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Hanging Mercury Drop Electrodeposition Technique for Carbon Filament Flameless Atomic Absorption Analysis

Application to the Determination of Copper in Sea Water

Charles Fairless and Allen J. Bard

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

Flameless atomic absorption analysis (AA) methods have a sensitivity which is 2 to 3 orders of magnitude greater than their counterpart flame methods (1), although molecular absorption and matrix interference effects are more serious in the flameless techniques (2). A number of current studies have concentrated on developing methods for isolating trace elements from complex supporting matrices. Most of these isolation methods involve the use of precipitation, ion exchange, or extraction (3-9) where large volumes of extraneous chemicals are brought into contact with the analysis sample. Such methods may introduce interfering impurities and are often time-consuming and tedious.

We describe here a method of coupling controlled potential electrodeposition as a simultaneous separation-concentration step to carbon filament AA. Usually no extraneous reagents need be added. The technique is applied to the analysis of Cu in sea water, which cannot be determined directly by AA because of severe salt interferences (10). [The current procedure for trace metal analysis of unpolluted sea water is a complex extraction process (6).] Experiments were conducted on synthetic sea water samples containing only the two salts that are known to be the major interfering substances for direct flameless atomic absorption analysis of Cu in sea water (10) as well as actual sea water, to demonstrate the feasibility of the technique.

We have previously described (11) two techniques for coupling electrodeposition with AA as a means of concentration and elimination of interferences from complex supporting matrices. Both methods involved direct electrodeposition of a trace metal onto a xylene pretreated carbon filament. Thus, application of these techniques is limited to those metals that can be deposited on carbon [e.g., Ag, Cd, Cu, Fe, Hg, Ni, Pb, and Sn (12)]. Moreover, the porosity and tendency of carbon to crumble make it a relatively undesirable electrode material for electrodeposition. Mercury, on the other hand, is better behaved in electrochemical studies and is a commonly employed electrode (13). Moreover, because of mercury's low boiling

point, separation from an electrodeposited metal by selective volatilization should be feasible. In the work reported here, we have coupled controlled potential electrolysis at a hanging mercury drop electrode (HMDE) with carbon filament AA. In addition, in this technique, sample size is limited only by the electrolysis apparatus configuration, total amount of trace metal, and time, and is not restricted to the microliter capacity of the carbon filament.

EXPERIMENTAL

Apparatus. A Perkin-Elmer Model 306 AA spectrometer equipped with a HGA-70 flameless atomic absorption attachment was used. The graphite furnace atomizer was replaced by a water-cooled carbon filament atomizer which has been previously described (11); "West" type carbon filaments were used. The HGA-70 control unit provided electrical current to the atomizer via program 5, voltage, 3.7; dry cycle, 15 sec; ash cycle, 100 sec; and atomize cycle, 12 sec. The wavelength monitored was 324.7 nm. A Wenking 61RH potentiostat was employed for electrodepositions. The comparative flameless atomic absorption analyses were also performed with the HGA-70 graphite furnace.

Reagents. Reagent grade chemicals were used for all solutions. The water was deionized and then distilled in a glass apparatus. The laboratory prepared "synthetic sea water" consisted of 30.2 g/l. NaCl and 3.8 g/l. Na₂SO₄, corresponding to 35‰ salinity sea water (10, 14). The natural sea water samples were collected thirty-five miles offshore from Port Aransas, Texas, and were filtered through a glass frit (salinity, 39‰. The mercury used was triply distilled and pre-electrolyzed.

