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A new mercury drop electrode for trace metal analysis

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Received 10 July 1996; revised 16 October 1996; accepted 20 October 1996

Abstract

A new mercury drop electrode, model-1 (MDE-1, Eco Chemie, Utrecht, Netherlands) is described. The sensitivity and the reproducibility of the electrode were tested for the determination of dissolved trace metals in natural aquatic systems using differential pulse anodic stripping voltammetry (ASV). The measurements were performed at pH=7.8 using a quartz cell, with a plastic stirrer and a glass reference electrode. The results obtained showed significant adsorption of the dissolved trace metal. The adsorption mainly takes place at the surface of the cell assembly (a plastic stirrer and a reference electrode made of glass), whereas only 1.5% of dissolved copper(II) is adsorbed on the walls of the quartz cell. The adsorption of trace metals is significantly suppressed when the plastic stirrer and the sinter glass tip of the reference electrode are made of quartz. The reproducibility of the current response of the repetitive measurements of anodic peak currents of the acidic solution for the concentration range between 10^{-7} and 2×10^{-10} M Cd^{2+} showed variation coefficients from 0.7% to 3.5%, respectively. The MDE-1 detection limit of 2.5×10^{-11} M Cd^{2+} was obtained under the given experimental conditions.

Keywords: Stripping voltammetry; Sensitivity; Reproducibility; Trace metals

1. Introduction

The determination and the speciation of dissolved trace metals in environmental aquatic systems are essential for an understanding of their entire biogeochemical cycles [1–3]. Determination of low concentrations of trace metals present in natural waters (below 10^{-8} M) requires selective and highly sensitive techniques and methods [2,3]. Further development of analytical procedures is essential for achieving accurate results of the distribution of physico-chemical forms of trace metals.

Anodic stripping voltammetry (ASV) with various scanning operating modes, is a very suitable technique for the determination of dissolved trace metals, due to its low detection limit and specific sensitivity for different chemical forms of the dissolved metals [4,5]. An ASV technique is much more advantageous for the speciation studies in natural water systems than other techniques (i.e. cathodic stripping voltammetry, atomic absorption spectroscopy, etc.) because it requires neither chemical preconcentration nor the addition of chemical reagents.

Well-controlled geometry and hydrodynamics of electrochemical systems are necessary for the accurate and reproducible determination of dissolved trace metals using ASV.

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Different types of working electrodes which are applied in the determination of trace metals are described elsewhere. Thin mercury film glassy carbon disk electrode (TMFGCDE) appears to be the most sensitive one for this purpose [3,5–10]. However, the mercury drop electrode is the most utilized polarographic and voltammetric electrode, due to its well-documented characteristics. A number of various designs of a dropping mercury electrode (DME) and a hanging mercury drop electrode (HMDE) are described elsewhere [11–20]. Mercury drop electrodes with a solenoid activated valve have recently been developed [14–20]. EG & G Princeton Applied Research static mercury drop electrodes (SMDE) Model 303 and 303A are widely used [14]. Several mercury drop electrodes based on the mechanical blocking of the mercury flow with a metal needle (activated by a solenoid or pneumatically) are described elsewhere [17–20]. These electrodes are commercially produced by Tacussel and Metrohm.

Very simple and reproducible renewal of the mercury drop surface, as compared to a solid electrode, makes this electrode very efficient for the automation of various voltammetric measurements.

The determination of trace metals speciation in natural waters is usually associated with problems dealing with the reproducibility of the electrode response and the adsorption of dissolved trace ions onto electrochemical cell assembly [21–23]. The adsorption of trace metals onto the sampling and storing containers as well as the measuring vessels, presents a problem in the determination of dissolved and total metal concentrations in natural water samples. This can partly be overcome by placing these containers under natural conditions so as to equilibrate the active sites prior to a sampling procedure. However, the adsorption–desorption equilibrium in containers could be disturbed after the sampling procedure, due to the release or additional adsorption of dissolved trace metals. The dissolved metal concentration in the sample increases by the standard addition method, thus enhancing the adsorption. It is shown that the adsorption of dissolved trace metals increases the virtual metal complexing capacity and the results consequently obtained are not representative for natural water samples [23]. The use of non-

adsorbable materials for the cell assembly could solve these problems.

