

A New Voltammetric Method for the Simultaneous Determination  
of Cu and Hg in Sea Water

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S u m m a r y

A new voltammetric method for the simultaneous determination of Cu and Hg in sea water with the rotating twin gold electrode is described.

R é s u m é

Une nouvelle méthode voltammétrique pour la détermination simultanée du Cu du Hg dans l'eau de mer a l'aide d'une électrode jumelée d'or est décrite.

Copper and mercury belong to two different important groups of trace metals, present in the marine environment. While mercury is known as one of the most hazardous toxic metals, even if present in very low concentrations, Cu has an essential function for living organisms below a critical threshold level above which it causes also toxic effects. An accurate and precise knowledge of the concentration and species distribution of both trace metals in sea water is thus of

particular importance.

The introduction of differential pulse anodic stripping voltammetry (DPASV) at the mercury film electrode (MFE) on glassy carbon carrier has provided a particularly sensitive and reliable way to determine simultaneously Cd, Pb and Cu in sea water from coastal regions and the open sea (1,2). A reliable voltammetric method for the determination of mercury with the rotating gold twin electrode in the subtractive DPASV-mode has been also introduced by us recently (3). The application of the subtractive mode has yielded in the past also significant improvements in the performance of conventional linear scan anodic stripping voltammetry in connection with a twin electrode of the mercury coated glassy carbon type (4). The application of mercury coated glassy carbon electrodes faces, however, for the determination of Cu some inconvenience and risks, if it is not taken into account that the solubility of Cu in mercury is rather limited and consequently two Cu-phases may occur (5,6).

In the present paper a new voltammetric method is described which enables in a very convenient manner the simultaneous determination of Cu and Hg by DPASV at a gold electrode. However, the determination of Pb and Cd is not possible with this electrode and has to be performed with the previously described glassy carbon based MFE. The measurements are made in two steps:

i) The concentration of Hg is determined with differential pulse anodic stripping voltammetry in the subtractive mode (DPASV-S) at a twin disc gold electrode after medium exchange to 0.1 M perchloric acid spiked with  $2 \times 10^{-3}$  M HCl. The electrode rotates with 3000 rpm during the cathodic deposition

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while a particular program of polarization with short intermittent anodic pulses (5a) is applied for elimination of deposited Cu. This ensures identical background currents on both halves of the working electrode. The concentration of Hg is evaluated by the standard addition method. ii) For the subsequent Cu-determination the utilization of programmed polarization during cathodic deposition and of the subtractive mode during stripping can be omitted and conventional DPASV at the gold electrode is applied. Other-wise the Cu-determination follows the same procedure as described before Hg. Between each deposition and stripping the electrode is electrochemically activated.

A simple home made microcomputer in connection with a modified PAR 174 A polarograph supplies the potential program necessary during the deposition of Hg, the switching off and on of the electrodes during medium exchange and performs automatically the other necessary controls during the measurements.

As Hg and Cu tend to be strongly chelated by dissolved organic matter (DOM) sea water samples are divided before voltammetric determination into two subsamples. One subsample is subjected to UV-irradiation (6h, 150 W, 60°C) to release Cu and Hg from eventually present strong organic chelates.

The new voltammetric procedure has determination limits of 2 ng/l and 20 ng/l for Hg and Cu, respectively, and with an error of + 20 % a rather good precision. It provides therefore a particularly reliable approach for the determination of ultra-trace levels of both metals in sea water and other natural water types.

#### REFERENCES

1. Nürnberg, H.W., Valenta, P., Mart, L., Raspor, B. and Sipos, L. (1976), The polarographic approach to the determination and speciation of toxic trace metals in the marine environment. *Z. Anal. Chem.*, 282, 357-367.

2. Nürnberg, H.W., Mart, L. and Valenta, P. (1977), Concentration of Cd, Pb and Cu in Ligurian and Tyrrhenian Waters. *Rapp. Comm. int. Mar. Médit.* 24 (8), 25-29.
3. Sipos, L., Valenta, P., Nürnberg, H.W. and Branica, M. (1977), A new voltammetric method for the study of mercury traces in sea waater and inland waters, *J. Electroanal. Chem.*, 77, 263-266.
4. Sipos, L., Kozar, S., Kontušić, I. and Branica, M. (1977) Subtractive anodic stripping voltammetry with rotating mercury coated glassy carbon electrode, *J. Electroanal. Chem.*, 87, 347-352.
5. Branica, M., Sipos, L., Bubić, S. and Kozar, S. (1976), Electroanalytical determination and characterization of some heavy metals in sea water. Proceedings of the 7th IMR Symp., Oct. 7-11, 1974, Gaithersburg, Md., USA, NBS Spec. Publ. 422, 917-928.
6. Valenta, P., Mart, L. and Rützel, H. (1977), New potentialities in ultratrace analysis with defferential pulse anodic stripping voltammetry, *J. Electroanal. Chem.*, 82 327-343.

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## DISCUSSION

## Questions and comments:

1. Why didn't you measure copper and mercury at natural pH?  
I believe that this information is very important with respect to evaluate the toxicity of heavy metals for certain organisms as some unicellular algae (R. FERRARA, Italy)
  - The measurements at natural pH are connected with experimental difficulties of maintaining constant pH during deaeration of the samples. During deaeration the pH increases due to elimination of  $\text{CO}_2$  from the system and hydrolysis; Precipitation and/or adsorption of trace metals on cell walls may occur. For routine measurements it is therefore more advisable to work at pH 2 which is much better defined and more stable than the natural pH of the sea water sample.
2. Could you give us some details about the destruction of organic matter by UV irradiation: power, time of irradiation, oxidizing agent used, etc. (G. CAUWET, France)
  - The UV irradiation of the sample was carried out in a air cooled reactor with a 150 W mercury arc lamp in closed quartz tubings for 6 hours in the presence of 0.5 ml 30%  $\text{H}_2\text{O}_2$ /l sample. The temperature of the sample was  $60^\circ\text{C}$ .
3. How do you explain the influence of UV treatment on the signal (shape and height of the peak)? (B. ČOSOVIĆ, Yugoslavia)
  - Generally, by U.V. irradiation the peak height increases due to release of trace metals from strong chelates with dissolved organic matter and becomes better defined because of the absence of organic matter causing nonlinear background currents and hindering the electrode process.

4. What is the reason that the peak height of copper is higher in not UV radiated sample than in the radiated one?

(H. BILINSKI, Yugoslavia)

- The stripping peak of copper is not higher in non-irradiated samples. It is only distorted by the nonlinear background current due to the presence of the organic matter.

5. By total oxidation of sample we can destroy information about the content of inorganic mercury and mercury chelated with organic matter. How do you avoid this?

(A. BALLESTER, Spain)

- In many natural samples it was possible to measure Hg without U.V. irradiation; that means in such samples one can distinguish total Hg and electroactive Hg content. Distinguishing inorganic from organic Hg using this technique is difficult because some organic mercury compounds (i.e. methyl mercury) are also electroactive.