, with the high solution flow rates, losses of deposited metal occurred. Such losses could possibly be minimized by lowering the flow rate in the wash cycle; however, this necessitated a longer washing time with the possibility of deposition of metals from the wash solution.

We have noted that the major sources of error in the technique lie in the electrode washing and transfer steps, which

Table I. Electrode Reproducibility by ASV and AA^a

Electrode No.	Added Pb concn, $\mu\text{g L}^{-1}$	ASV peak current, μA	AA absorbance
1	2.1	14.7	0.48
2	2.1	14.7	0.41
3	2.1	12.8	0.37
4	2.1	14.5	0.37
5	2.1	14.5	0.40
6	2.1	13.9	0.35
7	2.1	14.4	0.37
8	2.1	15.2	0.48
9	2.1	13.3	0.34
10	2.1	13.0	0.47
9 ^b	2.1	14.0	0.34
10 ^b	2.1	13.7	0.41
11	1.0	6.6	0.20
12	1.0	6.2	0.16
13	1.0	6.7	0.22
14	0	1.4	0.04
16 ^c	0	...	0.01

^a 5-min deposition at -0.85 V vs. Ag/AgCl , 120 mL min^{-1} flow. Electrolyte: 0.5 M NaCl , 0.012 M acetate ($\text{pH } 4.6$), $1.5 \times 10^{-4}\text{ M Hg}(\text{NO}_3)_2$. ^b Repeat analyses on fired tubes. ^c Tube blank, no deposition.

Table II. Determination of Lead in Seawater

Method	Labile Pb, $\mu\text{g L}^{-1}$	Total Pb, $\mu\text{g L}^{-1}$
Electrodeposition-AA	0.20 ± 0.04	0.42 ± 0.06
ASV	0.16 ± 0.02	0.35 ± 0.04

should be performed carefully. Traces of sodium chloride adhering to the outside of the tube may cause smoking during the atomization step, but this does not interfere with the absorption measurements. We are currently experimenting with a fully immersible electrode through which solution can be cycled. Preliminary results indicate improvements in the ease with which the tube can be washed and removed.

Electrode Reproducibility. The reproducibility of film deposition was tested on 10 different tubes by both ASV and AA. For ASV measurements, mercury was deposited in situ with lead for a 5-min period, stripped by an anodic voltage scan, and the lead peak current measured (21). The lead deposited in a second 5-min period was then washed and analyzed by AA. The results (Table I) show a relative standard deviation (RSD) by ASV of 6%, and this increased to 13% for AA measurements after electrodeposition, for $2.1\text{ }\mu\text{g L}^{-1}$ Pb. Both peak currents and absorbances showed a linear dependence in the range studied. Repeated deposition and firing of the same tubes produced no significant changes to the measured absorbance.

The problem of contamination in the flow-through system can be serious. Care should be taken that all tubing and surfaces which the sample solutions contact, are rinsed well with acid before use (22). In the 0.5 M NaCl solutions studied, the blank lead concentration was $0.23\text{ }\mu\text{g L}^{-1}$. The lead absorbance blanks on fired tubes were negligible.

Determination of Lead. The analyses of a seawater sample for both labile and total lead were compared using ASV and AA techniques (Table II). Labile lead was determined after the addition of acetate buffer ($\text{pH } 4.6$), while total lead was measured after boiling a 25-mL sample with 2 mL of 2 M HNO_3 (21), followed by the addition of 1 mL of 2 M sodium acetate. Ten-minute depositions were performed at -0.85 V vs. Ag/AgCl with lead concentrations being determined by the standard addition procedure. The results for both techniques agreed well.

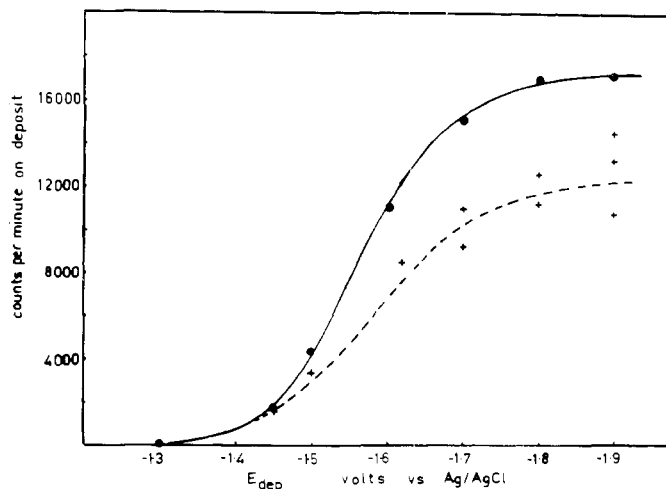


Figure 4. Effect of potential on cobalt-60 deposition in the presence of $1.5 \times 10^{-4}\text{ M Hg}(\text{NO}_3)_2$ and without $\text{Hg}(\text{NO}_3)_2$ (dashed line). $5.9\text{ }\mu\text{g L}^{-1}\text{ Co}$, 0.5 M NaCl , 0.012 M acetate ($\text{pH } 4.6$), 10-min deposition

