

## Application of Vibrating Dropping Mercury Electrode for Trace Metal Speciation

M.Lovrić, T.Magjer and M.Branica

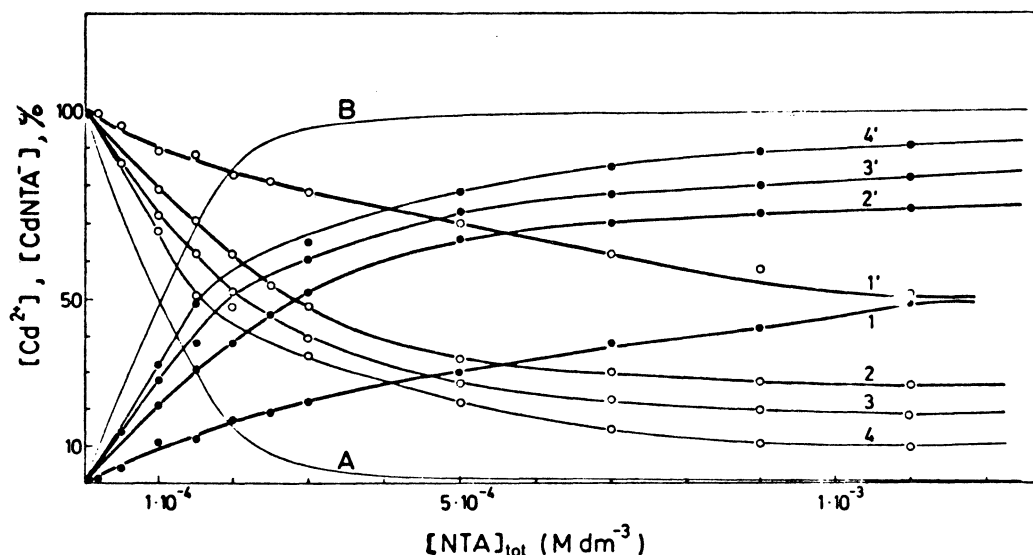
Center for Marine Research Zagreb, "Rudjer Bošković" Institute, Zagreb, Croatia, Yugoslavia

**Summary** The application of VDME for the characterisation of ionic species and for electroanalytical measurements of metal ions concentrations in strongly polluted water samples with different kinds of surface active substances is reported.

**Résumé** : Nous développons ci-après une étude sur l'application du VDME à la caractérisation d'espèces ioniques et aux mesures électroanalytiques des concentrations d'ions métalliques dans des échantillons d'eau fortement polluée par différentes sortes de substances actives en surface.

One of the critical points in the speciation of dissolved metal traces in marine environment is the recognition between the real distribution of the species in the bulk of investigated solution and artefacts caused by the reactions in the vicinity of the electrode.

Fig. 1



This paper describes the application of newly developed (1) vibrating dropping mercury electrode (VDME) with a very short drop time (down to 5 ms.) for the speciation studies. As a model system, the interactions of Cd with NTA were investigated. At the same time, the proposed VDME has some advantages in excluding the influence of surface active substances (SAS) on the electrode processes of metal ions.

Figure (1) shows the polarographic results for the titration of  $\text{Cd}^{2+}$  with  $\text{Na}_2\text{HNTA}$  at  $\mu=0.1$  ( $\text{mol}/\text{dm}^3$ ) and  $\text{pH}=6$  in citrate buffer. The diffusion currents of "free"  $\text{Cd}^{2+}$  and  $\text{CdNTA}^-$  waves are plotted

against the total concentration of  $\text{Na}_2\text{HNTA}$  added. The experiment was performed with the DME (drop life time  $t=4\text{s}$ ) using d.c. (curves 1 and 1') and pulse (curves 3 and 3') polarographic excitation techniques and with the VDME using d.c. polarography at dropping rates of 10 drops/s (curves 2 and 2') and 100 drops/s (curves 4 and 4'). The curves A and B represent theoretically calculated equilibrium concentrations of  $\text{Cd}^{2+}$  and  $\text{CdNTA}^-$  ions if no citrate ions are present. From the experiment, the stability constant of  $\text{CdNTA}^-$  complex, at  $\text{pH}=6$ , was calculated:  $K_{\text{CdNTA}} = (2.1 \pm 0.1) \cdot 10^{10} \text{ (dm}^3/\text{mol)}$  which is in a fair agreement with the literature data (2).

The electroanalytical measurements in natural samples can be significantly complicated by the adsorption of electroactive, naturally existing, surface active substances. One of the most commonly used model substances for the investigation of the SAS influence on the electrochemical reactions is Triton-X-100 (3). The concentration of T-X-100 required for the total suppression of  $\text{Cd}^{2+}$  reduction current at the VDME with  $t=10 \text{ ms}$  is more than an order of magnitude higher (700 mg/l) than for the suppression of the current on the DME with  $t=2 \text{ s}$  (40 mg/l) (3).