Procedure. Timed electrolyses at a controlled potential of -0.35 V vs. SCE were conducted with a simple three-electrode arrangement (Figure 1). A Brinkmann HMDE provided a reproducible mercury drop (MD) with an area of 0.067 cm² and a weight of 0.0223 gram. The solution volume was 2.5 ml. Deaeration of analysis solutions was accomplished by bubbling nitrogen for 5 minutes prior to electrolysis and then by passing nitrogen over the solution during electrolysis. After electrolysis, two procedures were followed to examine relaxation losses. In one procedure, the potentiostat was turned off first, then in rapid sequence; the whole HMDE assembly was removed from solution, the MD rinsed with approximately 1 ml of water from a dropper, and any adhering rinse water blotted. The MD was then transferred directly to a carbon filament which had been prepositioned in the atomizer. The other procedure was to remove the whole HMDE assembly from solution first, followed in rapid sequence by the same rinsing and blotting procedure and then turning off the potentiostat. Again, the MD was transferred directly to a prepositioned carbon filament. No significant differences were observed between results obtained with the two procedures. Five microliters of *p*-xylene was used to pretreat the filament cavity. The mercury was volatilized completely by heating the filament at approximately 425 °C (just above the boiling point of Hg), then the Cu was atomized. Blanks were determined by electrolysis of supporting matrices alone. Accuracy was checked by the method of standard additions.

RESULTS AND DISCUSSION

Typical results of carbon filament analysis of Cu solutions electrolyzed at a HMDE are shown in Table I. The

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Table I. Electrodeposition Coupled to Carbon Filament Atomic Absorption Analysis of Cu

Concn of Cu, $\mu\text{g l}^{-1}$	Sample vol, ml	Support. matrix	Total Cu (μg) $\times 10^3$	Time of electrolysis, min	Absorption signal, peak ht	% Electro-deposited
738	2×10^{-3}	Water	1.47	a	12.4	...
738	5×10^{-3}	Water	3.69	a	31.7	...
738	1×10^{-2}	Water	7.38	a	61.1	...
1.48	2.5	1.0M H ₂ SO ₄	3.69	30	7.4	23.5
2.96	2.5	1.0M H ₂ SO ₄	7.38	30	16.5	27.4
5.92	2.5	1.0M H ₂ SO ₄	14.7	30	35.8	29.3
1.48	2.5	Synthetic sea water	3.69	30	8.2	25.7
$x(0.72)^b$	2.5	Natural sea water	$y(1.81)$	30	4.3	(26.0)
$x + 1.48$	2.5	Natural sea water	$(3.69 + y)$	30	12.4	...
$x + 2.96$	2.5	Natural sea water	$(7.38 + y)$	30	20.0	...
$x + 4.43$	2.5	Natural sea water	$(11.07 + y)$	30	29.1	...

^a Samples were injected directly into the carbon filament cavity. ^b The natural sea water Cu concentration (x) was determined to be 0.72 $\mu\text{g Cu l}^{-1}$ by direct electrodeposition coupled to AA analysis using the method of standard additions.