This paper describes a newly constructed mercury drop electrode (MDE-1) where the drop formation is electromagnetically controlled by a needle valve. Following the adjustments to certain parts of the electrochemical cell assembly, good reproducibility, sensitivity and applicability of the system for the characterization of natural water samples were achieved.

2. Instrumentation and chemicals

Voltammetric measurements were performed using μ AUTOLAB multimode polarograph (Eco Chemie, Utrecht, Netherlands) connected to an IBM PC 486 compatible computer and the corresponding Electro Analytical System software version 2.4 (EAS), which offers variety of the polarographic and voltammetric techniques: Square-wave, differential and normal pulse, sampled dc, ac and ac 2nd harmonic, both normal and stripping mode.

For the determination of trace metal concentrations, using a standard addition method, the additions of the stock solution to the sample were carried out automatically by a Cávro burette system (Cávro XL 3000 Modular Digital Pump).

A three-electrode system was used in all measurements. A new mercury drop electrode was used as a working electrode, where the glass capillary was manufactured by Metrohm (Herisau), for the VA-Stand 663. The reference electrode was an Ag/AgCl/sat. NaCl electrode, and a platinum wire was used as a counter electrode.

The chemicals were either of “suprapur” (NaCl and concentrated HNO_3) or of “analytical-reagent” grade (Merck, Darmstadt). Sea water samples ($S=32\%$, $\text{pH}=8.1$) were collected from the Šibenik Bay and stored at 4°C prior to analysis.

The pH of the solutions was adjusted to 7.9 ± 0.1 with a $5\times 10^{-3}\text{ M}$ borate buffer solution ($\text{H}_3\text{BO}_3+\text{NaOH}$) and to 3.5 or 2 by the addition of a “suprapur” conc. HNO_3 . pH of the solution was controlled by an Orion Research pH meter (EA 920) connected to a glass pH electrode.

Prior to measurements, the solutions were purged with extra-pure nitrogen for 15 min (no changes of

pH were observed after purging); a nitrogen blanket was maintained thereafter. A Milli-Q water was used in all experiments.

A differential pulse anodic stripping voltammetry, DPASV, as a scanning operating mode, was applied under controlled conditions of deposition potential (E_{dep}), differential pulse amplitude (A), potential step increment ($E_{\text{st inc}}$), deposition time (t_{dep}), time between pulses (t_{int}), and pulse duration (t_{dur}).

3. The electrochemical cell assembly of MDE-1

The electrochemical cell assembly of a new mercury drop electrode MDE-1 (home-made) is illustrated in Fig. 1. The electrochemical cell assembly consists of an electrochemical home-made quartz cell with a working volume of 50 ml (1), reference

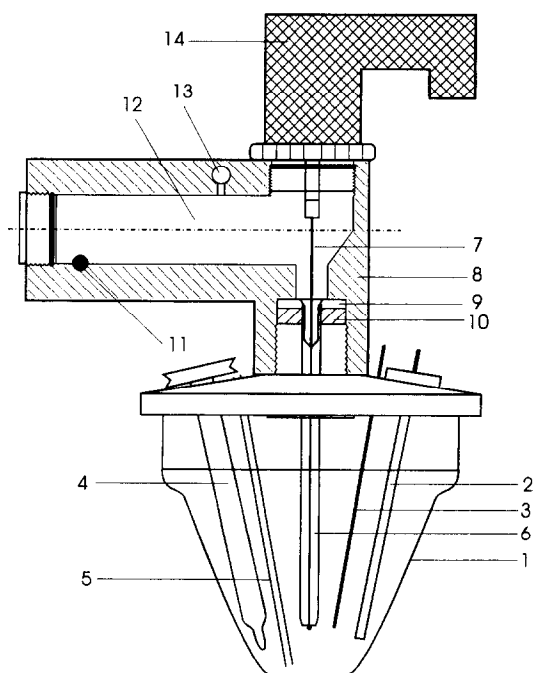


Fig. 1. The scheme of the electrochemical cell assembly of the electromagnetic valve multimode mercury drop electrode (MDE-1); (1) electrochemical cell, (2) reference electrode, (3) counter electrode, (4) rotating stirrer, (5) tube for nitrogen, (6) glass capillary, (7) locking needle, (8) plexiglass body, (9) PTFE ring, (10) silicon ring, (11) electrical contact, (12) mercury reservoir, (13) nitrogen connector, (14) electromagnet.

and counter electrodes (2 and 3), a rotating stirrer (4), a PTFE tube for nitrogen input (5) and a glass capillary (6) connected to a device for the mercury drop formation (7–14).

