

SUBTRACTIVE DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY AT A STATIONARY MERCURY-COATED GLASSY CARBON ELECTRODE

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ABSTRACT

The application of subtractive mode differential pulse anodic stripping voltammetry (SDPASV) at a stationary mercury-coated glassy carbon electrode for the analysis of labile Zn(II), Cd(II), Pb(II) and Cu(II) is described. It is shown that the method has an improved sensitivity to Cu(II) owing to elimination of high background currents normally encountered in normal mode DPASV at the TFME. The sensitivity limits of the present method to Cd(II) and Cu(II) is estimated to be 0.025 and 0.067 ppb respectively, when a 2 min deposition time is used. It is suggested that the high sensitivity of the method coupled to the relative simplicity of the stationary electrodes could make the method useful in environmental and natural water studies.

INTRODUCTION

Anodic stripping voltammetry (ASV) which increases sensitivity by preconcentration has been shown to be applicable for trace analysis of heavy metals in the sub ppb ($\mu\text{g/l}$) levels [1–6]. The method is attractive due to its apparent simplicity which could make it suitable for the design of environmental monitors and other field instrumentation if the detection level can be made low enough. Sensitivity improvements have been achieved by applying pulse and differential pulse techniques [5–8] and by applying two electrodes in the subtractive mode [9], using a flow cell [10] or a rotating glassy carbon split disc electrode [11].

In the present study we investigated the method of subtractive differential pulse ASV (SDPASV) for determination of Zn(II), Cd(II), Pb(II) and Cu(II) in seawater. A similar approach was applied previously by Sipos et al. [12] for ASV analysis of Hg at the rotating twin disc gold electrodes. As the method was intended to be used in conjunction with a flow-through cell on board ship we

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explored the possibility of applying a stationary, rather than the more elaborate rotating disc electrode. The main objective was to improve the sensitivity of analysis and thereby to permit short deposition times with a stationary electrode so as to save expensive ship time.

EXPERIMENTAL

Instrumentation

Measurements were made with a Ben—Gurion University (B.G.U.) Model EI224 polarographic analyzer and recorded with a Perkin—Elmer Model 56 strip chart recorder. The polarographic analyzer was developed and built at the Department of Electrical Engineering of B.G.U. It can operate in manual or computer-controlled modes and is capable of performing ASV analysis in a linear sweep, pulse and differential pulse modes. The option to use two working electrodes for subtractive ASV is built in. The basic electronic configuration of the polarographic analyzer is given in Fig. 1.

When operated in the differential pulse mode as applied here, the polarographic analyzer uses a staircase-type waveform on which a pulse is superimposed (Fig. 2). This pulse-form is similar to that recently investigated by Turner et al. [13] and found to increase the sensitivity of analysis. The subtractive method used here is similar to the procedure described by Sipos et al. [11].

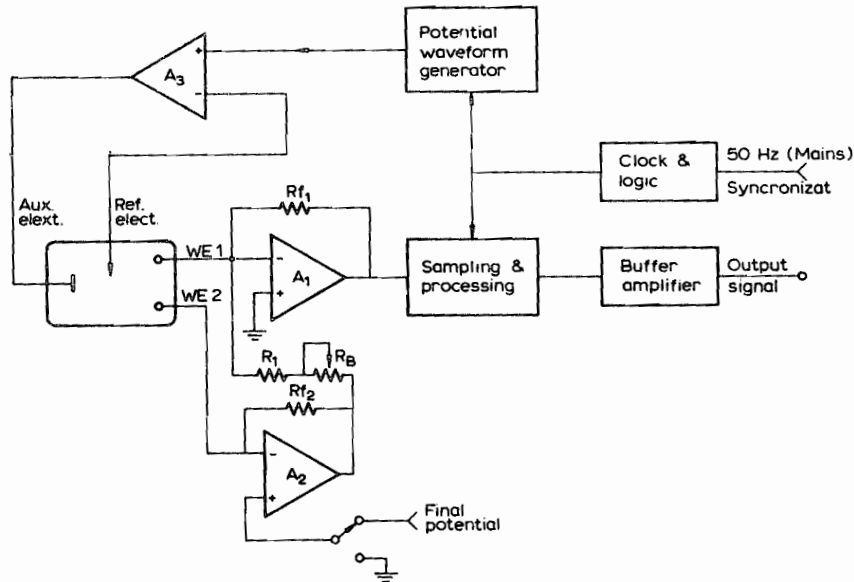


Fig. 1. Basic electronic configuration of the polarographic analyzer used in this study. The change-over switch controls the extra stripping of WE2.