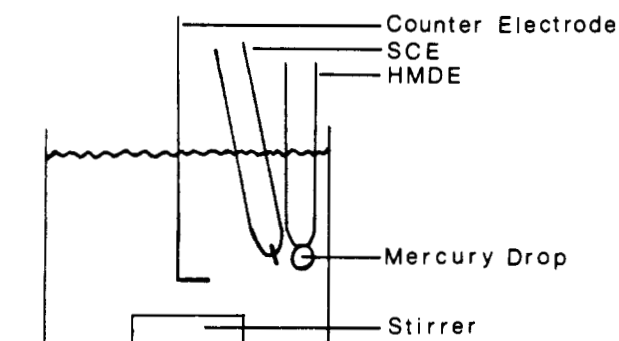


Figure 1. Electrode arrangement

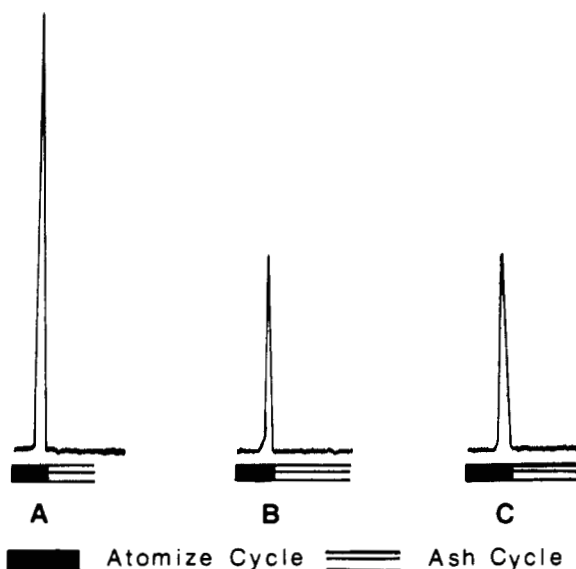


Figure 2. Carbon filament atomizer tracings for the determination of Cu

A. Directly injected 5- μl sample of aqueous Cu solution (1.9 ng Cu). B. MD electrodeposited with Cu from a 1.0M H₂SO₄ solution (total Cu in solution = 1.9 ng). C. MD electrodeposited with Cu from sea water (total Cu in solution = 1.9 ng)

natural sea water analyzed here (0.72 $\mu\text{g Cu l}^{-1}$) is within the range of Cu concentration in unpolluted sea water (1–2 $\mu\text{g Cu l}^{-1}$) (15). The practical detection limit for

(15) J. P. Riley and G. Skirrow, "Chemical Oceanography," Vol. 2, Academic Press, London, 1965, pp 343–60.

this technique with this electrode configuration, solution volume, and electrolysis time is 0.2 $\mu\text{g Cu l}^{-1}$. This could be lowered by appropriate electrolysis apparatus design such that 100% electrolysis is accomplished in a reasonable time. The absolute detection limit of the carbon filament atomizer is about 5×10^{-11} gram of Cu (essentially the same value as the sensitivity per 1% absorption). This represents the minimum amount of Cu that must be present in the analysis solution for 100% electrolysis. The relative standard deviation of 15% is comparable to most flameless AA techniques, except for the direct injection of some aqueous samples. Thus, these results indicate that coupling controlled potential electrolysis with carbon filament AA is a suitable technique for the determination of Cu in unpolluted sea water with matrix interferences apparently eliminated and selective volatilization of Hg without covolatilization of Cu accomplished. The technique may, therefore, provide an adequate alternative to long, tedious, and sometimes complicated matrix separation procedures in the fields of biological trace metal analysis (6, 7, 16), health studies (17, 18) food and agriculture (8, 19, 20), geochemistry (9, 20–22), metallurgy (23), and industrial development and control (24).

The tracings in Figure 2 illustrate that essentially the same type of signal is obtained from a sample electrodeposited on a MD as from a directly injected aqueous sample.

Graphite furnace AA analysis of the electroplated MD was not successful, however. A satisfactory method of positioning the MD at the focal point of the hollow cathode source within the graphite tube reproducibly was not achieved. Introduction of the MD through the standard sample port resulted in deposition of a blackish coating on the pipet tip and irreproducible positioning of the MD in

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the graphite tube. Occasionally the MD broke into droplets which scattered along the length of the tube. Erratic absorption signals resulted. Introduction of the sample through the end opening of the graphite tube were also unsuccessful. The MD had to be rolled horizontally along the tube walls for proper positioning. This apparently resulted in a loss of Cu on the walls, since again erratic absorption signals were obtained. The use of the newly announced grooved tube accessories (25) or the commercially available solid sample adaptor could make graphite furnace atomization of an electroplated MD feasible.

The technique of coupling controlled potential electro-

(25) F. J. Fernandez, *At. Absorption Newslett.*, **11**, 123 (1972).

ysis with carbon filament AA is currently being exploited to establish a practical detection limit for Ag, Cd, Co, Cr, Mn, Ni, Pb, V, and Zn in unpolluted sea water.