A device for the mercury drop formation is the main part of the whole electrode. An electronically controlled electromagnet (14), connected to a stainless steel locking needle (7), lifts the needle above the capillary. The needle must be carefully positioned so as to avoid any damage of the glass capillary and/or the needle tip. The pressure of 1 bar, maintained by nitrogen over the connector (13), is necessary for the mercury drop formation because of the small capillary diameter ($\phi=50\text{ }\mu\text{m}$).

The rotating stirrer strapped to the electromotor with a neoprene pulley, operates alternatively at six rotating rates.

The mercury drop electrode MDE-1 can operate in two modes: as a hanging mercury drop electrode (HMDE) or as a free dropping mercury electrode (DME).

The mercury drop in the HMDE operation mode is formed by the lifting of the locking needle. The electrode in the HMDE operating mode allows three different times for the mercury drop formation corresponding to drop radii, denoted as small ($r_s=150\text{ }\mu\text{m}$), medium ($r_M=170\text{ }\mu\text{m}$) and large ($r_L=190\text{ }\mu\text{m}$).

In the DME operation mode, the needle is constantly above the capillary entrance and mercury flows continuously through the capillary. A mercury drop time is controlled by an electronic circuit connected to the electromagnetic knocker.

During the testing of the MDE-1, the adjustments were made by replacing the stirrer (4) and the reference electrode (2) material with quartz.

All operations of the mercury drop electrode system (mercury drop formation, stirring and deaeration) were entirely automatically controlled by the computer equipped with the corresponding electrochemical software (EAS).

4. Experimental procedures and results

The cell assembly consisting of the originally constructed electrode system (prior to adjustments) included a plastic stirrer and a glass reference

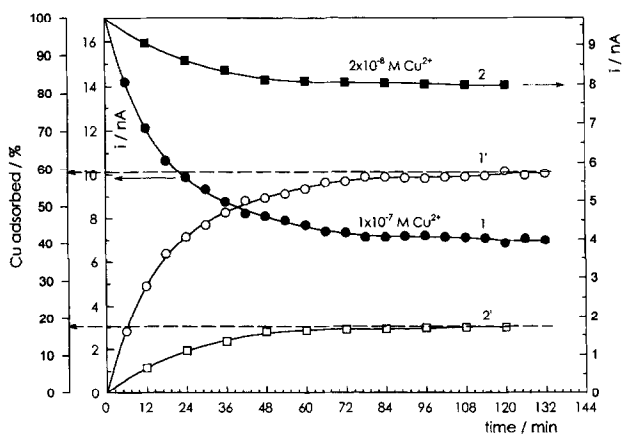


Fig. 2. Dependence of 10^{-7} and 2×10^{-8} M Cu^{2+} anodic peak heights (curve 1 and 2) and percentage of dissolved copper(II) ions adsorbed onto the cell system (curve 1' and 2') vs. the adsorption time; (curves 1 and 1' obtained in the original cell assembly, curves 2 and 2' obtained in the quartz adjusted cell assembly) supporting electrolyte 0.55 M NaCl, pH=7.8; DPASV parameters: $E_{\text{dep}}=-0.4$ V, $A=0.05$ V, $t_{\text{dep}}=300$ s (curve 1), $t_{\text{dep}}=600$ s (curve 2) $t_{\text{int}}=0.2$ s, $t_{\text{dur}}=0.0$ s.

electrode. The decrease of the metal anodic peak current was observed when the measurements were performed at pH of about 8, due to the adsorption of dissolved trace metals onto parts 1–6 of the electrochemical cell assembly. Repetitive measurements performed in 0.55 M NaCl, at pH=7.8 (Fig. 2) showed a decrease of the copper(II) anodic peak current (curve 1) and an increase of the corresponding percentage of the total copper(II) adsorbed (curve 1') with time. Initial results of the copper(II) peak current were obtained 6 min after the addition of a 10^{-7} M of copper(II) ion to the solution. About 60% of the initially added copper(II) ions were adsorbed onto the cell assembly after 130 min. About 30% of copper(II) was only adsorbed after 12 min. This suggests that the measurements performed under conditions corresponding to natural seawater (pH about 8) will yield biased results. The results illustrated in Fig. 2 indicate that the analysis of dissolved trace metals of natural water samples (pH=8) are strongly influenced by the adsorption onto the electroanalytical assembly.