For samples having higher lead concentrations, shorter deposition times should be used so that absorbance readings are kept near 0.4 for optimum accuracy. It is important that measurements after the standard addition be made using the same deposition time as that used for the sample, to account for differences in the plating efficiencies. For the analysis of seawater using the AA method, for a 10-min deposition, a RSD of 17% was obtained with a characteristic concentration (0.0044 absorbance) of $0.01\text{ }\mu\text{g L}^{-1}$.

Direct additions of a standard lead solution to the graphite furnace showed that 0.4 ng of lead gives an absorbance of 0.15 . On the above seawater sample, 0.3 ng of lead deposits during 10 min, representing less than 5% of the available lead in the 50-mL sample.

Determination of Cobalt. The reduction of cobalt at a mercury electrode occurs irreversibly in chloride media, but becomes more reversible in complexing electrolytes such as thiocyanate or pyridine (24). Studies of the stripping voltammetric behavior at the hanging mercury drop (25–27) have shown, however, that anodic stripping peaks can be obtained even in chloride solutions, where the minimum detectable cobalt concentration was $30\text{ }\mu\text{g L}^{-1}$. This was lowered to $3\text{ }\mu\text{g L}^{-1}$ in SCN^- or in pyridine. In all cases, for depositions at -1.4 V vs. SCE, cobalt stripping peaks occurred at potentials more positive than -0.3 V vs. SCE. Problems arise owing to the low solubility of cobalt in mercury, and continued electrolysis leads to a mixture of cobalt amalgam and cobalt metal suspension in the electrode surface. The stripping process is kinetically controlled, the rate being dependent on the concentration of complexing agent present and the degree of saturation of the mercury electrode. Although this places restrictions on the suitability of ASV for cobalt analysis, there should be no such impediments to the use of AA for the measurement of cobalt electrodeposited with mercury on a graphite cathode.

One aim of these studies was to provide analytical methods whereby the chemical speciation of metals such as cobalt in seawater could be studied using the speciation scheme described in an earlier paper (28). It was therefore undesirable that the natural sample be perturbed by the addition of any complexing electrolyte, and studies were confined to measurements in chloride media.

To select the optimum voltage for electrodeposition, cobalt spiked with cobalt-60 tracer was deposited with mercury on the pyrolytic graphite electrodes from 0.5 M NaCl , buffered to $\text{pH } 4.6$ with acetate. The deposited metal film was dissolved in nitric acid and the solution activity determined by γ -

Table III. Determination of Cobalt and Nickel in Seawater

Source of Sample	Labile metal, $\mu\text{g L}^{-1}$		Total metal, $\mu\text{g L}^{-1}$		Reference
	Co	Ni	Co	Ni	
Botany Bay, Australia	0.19	2.6	0.25	3.8	This work
Cronulla Beach, Australia	0.15	1.8	0.21	2.5	This work
Port Hacking, Australia	0.16	2.3	0.25	2.9	This work
North Central Pacific Ocean	0.24	3.2	(29)
North West Coast, U.S.A.	0.13	1.1	(29)
Menai Straits, U.K.	0.07	1.9	(30)
Shibukawa, Japan	0.07-0.16	...	(31)

