

# Mercury Thin Film Electrodeposition Technique for flameless Atomic Absorption Determination of Copper in Seawater

by

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## Abstract

Copper was extracted from seawater by electrodeposition into a mercury thin film. It was then stripped out of the film into a small volume of distilled water. This solution was then analyzed by flameless atomic absorption spectrometry. The limit of detection was found to be about 0.03 micrograms/liter.

## Résumé

Le cuivre a été extrait de l'eau de mer par électrodeposition sur une couche mince de mercure. Il a été redissous dans un petit volume d'eau distillée. Cette solution a été analysée par la spectroscopie d'absorption atomique sans flamme. La limite de détection est environ 0,03 microgramme/litre.

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The flameless atomic absorption technique has a limit of detection for copper of about three picograms in aqueous solution [1]. This corresponds to a solution concentration of about 0.06 micrograms/liter. This is somewhat below the concentration of copper in the open ocean [2]. However, to measure copper in such seawater the copper must be extracted to concentrate it and, more importantly, to remove the interference of the NaCl. Most of these isolation methods involve the use of precipitation, ion exchange, or extraction in which relatively large volumes of chemicals are mixed with the sample [3]. Such methods may introduce interfering impurities as well as being time-consuming and tedious. Recently, the extraction has been accomplished by electrodepositing the copper into a hanging mercury drop electrode [4]. The drop was then transferred to a flameless atomic absorption apparatus. The limit of detection of this system was about 0.1 microgram/liter of seawater. The main advantages of this electrodeposition method are the lack of extraneous reagents and the relative brevity of the extraction.

We also have extracted copper electrochemically from seawater by depositing all the copper in a mercury film. Then the copper was completely stripped out of the mercury film into a small volume of acidified distilled water. An aliquot of this solution was analyzed by flameless atomic absorption spectrometry. All operations, except the transfer of an aliquot of the final solution to the atomic absorption spectrometer, were carried out in a laminar flow hood. The concentration of copper was increased by a factor of about 100 in this process. This gives a theoretical limit of detection of 0.6 ppt or  $6 \times 10^{-4}$  micrograms/liter of seawater, less than 1 % of the concentration of copper in the open ocean. The advantage of using a thin film of mercury over a hanging drop is that the greatly increased surface area (100-200 times greater) allows the analysis of a much larger volume of sample in a comparable time. The advantage

of stripping back into an aqueous solution instead of putting the mercury solution directly into the graphite tube furnace is that the direct insertion of aqueous samples is more precise and since the sample is not introduced all at one time, several determinations can be made of the same electrolysis to check for errors and to determine precision. Of course, sensitivity may be lost in that the concentration of the solution analyzed may not be as high as in the corresponding mercury drop.

We have measured several samples of seawater ranging in copper concentration from less than 0.03 to 0.7 ( $\pm 10\%$ ) micrograms/liter. The values obtained were in agreement with those obtained by anodic stripping voltammetry. We have also purified electrolyte solutions as well as seawater itself, electrochemically and then spiked to certain values. We analyzed these spiked samples and found the appropriate values.

This method should be applicable to the measurement of any metallic ion which can be electroplated and subsequently stripped from a mercury electrode. These include Ag, Ba, Bi, Cd, Cu, Ga, Ge, In, K, Mn, Na, Ni, Pb, Pt, Sb, Sn, Sr, Tl and Zn [5]. Experiments are now being carried out to ascertain if this method is applicable to those metals which will electrodeposit on bare graphite.

#### References

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