By replacing certain parts of the cell assembly (1–6) with clean ones, after the adsorption of dissolved copper(II) from the solution (130 min), we attempted

to identify the parts which were primarily responsible for the adsorption process. The experiments are described as follows:

- After the adsorption (130 min) of 10^{-7} M copper(II) onto the initial cell assembly (1–6), the electrochemical quartz cell (1) was detached from the other parts (2–6) which were then immersed into a clean quartz cell containing 50 ml of supporting electrolyte (0.1 M NaCl, pH=2). The desorption of copper(II) from the cell assembly (2–6) resulted in 6×10^{-8} dissolved copper(II) (Fig. 3, curve A).
- A 50 ml of the solution, which remained in the initial quartz cell (1) (pH=8), was transferred to another clean assembly (1–6) and acidified with HNO_3 to pH=2. The same copper(II) concentration of 4×10^{-8} M was found in the acidic solution as well as in the solution (pH=8) after the adsorption process (Fig. 3, curve B).
- The initial quartz cell (1) was refilled with 50 ml of fresh supporting electrolyte (0.1 M NaCl, pH=2) and analyzed for the copper(II) concentration. The copper(II) concentration of only 1.5×10^{-9} M was found (Fig. 3, curve C). Such a small portion of copper(II) (1.5%) can be attributed to the desorption from the walls of the initial quartz cell (1).

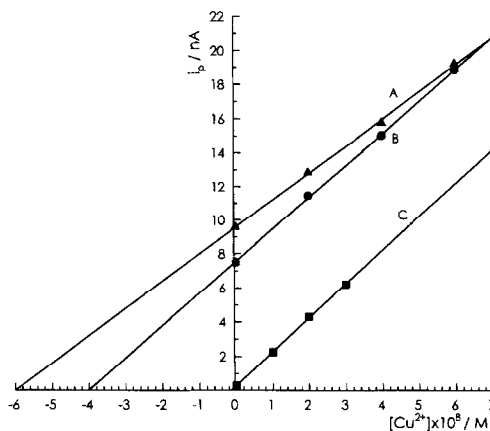


Fig. 3. Partitioning of copper(II) concentration (10^{-7} M) between the parts of cell system after 130 min of adsorption time (see Fig. 2 curves 1 and 1'); Concentration axis intercepts: (A) copper(II) adsorbed onto cell assembly, (B) dissolved copper(II) found in the solution, and (C) copper adsorbed onto quartz cell; DPASV parameters: $E_{\text{dep}}=-0.4$ V, $A=0.025$ V, $t_{\text{dep}}=300$ s, $t_{\text{int}}=0.2$ s, $t_{\text{dur}}=0.05$ s.

These experiments showed that most (60%) of 10^{-7} M copper(II) added to the solution (pH=8) was adsorbed onto the surfaces of the cell assembly (2–6), while only 1.5% of the adsorption took place at the quartz cell (1).

To suppress the adsorption of dissolved trace metals from natural waters (pH=8) onto the cell assembly, the material of the cell assembly parts (plastic stirrer (4) and the glass reference electrode (2)) was replaced with quartz.

Figure 2 (curves 2 and 2') illustrates that the suppression of the adsorption of copper(II) on the cell assembly (less than 20%) is achieved, even at the dissolved copper(II) concentrations (2×10^{-8} M) lower than those in previous experiments (10^{-7} M). It was confirmed that practically the largest part of adsorption of trace metals took place at the plastic stirrer and the reference electrode with sintered glass tip.