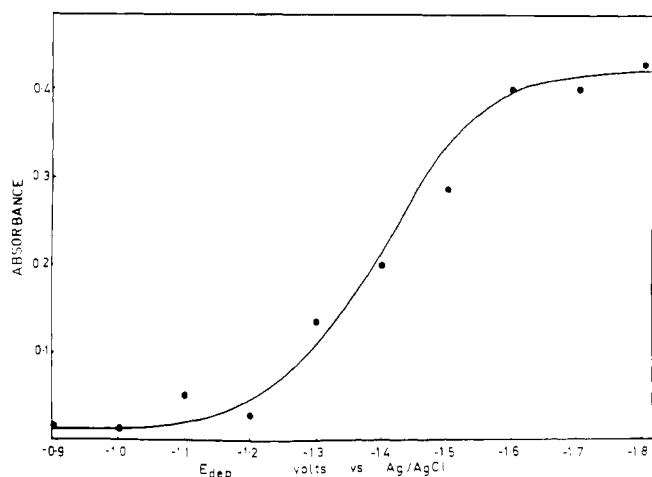


Figure 5. Effect of potential on the deposition of $5.9 \mu\text{g L}^{-1}$ Ni. 0.5 M NaCl , $0.012 \text{ M acetate (pH 4.6)}$, $1.5 \times 10^{-4} \text{ M Hg(NO}_3)_2$, 5-min deposition

counting. The results of these experiments plotted in Figure 4 show the expected polarographic-type curve for cobalt activity vs. deposition potential. At the more negative potentials, hydrogen is obviously being evolved simultaneously with deposition, but with no detrimental effects in the flowing system. By contrast, similar experiments carried out previously at a hanging mercury drop electrode, showed a lack of reproducibility in deposited cobalt activity at potentials more negative than $-1.60 \text{ V vs. Ag/AgCl}$. This is a result of inefficient stirring near the electrode surface where interferences are caused both by the evolution of hydrogen and the resulting increases in pH in the diffusion layer. Rapid solution flow in the tubular electrode efficiently removes hydrogen as it is formed with no apparent hindrance to cobalt deposition. In the absence of mercury, less cobalt was deposited at the tubular electrode and the results were not reproducible at very negative potentials. A potential of $-1.80 \text{ V vs. Ag/AgCl}$ was selected for analytical cobalt deposition.

Results obtained from both tracer studies and AA measurements showed the amount of cobalt deposited was a linear function of solution concentration up to $5.9 \mu\text{g L}^{-1} \text{ Co}$. The RSD of measurements at the $1 \mu\text{g L}^{-1}$ level was 12%. No significant differences were observed between results obtained using a pre-formed mercury film and those with mercury deposited in situ with cobalt.

The method was applied to the determination of cobalt in several seawater samples and the results for both labile and total cobalt concentrations are shown in Table III. For 15-min depositions, the RSD for cobalt measurements was 15%, while a characteristic concentration of $0.02 \mu\text{g L}^{-1} \text{ Co}$ was observed. Cobalt blanks on added reagents were negligible. The results for total cobalt are of the same order as those obtained using analytical methods involving solvent extraction in the presence of complexing agents, followed by x-ray fluorescence (29, 30) or spectrophotometric (31) analysis. However, on the basis

of studies by Lowman and Ting (32), it seems unlikely that such extraction methods measure total cobalt.

Determination of Nickel. As for cobalt, the reduction of nickel in chloride solutions is irreversible, although the polarographic half-wave potential is several hundred millivolts more positive (33), and similar attempts have been made to determine nickel by ASV. Markova and Sinyakova (25) reported a detection limit of $9 \mu\text{g L}^{-1}$ in Cl^- , while in SCN^- solutions, limits in the range $0.6 - 3 \mu\text{g L}^{-1}$ have been obtained in ASV at graphite (25), carbon paste (34), and hanging mercury drop (35) electrodes.

The effect of deposition potential on the concentration of nickel deposited with mercury from 0.5 M NaCl (pH 4.6) on the pyrolytic graphite electrode, was determined from AA measurements (Figure 5). The expected positive potential shift of the plating curve from that for cobalt, was observed and a potential of $-1.60 \text{ V vs. Ag/AgCl}$ was selected for analytical nickel deposition.

Results for the analyses of nickel in seawater are compared with data obtained by other methods in Table III. Typical values for nickel in seawater are an order of magnitude higher than those for cobalt, and shorter deposition times were therefore possible. A RSD of 15% for 10-min depositions and a characteristic concentration of $0.02 \mu\text{g L}^{-1}$ were obtained.

