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ELECTRODEPOSITION TECHNIQUES FOR CARBON ROD
FLAMELESS ATOMIC ABSORPTION ANALYSIS

KEY WORDS: atomic absorption spectrometry, controlled potential electrolysis,
carbon rod atomizer

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ABSTRACT:

Two techniques involving electrodeposition of Cu on a carbon rod (CR) prior to atomic absorption (AA) analysis are described. The in situ technique involves electrodeposition from μl samples contained in the well of the CR in an attempt to decrease matrix effects. The bulk electrolysis technique allows preconcentration of Cu on the CR from very dilute metal ion solutions. Analysis of Cu in solutions as dilute as 1.6×10^{-10} M (70 ml volume) appears possible.

INTRODUCTION:

Atomic absorption (AA) analysis using a carbon rod atomizer (CRA) has been widely employed for metal analysis in small solution volumes.¹ In the conventional technique a small (1-100 μl) sample is injected into the well of a carbon rod, pretreated with xylene to prevent absorption into the carbon, and then subjected to a heating cycle which evaporates the solvent and ultimately vaporizes the metal salts. This approach may suffer from matrix effects² and the need for chemical pretreatment of the sample,³ poor reproducibility,¹ and the need for extremely small sample volumes.⁴ In 1968 Brandenberger⁵ suggested the electroplating of metals onto a wire spiral

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followed by electrical heating for metal vaporization and AA analysis. This technique has not been widely used, however, nor has it been extended to carbon rod techniques.

We report here preliminary experiments utilizing electrodeposition on a carbon rod as a preliminary step to the AA analysis of copper. Two different electrolysis techniques were employed. In the in situ technique electrodeposition from microsamples directly in the well of the carbon rod was attempted with the hope of decreasing matrix effects and improving reproducibility. In the bulk electrolysis technique the carbon rod was immersed in a larger volume of sample solution (ca 100 ml) and long term controlled potential electrolysis was employed to preconcentrate the metal from very dilute solutions prior to AA analysis.

EXPERIMENTAL:

The AA unit consisted of a Beckman Model DU spectrophotometer in conjunction with a Model 1300 AA accessory and a copper hollow cathode lamp. The CRA was constructed of an aluminum block to hold the CR while argon gas was passed over the assembly through the AA flame gas ports. Power to the CR came from a Miller 7.2 kw arc welder power supply. The AA spectrometer signal was recorded with time during the heating cycle with a Sargent SR recorder. Electrodepositions were carried out with a Wenking 61 RH potentiostat.

Reagent grade chemicals were employed for all solutions. The water was deionized and then distilled twice in a Pyrex apparatus.

The in situ electrolysis was performed with the electrode arrangement shown in Fig. 1. The well of the CR served as the solution container and the CR was the working electrode. A platinum wire auxiliary electrode and a saturated calomel electrode (S.C.E.) with a fine capillary salt bridge were also employed. This cell and electrode assembly was positioned in the usual

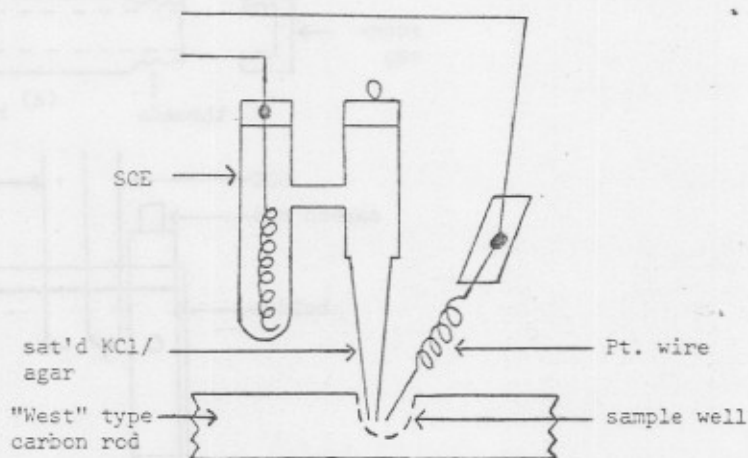


Fig. 1 In situ electrodeposition apparatus

CR location in the AA CRA. About 8 μ l of p-xylene were added to the CR well to prevent the test solution from soaking into the rod. Then 3-5 μ l of test solution, containing 5.8×10^{-9} moles to 5.8×10^{-11} moles of Cu(II) were added and electrolytic plating of Cu carried out for a 15 sec to 2 min duration. The auxiliary electrode and the S.C.E. were lifted away, the test solution was removed with a pipet and the Cu deposit on the CR washed with about 25 μ l of water. Conventional AA analysis followed.

Bulk electrolysis was carried out in a conventional manner using the apparatus shown in Fig. 2. The CR was held in a precision drilled Teflon holder so that only the CR well was exposed to the test solution for electrodeposition. As in in situ analysis, p-xylene was injected into the CR well to prevent solution soaking. Electrodeposition of Cu from the solution volume of 70 ml was carried out at a potential of 0.18 V. vs. S.C.E. for 35-60 min. The rod was removed from the solution following electrodeposition, rinsed with water, and positioned in the CRA assembly.