Further results were obtained using only the adjusted cell assembly. Reproducibility of the response of the MDE-1 was determined at four different concentration levels of cadmium(II) (10^{-7} , 10^{-8} , 10^{-9} and 2×10^{-10} M), in the supporting electrolyte of 0.03 M HNO_3 , pH=2. Fig. 4 shows the current responses of cadmium(II) obtained after

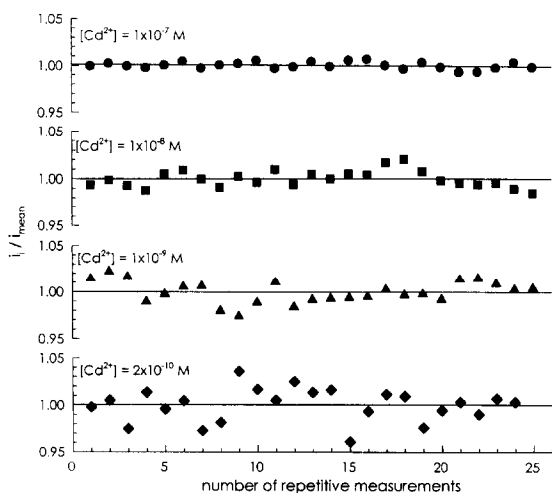


Fig. 4. Repetitive anodic peak currents of 10^{-7} , 10^{-8} , 10^{-9} , 2×10^{-10} M Cd^{2+} normalized to their mean value (176, 16.4, 1.45 and 0.64 nA, respectively); supporting electrolyte 0.03 HNO_3 , pH=2; DPASV parameters (for 10^{-7} , 10^{-8} , 10^{-9} M Cd^{2+}): $E_{\text{dep}}=-0.8$ V, $A=0.05$ V, $t_{\text{dep}}=600$ s, $t_{\text{int}}=0.2$ s, $t_{\text{dur}}=0.05$ s.; DPASV parameters (for 2×10^{-10} M Cd^{2+}): $E_{\text{dep}}=-0.8$ V, $A=0.05$ V, $t_{\text{dep}}=900$ s, $t_{\text{int}}=0.2$ s, $t_{\text{dur}}=0.04$ s.

repetitive measurements. The anodic peak currents were normalized to their mean value. Confidence limits of the determination of cadmium(II) at the concentrations of 10^{-7} , 10^{-8} , 10^{-9} and 2×10^{-10} M, (for the confidence interval of 95%), under given experimental conditions, are 1.000 ± 0.007 , 1.000 ± 0.017 , 1.000 ± 0.024 and 1.000 ± 0.035 , respectively [24,25]. Reproducibility of the results decreases with lowering the concentration of cadmium(II) because of a relative increase of the current noise. Even the measurements of the peak current at the concentration level of 2×10^{-10} M Cd^{2+} gives a variation coefficient of about 3.5%, only. This suggests that the reproducibility of the MDE-1 response, even at low metal concentrations, is sufficient enough for the accurate metal determination in natural water samples.

Figure 5 shows the original and smoothed voltammograms and the calibration curve of the standard addition method for the determination of cadmium(II) concentrations. The measurements were performed in a supporting electrolyte of 0.03 M HNO_3 , pH=2, using differential pulse anodic stripping voltammetry. Well-defined voltammetric curves were obtained. For each addition of cadmium(II), three repetitive measurements of the current response were carried out. The anodic voltammograms were smoothed by the Savitzki–Golay method, level 4,

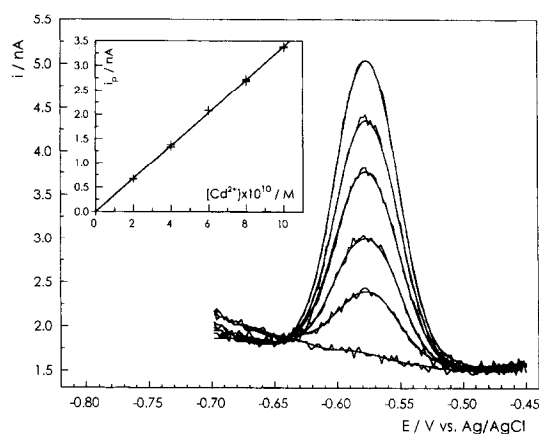


Fig. 5. Calibration graph and original and smoothed DPASV voltammograms for the standard addition method of cadmium(II); limit of detection: 2.5×10^{-11} M Cd^{2+} ; supporting electrolyte 0.03 M HNO_3 , pH=2; DPASV parameters: $E_{\text{dep}}=-0.8$ V, $A=0.05$ V, $t_{\text{dep}}=900$ s, $t_{\text{int}}=0.2$ s, $t_{\text{dur}}=0.04$ s.