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LITERATURE CITED

- (1) R. B. Cruz and J. C. van Loon, *Anal. Chim. Acta*, **72**, 231 (1974).
- (2) D. A. Segar and A. Y. Cantillo, "Analytical Methods in Oceanography", *Adv. Chem. Ser.*, **147**, 56 (1975).
- (3) T. H. Donnelly, J. Ferguson, and A. J. Eccleston, *Appl. Spectrosc.*, **29**, 158 (1975).
- (4) D. A. Segar and J. D. Gonzalez, *Anal. Chim. Acta*, **58**, 7 (1972).
- (5) H. Brandenberger and H. Bader, *At. Absorp. Newsl.*, **6**, 101 (1967).
- (6) C. Fairless and A. J. Bard, *Anal. Lett.*, **5**, 433 (1972).
- (7) C. Fairless and A. J. Bard, *Anal. Chem.*, **45**, 2289 (1973).
- (8) F. O. Jensen, J. Dolezal, and F. J. Langmyhr, *Anal. Chim. Acta*, **72**, 245 (1974).
- (9) M. P. Newton, J. V. Chauvin, and D. G. Davis, *Anal. Lett.*, **8**, 89 (1973).
- (10) M. P. Newton and D. G. Davis, *Anal. Chem.*, **47**, 2003 (1975).
- (11) J. B. Dawson, D. J. Ellis, T. F. Hartley, M. E. A. Evans, and K. W. Metcalf, *Analyst (London)*, **99**, 602 (1974).
- (12) W. Lund and B. V. Larsen, *Anal. Chim. Acta*, **70**, 299 (1974).
- (13) W. Lund and B. V. Larsen, *Anal. Chim. Acta*, **72**, 57 (1974).
- (14) Y. Thomassen, B. V. Larsen, F. J. Langmyhr, and W. Lund, *Anal. Chim. Acta*, **83**, 103 (1976).
- (15) Kh. Z. Brainina, *Talanta*, **18**, 513 (1971).
- (16) R. E. Sturgeon and C. L. Chakrabarti, *Anal. Chem.*, **49**, 90 (1977).
- (17) W. R. Seitz, R. Jones, L. N. Klatt, and W. D. Mason, *Anal. Chem.*, **45**, 840 (1973).
- (18) W. D. Mason and C. L. Olson, *Anal. Chem.*, **42**, 548 (1970).
- (19) S. H. Lieberman and A. Zirino, *Anal. Chem.*, **46**, 20 (1974).
- (20) A. Zirino and S. H. Lieberman, *Ref. 2*, p. 82.
- (21) G. E. Batley and T. M. Florence, *J. Electroanal. Chem.*, **55**, 23 (1974).
- (22) G. E. Batley and D. Gardner, *Water Res.*, in press.
- (23) T. R. Copeland, J. H. Christie, R. K. Skogerboe, and R. A. Osteryoung, *Anal. Chem.*, **45**, 995 (1973).
- (24) B. K. Hovsepian and I. Shain, *J. Electroanal. Chem.*, **12**, 397 (1966).
- (25) I. V. Markova and S. I. Sinyakova, *J. Anal. Chem. USSR*, **23**, 891 (1968).
- (26) I. V. Markova and S. I. Sinyakova, *J. Anal. Chem. USSR*, **26**, 1021 (1971).
- (27) I. V. Markova and S. I. Sinyakova, *J. Anal. Chem. USSR*, **29**, 924 (1974).
- (28) G. E. Batley and T. M. Florence, *Mar. Chem.*, **4**, 347 (1976).
- (29) B. Armitage and H. Zeitlin, *Anal. Chim. Acta*, **53**, 47 (1971).

- (30) A. W. Morris, *Anal. Chim. Acta*, **42**, 397 (1968).
(31) S. Motomizu, *Anal. Chim. Acta*, **64**, 217 (1973).
(32) F. G. Lowman and R. Y. Ting, "Radioactive Contamination of the Marine Environment," IAEA Symposium Series 158, Vienna, 1973, p. 369.
(33) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience, New York, N.Y., 1952, p. 475.

- (34) R. U. Vakhobova and R. D. Yurina, *Dokl. Akad. Nauk Tadzhik. SSR*, **15**, 29 (1972). (*Anal. Abstr.*, **26**, 2086 (1974)).
(35) H. Grubitsch and J. Schukoff, *Fresenius' Z. Anal. Chem.*, **253**, 201 (1971).

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Subnanogram Fluorine Determination by Aluminum Monofluoride Molecular Absorption Spectrometry

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The diatomic molecule of aluminum monofluoride, AlF, gives a sharp absorption band spectrum at 227.5 nm in both flames and a carbon rod furnace. The absorption intensity is high enough so that it can be used for a sensitive analytical method of fluorine determination. The best sensitivity observed is 0.021 ng of fluorine with the carbon rod furnace, which is the best so far reported for this element and is also superior to that obtained with the $N_2O-C_2H_2$ flame, i.e., 24 μg F/mL. An excess aluminum solution is applied first to the furnace before the fluorine containing sample is pipetted, so that the AlF molecule is effectively formed inside the furnace. A certain amount of strontium and nickel is found to enhance the signal with decreasing the background. The method has been successfully applied to biological samples and also to organofluorine compounds.