The AA CRA analysis was carried out by clamping the CR between two aluminum blocks attached to the a.c. power supply. The current supplied to

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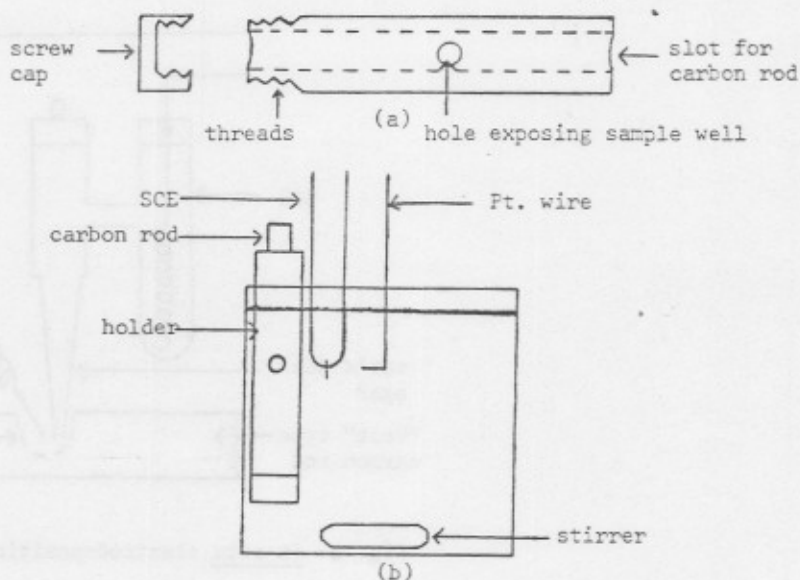


Fig. 2 (a) Detail of Teflon carbon rod holder
(b) Bulk electrolysis apparatus

the CR was manually ramped from 0 to 90 A, held for 3 sec to vaporize the p-xylene and then ramped to 125-135 A and held for 2 sec while the AA signal was recorded. The peak height of the recorded signal was used as a measure of the amount of Cu.

RESULTS AND DISCUSSION

Typical results for CRA analysis of a solution containing $1.15 \times 10^{-5} \text{ M}$ Cu(II) are shown in Table I. Compared in this table are experiments in which 1.0 μl of solution was injected directly into the CR cavity and subject to the usual CRA AA procedure (listed as the "direct method"), experiments in which 5.0 μl of sample were injected into the cavity and subjected to the in situ electrodeposition procedure for 60 sec before AA analysis, and experiments in which the bulk electrolysis technique preceded AA analysis. In the bulk electrolysis experiments 1.0 μl of sample was introduced into a solution prepared from 68 ml of water and 2 ml concentrated sulfuric acid resulting in a solution containing $1.64 \times 10^{-10} \text{ M}$ Cu(II); the electrolysis

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Table I. Comparison of Results of Electrodeposition Techniques
With Conventional Carbon Rod Atomizer Atomic Absorption
Analysis

Method	Direct	In Situ Electrolysis	Bulk Electrolysis
Run	Signal Level	Signal Level	Signal Level
1	5.6	0.31	6.1
2	6.0	0.32	5.6
3	5.4	0.32	6.4
4	6.0	0.34	5.7
Avg.	5.8	0.32	6.0
Rel. Std. Dev.	5.3%	4.0%	6.2%

times employed were about 50 min and deposition of the Cu in solution was essentially complete in this time.

The results of these preliminary experiments suggest that electrodeposition techniques coupled with AA analysis may be useful in decreasing matrix effects and carrying out analyses of very dilute solutions. The *in situ* technique with short electrodeposition times can be used in separating Cu from an aqueous solution and eliminating matrix interferences. However, only about a tenth of the total Cu in the sample is plated in this technique. This necessarily limits the technique to samples with higher Cu concentrations where separation of the metal or elimination of matrix effects is of primary importance. There is obviously no improvement in absolute sensitivity. The maximum sample solution volume is restricted by the CR well capacity to about 10 μ l with a minimum volume of about 3 μ l required for electrode contact.

Controlled potential bulk electrolysis for preconcentration coupled with CRA does afford the capability of expanding the allowable solution

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volume in which the metal is contained to the 100 ml to liter range. Although this technique does not increase the CRA absolute sensitivity (in terms of μ moles of Cu required per AA experiment), it does expand the useful sample concentration range some 10^5 -fold, providing an adequate sample volume is available for analysis. This technique would be especially useful for the analysis of natural waters or industrial waste streams for trace metals.

Experiments are continuing on extensions of this technique to other metals, to an investigation of the extent of elimination of matrix effects in real samples, and to modifications and improvements in the electro-deposition techniques.

REFERENCES

1. G. F. Kirkbright, *Analyst*, 96, 609 (1971).
2. D. Alger, R. G. Anderson, I. S. Maines, and T. S. West, *Anal. Chim. Acta*, 57, 271 (1971); M. Glenn, J. Savoy, L. Hart, T. Glenn, and J. Winefordner, *ibid.*, 263 (1971).
3. J. P. Matousek and B. J. Stevens, *Clin. Chem.*, 17, 363 (1971).
4. M. D. Amos, P. A. Bennett, K. G. Brodie, P. W. Y. Lung, and J. P. Matousek, *Anal. Chem.*, 43, 211 (1971).
5. H. Brandenberger, *Chimia*, 22, 449 (1968).

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