## References

- 1) T. Magjer, M. Lovrić and M. Branica: "A Device for Vibrating Dropping Mercury Electrode", *Croat. Chem. Acta* **53** (1980) 101.
- 2) L.G. Sillen and A.E. Martell: "Stability Constants of Metal-ion Complexes", *Chem. Soc. London*, 1964.
- 3) Z. Kozarac, S. Nikolić, I. Ružić and B. Čosović: "Inhibition of the Electrode Reaction in the Presence of Surfactants Studied by Differential Pulse Polarography. Cadmium(II) in Seawater in the Presence of Triton-X-100", *J. Electroanal. Chem.* **137** (1982) 279.

Lovrić, M., Magjer, T., Branica, M.

"Application of vibrating dropping mercury electrode for trace metal speciation"

Paper presented by M. Lovrić (Yugoslavia)

## Discussion

P. Valenta: The comparison of the new method with pulse polarography has to be corrected by two points.  
A) The dissociation rate of a complex depends also on the concentration of the complex at

the electrode surface. Therefore, working with pulse polarography and going to lower bulk metal concentrations (typically  $10^{-7}$  M) the same effect is accomplished, i.e., the lower rate of the dissociation of the complex. The new method (vibrating dropping Hg electrode) cannot go to lower concentrations because of the lower faradaic current/charging current ratio.

B) The short time of contact with the electrode is also attainable by normal pulse polarography adjusting the starting potential of the pulse outside of the potential range of adsorption, i.e., to more positive or negative potentials. Mostly organic substances desorb at potentials higher than about -1.2 (V) vs. SCE. Short contact of the electrode with the solution can also be accomplished by the Hg-streaming electrode introduced by Heyrovsky some 30 years ago. On the whole, the main advantage of the proposed method is its very simple electronic instrumentation.

M. Lovrić:

Dr. Valenta is right that the dissociation rate of a certain complex ML depends on its concentration, but the dissociation of ML is the first-order-reaction, so the kinetic contribution to the polarographic wave of "free" metal ion does not depend on complex concentration but only on the time of measurement, the dissociation rate constant, the stability constant and the free ligand concentration. For the simple

reaction:  $M + L \rightleftharpoons ML$ , we can define

$$v_{\text{diss.}} = k_{\text{diss.}} [ML];$$

$v_{\text{ass.}} = k_{\text{ass.}} [M][L]$  and the bulk (equilibrium) concentrations  $[ML]_0 = K [M]_0 [L]_0$ . On the

plateau of the wave, the concentration of free metal ion near the electrode surface will be close to zero, so the association rate can be neglected and the dissociation of the complex species will prevail. For dissociation process corresponding relations are valid:  $[ML]_t = [ML]_0 \exp(-k_{\text{diss.}} t)$

or:

$$[ML]_0 - [ML]_t = [ML]_0 [1 - \exp(-k_{\text{diss.}} t)]$$

The ratio between the kinetic contribution to the polarographic wave of "free" metal ion and its purely diffusional limiting current can be approximated by the expression:

$$([ML]_0 - [ML]_t) / [M]_0 = [L]_0 K (1 - \exp(-k_{\text{diss.}} t)).$$

The second remark is only correct, but only in principle. The potential range in which a certain SAS adsorbs could be so broad that it would be impossible to choose the starting potential outside this range (because of mercury oxidation or hydrogen evolution, for instance).

#### M. Branica:

In the last decades the electro-analytical methods developed in two directions: (i) by the application of more sophisticated instrumentation changing the form of excitation signals (and the response recording) and (ii) by the development of new types of electrodes. The present communication ment to to be a contribution to the development of a new type of electrode, what was not explicated enough.

H.W. Nürnberg:

The kinetic potentialities of the vibrating DME are obvious and they can become, depending on the vibration frequency, comparable to pulse methods, but the similar favourable signal-to-noise ratios ( $i_F/i_C$ ) as in pulse methods are not attained. With respect to kinetic effects in studies of ML formation (L = NTA, EDTA, etc.), i.e., dissociation kinetics of ML, they tend to be negligible provided measuring time is small and reactant concentration low (pulse methods) and the stability of ML is not too low. Practical existence of equilibrium conditions can be tested experimentally and theoretically, e.g., if the correct stability constant can be evaluated from the experimental data.

M. Lovrić:

Dr. Nürnberg is right that the low signal-to-noise ratio at VDME is the biggest vice of this technique and we are working on the increasing of VDME sensitivity. The answer to this comment is already partially given. The experimentally obtained stability constant cannot be tested theoretically (by comparing with literature data) because the literature data vary very much. The only rigorous method of testing the obtained constants is to repeat the measurement at shorter measurement time. If the constant does not change by shortening of the time of contact it is realistic.