Atomic absorption spectrometry has been extensively developed as a useful analytical method for various metallic elements. However, its applications to nonmetallic elements have many difficulties, mainly due to the fact that the resonance lines of these atoms are found in the vacuum ultraviolet region of the spectrum. Especially, it is impossible to determine fluorine using its atomic spectrum since its main resonance line is located at 95 nm.

As a method of determination of fluorine by atomic absorption, indirect spectrometry using Zr and Mg atomic absorption was reported by Bond et al. (1). However, this method is rather insensitive and inconvenient for practical use.

On the other hand, molecular emission spectra of some metal monofluorides have long been available for fluorine determination, e.g., CaF, SrF, and BaF in a d.c. arc (2) or in flames (3). Recently, Haraguchi and Fuwa (4) observed aluminum monofluoride, or AlF radical in air-acetylene flame, which gives a strong absorption spectrum with a linelike shape and a peak at 227.5 nm in the ultraviolet region.

The present paper demonstrates that the absorption spectrum of AlF both in flames and in the high temperature cuvette of the carbon rod furnace is useful for the determination of fluorine. The latter is particularly sensitive for both inorganic and organic forms, and it can be applied for the determination of subnanograms of fluorine in the biological samples (5).

EXPERIMENTAL

Apparatus. For the measurement of the absorption spectra, an atomic absorption spectrophotometer, AA-1, Mark-II, from

Nippon Jarrell-Ash Co., Ltd. was used. For the sample dispersing devices, a 10-cm slot burner was used for the air-acetylene and air-hydrogen flames, a 5-cm slot burner for the nitrous oxide-acetylene flame, and a carbon rod furnace (Nippon-Jarrell Ash FLA-100) for the high temperature cuvette.

As the continuous light source, a deuterium lamp of either the hollow cathode or the thermal cathode type from Hamamatsu TV Co., Japan, was used. Spectral band width of the spectrophotometer was 0.03 to 0.16 nm, and 0.08 nm was used unless otherwise defined.

Reagents. All the reagents used were of analytical grade purchased from Wako Pure Chemicals.

Fluorine standard solution was prepared by dissolving ammonium or sodium fluoride in distilled water. All the metal ions investigated were in the form of nitrates.

Sodium monofluoroacetate, trifluoroacetic acid, and *o*-fluorobenzoic acid were used as organofluorine compounds. These reagents were accurately weighed and dissolved in distilled water.

Procedure. The absorption spectrum of AlF was observed by aspirating the mixed solution of ammonium fluoride and aluminum nitrate into the flame at the rate of 3 mL/min. The fundamental conditions of the flames and the concentrations of the solutions are shown in Table I.

The measuring procedure with the high temperature cuvette is summarized in Table II. In practical measurements, the appropriate amount of nickel and strontium was added to the aluminum solution to increase both the sensitivity and precision of analysis.

In order to obtain the absorption spectrum of AlF in the flame, a wavelength scan was performed. For the high temperature cuvette, however, the absorption of AlF was measured at fixed wavelengths at intervals of 0.1–0.2 nm. In practical measurements, the AlF absorption peak at 227.5 nm was used for fluorine determination. In case it was necessary, the background intensity at 228.1 nm was subtracted from that at 227.5 nm.

Preparation of Biological Samples. The Standard Reference Material of Orchard Leaves from the National Bureau of Standards (SRM No. 1571) was chosen and prepared as an example for biological samples. A proper amount of powdered and dried (90 °C) sample was precisely weighed and ashed with 0.1 g Na_2CO_3 in a porcelain crucible at 550 °C for 10 h. The ash was dissolved in hot water and neutralized with 1 N nitric acid. The solution was diluted to a fixed volume. After the precipitate settled, the fluorine in the supernatant was measured according to the method mentioned above.

RESULTS AND DISCUSSION

AlF Absorption in Flames. The molecular absorption spectra of AlF in the air-acetylene and N_2O -acetylene flames are shown in Figure 1. In the air-hydrogen flame, the absorption spectrum of AlF observed was the same as that in the air-acetylene flame.

In N_2O -acetylene flame, the Al atom is generated, which gives a spectrum near that of AlF, i.e., 226.9 nm and 226.3 nm,