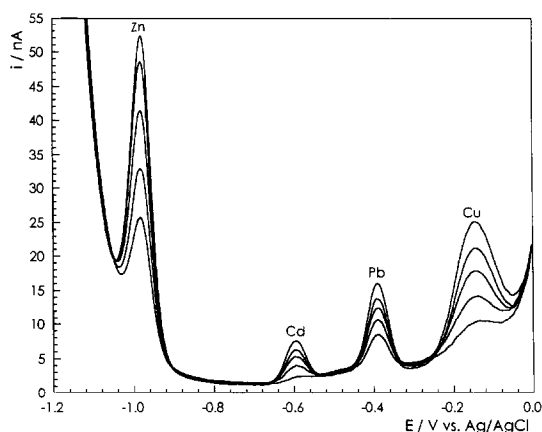


Fig. 6. DPAS voltammograms of standard addition method for determination of Zn, Cd, Pb and Cu in seawater sample (pH=3.5); DPASV parameters: $E_{\text{dep}} = -1.25$ V, $A = 0.05$ V, $t_{\text{dep}} = 600$ s, $t_{\text{int}} = 0.2$ s, $t_{\text{dur}} = 0.05$ s.

offered by the ElectroAnalytical Software (EAS), and the peak currents were determined from the smoothed voltammograms. For cadmium(II) a detection limit of 2.5×10^{-11} M was obtained from the calibration curve [25] (experimental conditions: $E_{\text{dep}} = -0.8$ V, $t_{\text{dep}} = 900$ s, $A = 50$ mV, $t_{\text{int}} = 0.2$ s, $t_{\text{dur}} = 0.04$ s). For the initial addition of cadmium(II) (2×10^{-10} M) the peak current was about 0.65 nA. Owing to a low background current noise of the instrument (± 0.024 nA) (μ AUTOLAB, Eco Chemie), it was possible to measure such small peak currents. The determination of very low metal concentration levels is possible considering the good sensitivity and reproducibility of this electrode.

An example of the trace metals determination in natural seawater samples (collected from the Šibenik area), is shown. The seawater samples were acidified to pH=3.5 to determine the "total" metal concentrations. Fig. 6 illustrates a series of differential pulse anodic stripping voltammograms recorded (smoothed) for zinc(II), cadmium(II), lead(II) and copper(II) using the standard addition method. Fig. 7 shows calibration curves from which the total dissolved trace metal concentrations of Zn, Cd, Pb and Cu were calculated, $8.3 \pm 1.1 \times 10^{-9}$, $1.5 \pm 0.3 \times 10^{-10}$, $1.5 \pm 0.1 \times 10^{-9}$ and $2.2 \pm 0.2 \times 10^{-9}$ M, respectively. Higher lead concentrations could probably be attributed to the traffic in the vicinity of the sampling station. The concentration of

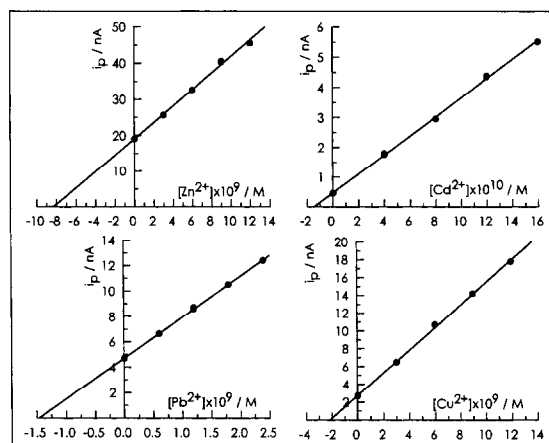


Fig. 7. Calibration curves of the standard addition method for determination of Zn, Cd, Pb and Cu in seawater sample (pH=3.5); DPASV parameters: $E_{\text{dep}} = -1.25$ V, $A = 0.05$ V, $t_{\text{dep}} = 600$ s, $t_{\text{int}} = 0.2$ s, $t_{\text{dur}} = 0.05$ s.

other trace metals are expected in seawater from coastal areas.