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Identification and Determination of Sulfur Trioxide in Sulfur Dioxide by Raman Spectrometry

Peggy A. Skotnicki, Alfred G. Hopkins, and Chris W. Brown

Department of Chemistry, University of Rhode Island, Kingston, R.I. 02881

The importance of the oxidation of SO₂ to SO₃ in air pollution reactions has led to several recent kinetic studies of the reaction (1-9). During the course of these investigations, problems of identifying and analyzing for SO₃ were encountered. Calvert and his coworkers (5) pointed out the lack of spectroscopic methods to identify SO₃ as the final product of the photochemical reaction, and Cox (9) has shown that the present methods of wet chemical analysis are unreliable at low pressures. Sethi (8) attempted to overcome both of these problems by measuring infrared spectra of SO₂-SO₃ mixtures condensed onto an Irtran-2 window in a conventional liquid N₂ infrared cell. He identified SO₃, but was unable to obtain reproducible quantitative estimates of SO₃ in the mixture. Details of the bands used to identify SO₃ are not given. Presumably, he used the doublet at ~1400 cm⁻¹, since these are the only strong bands of SO₃ in the transparent region of Irtran-2. However, polycrystalline SO₂ has a weak band at ~1400 cm⁻¹ and this could have caused difficulty with the analysis.

We have repeated the experiments performed by Sethi; however, we condensed the mixture onto a CsI substrate. Sethi claims that SO₃ attacks CsI crystals, but we did not find any evidence for such a reaction when small concentrations of SO₃ in SO₂ were slowly deposited onto the substrate. At high deposition rates or at high SO₃ concentrations, some reaction did take place and new bands were observed. The advantage of using a CsI substrate is that

the low frequency region (down to ~200 cm⁻¹) is transparent, and SO₃ has a very strong band at 465 cm⁻¹. Using this band, we have obtained reproducible quantitative estimates of SO₃ relative to SO₂; however, the analysis takes considerable time (from 3 to 5 hr) and is very tedious. In trying to eliminate these difficulties, we found a very simple, unique technique to analyze for SO₃ in SO₂. The technique consists of measuring the Raman spectrum of the gaseous mixture; the relative concentrations of the two components can be obtained from the band intensities. The entire analysis takes less than 10 minutes.

EXPERIMENTAL

Apparatus. Raman spectra were measured on a Spex Industries Model 1401 double monochromator using photon-counting detection and a CRL Model 52A argon-ion laser emitting at 4880 Å (~600 mW power at the sample). Photolysis experiments were carried out in a Rayonet Srinivasan-Griffin photochemical reactor equipped with lamps emitting a band centered at 3000 Å. A 35-cm long, 5-cm diameter borosilicate glass (or quartz) cell fitted with a Teflon (DuPont) stopcock was used both for the photolysis experiments and as the Raman cell.

Reagents. Gaseous SO₂ (Matheson lecture bottle, 99.98%) was vacuum distilled several times prior to use. Gaseous SO₃ was obtained by vaporizing Sulfan (stabilized monomers of SO₃, Allied Chemical Corp.).

Procedure. Prior to each photolysis experiment, the reaction cell was cleaned with successive washings of chromic acid, ammonium hydroxide, distilled water, and deionized water. It was then evacuated to 10⁻⁶ Torr and degassed by heating to ~300 °C. For a photolysis experiment, the cell was filled to the desired pressure (50 to 550 Torr) with SO₂ and placed in the photochemical reactor for 1 to 24 hr. After each irradiation, the Raman spectrum of the gas was measured by placing the cell directly in the laser beam, *i.e.*, the spectrum was recorded without removing the gas from the cell.

For calibration of the Raman band intensities, a known mixture of SO₃-SO₂ was prepared. For this experiment, a special cell was constructed. The cell consisted of a 1-liter spherical bulb with a 15-cm long, 3-cm diameter closed cylindrical tube at the bottom and a Teflon stopcock. A small side-arm was attached to the cylin-

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