5. Conclusions

The mercury drop electrode MDE-1 detection limit of 2.5×10^{-11} M Cd^{2+} is comparable to that of the solid electrode (TMFGCDE) (8×10^{-12} M Pb^{2+} [10]). The reproducibility of its response appears to be considerably better than that of the SMDE PAR 303A (EG & G) [24]. The capability of the renewal of the working electrode surface (MDE-1), with a good reproducibility, appears to be more suitable for the automation of the trace metals determination, speciation as well as complexing capacity determination in natural water samples.

By suppressing the adsorbability of the whole assembly for the added dissolved trace metals, the MDE-1 becomes appropriate for metal complexing capacity determination in the range above 10^{-9} M metal equivalent, as well.

Acknowledgements

The financial support of the Ministry of Science and Technology of the Republic of Croatia, EUR-

EKA-493- ELANI (EUROMAR) Project, as well as KFA, Jülich, within the bilateral agreement between Germany and Republic of Croatia, is gratefully acknowledged.

References

- [1] E.D. Goldberg (Ed.), *The Nature of Seawater*, Dahlem Konferenzen, Berlin, 1975.
- [2] M. Branica, *Environmental Research in Aquatic Systems*, Forschungszentrum Jülich, Scientific Series of Int. Bureau, Vol. 3., 1990.
- [3] T.M. Florence, *Analyst*, 111 (1986) 489.
- [4] J. Wang, *Stripping Analysis*, VCH Publishers, Deerfield Beach, Florida, 1985.
- [5] A.M. Bond, *Modern Polarographic Methods in Analytical Chemistry*, Marcel Decker, New York, 1980.
- [6] T.M. Florence, *J. Electroanal. Chem.*, 27 (1970) 233.
- [7] T.M. Florence, *J. Electroanal. Chem.*, 35 (1972) 237.
- [8] M. Plavšić, S. Kozar, D. Krznarić, H. Bilinski and M. Branica, *Mar. Chem.*, 9 (1980) 175.
- [9] M. Plavšić, D. Krznarić and M. Branica, *Mar. Chem.*, 11 (1982) 17.
- [10] D. Omanović and Ž. Peharec, T. Magjer, M. Lovrić and M. Branica, *Electroanalysis*, 6 (1994) 1029.
- [11] W. Kemula and Z. Kublik, *Anal. Chim. Acta*, 18 (1958) 104.
- [12] R. Dias, Cl. Buess-Herman and L. Gierst, *J. Electroanal. Chem.*, 130 (1981) 345.
- [13] M.L. Foresti and R. Guidelli, *J. Electroanal. Chem.*, 197 (1986) 159.
- [14] PAR Electrode, UK Patent Application GB 2013346A.
- [15] A.M. Bond, *J. Electroanal. Chem.*, 118 (1981) 381.
- [16] Z. Kowalski, K.H. Wong, R.A. Osteryoung and J. Osteryoung, *Anal. Chem.*, 59 (1987) 2216.
- [17] W.A. Byers and S.P. Perone, *Anal. Chem.*, 55 (1983) 412.
- [18] T. Novotny, *Electroanalysis*, 2 (1990) 257.
- [19] J. Pedrotti, L. Angnes and I.G.R. Gutz, *Electroanalysis*, 4 (1992) 635.
- [20] R.M. Town, M.-L. Tercier, N. Parthasarathy, F. Bujard, S. Rodak, C. Bernard and J. Buffle, *Anal. Chim. Acta*, 302 (1995) 1.
- [21] J.M. Diaz-Cruz, M. Esteban, M.A.G.T. van den Hoop and H.P. van Leeuwen, *Anal. Chem.*, 64 (1992) 1769.
- [22] V. Cuculić and M. Branica, *Analyst*, 121 (1996) 1127.
- [23] D. Omanović and Ž. Peharec, I. Pižeta and M. Branica, *Mar. Chem.*, 53 (1996) 121.
- [24] I. Pižeta, D. Omanović and M. Branica, *Anal. Chim. Acta*, 331 (1996) 125.
- [25] J.C. Miller and J.N. Miller, *Statistics for analytical chemistry*, Ellis Horwood Series in Analytical Chemistry, Ellis Horwood, Chichester, 1984, p. 115.