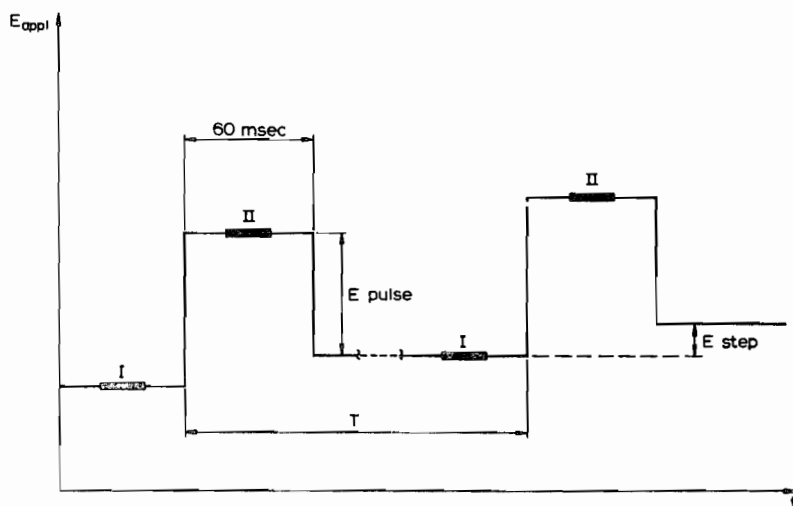


Fig. 2. Pulse shape used during the stripping phase of the DPASV analysis. Current samples are integrated over the periods marked by the heavier lines. The output signal of the polarographic analyzer is proportional to the difference between the two integrated currents ($\int_{II} i dt - \int_I i dt$). In the present analysis: $E_{step} = 10$ mV; $E_{pulse} = 80$ mV; $t = 640$ ms.

Electrodes and cell

Measurements were carried out in a 100 ml Teflon beaker fitted with a Teflon cover through which the electrodes and the tube carrying the oxygen purging gas (CO_2) were inserted. The solution was stirred with a Teflon-coated stirring bar.

A radiometer type K-401 saturated calomel electrode equipped with a Coleman fiber liquid junction (Perkin-Elmer C 003-0702) filled with 2 M KCl served as a reference electrode and a coiled platinum wire was used as an auxiliary electrode. The working electrodes (Fig. 3) were thin mercury film electrodes (TMFE) deposited on glassy carbon (GC) 3 mm in diameter (Ringesdorf Werke S-10). Two electrodes were included in one housing to form a double TFME (DTFME) as required for the subtractive mode. The DTFME was constructed by cementing two GC rod pieces, 10 mm long and 3 mm diameter, into a plexiglass disc of 14 mm diameter and 3 mm thickness. The distance between the two GC surfaces was 5 mm. A coaxial cable was attached by a conductive epoxy to the other side of the GC rods and the plexiglass disc, with the GC pieces, was glued to a plexiglass tube (od 15 mm, id 8.5 mm and 150 mm long) to form the DTFME. Finally, the tube was filled with epoxy cement (Buchler No. 20-8130-032 and No. 20-8132-20) to reduce errors due to surface current leakages and to fix the coaxial cables in place.

The electrode faces were polished with Hyprez Diamond Compounds of 6, 1, and 0.1 μm grade on a Hyprocel Pellon Cloth (Engis Ltd.). The surface finish was checked for scratches with a reflected light microscope.

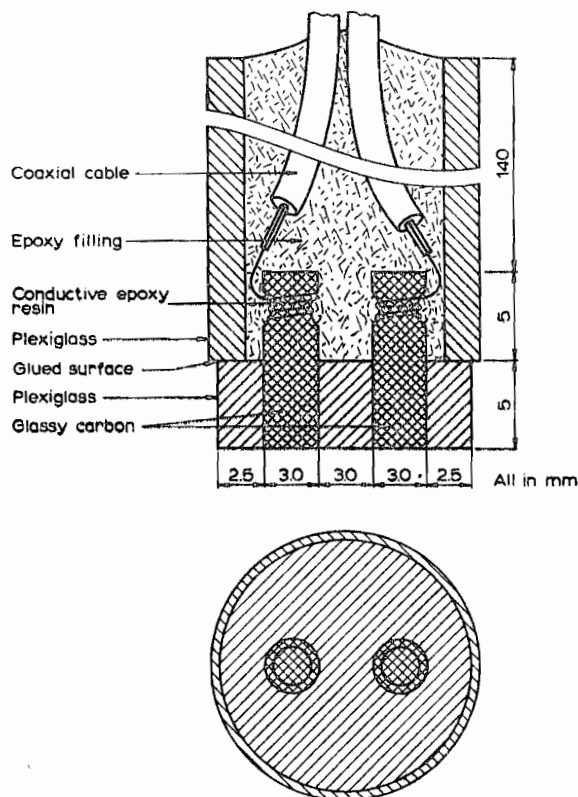


Fig. 3. Cross-section of the dual glassy carbon electrode used in this study.

Reagents and solutions

Gulf of Eilat (Red Sea) seawater was sampled and stored in 15 l containers which had been cleaned with 1 M HNO₃ and rinsed several times with the sampled water. Spike solutions were prepared from certified atomic absorption standard reference solution (Fisher Scientific Company). The plating solution was approximately 2×10^{-5} M mercuric nitrate prepared by dissolving the salt (Baker Analyzed Reagent) in seawater. A commercial CO₂ gas, treated with vanadous chloride solution, was used to purge the sample during the entire analysis cycle.

Procedure

The Teflon cover, through which the electrodes were inserted, was transferred to a 100 ml Teflon beaker containing the Hg plating solution and a -1400 mV potential was applied to both working electrodes (WE) for 20 min. Following the plating time, the potential was changed to -100 mV for another 3 min to strip any trace metal deposited during plating. The electrodes were then rinsed with double-distilled water and then placed in the tested solution (stored seawater). The solution was then deaerated for 7 min, after which the ASV

cycle was commenced. The analysis consisted of five steps:

- (1) Application of -1400 mV to both WE in a stirred solution for 110 s.
- (2) Changing the potential of WE2 to -100 mV for 10 s while WE1 is kept at -1400 mV.
- (3) Rest period of 30 s for both WE in unstirred solution at a potential of -1400 mV. At this time the polarographic analyzer is adjusted for zero output current by adjusting the gain of one (WE2) electrode.
- (4) Scanning from -1400 mV to -100 mV ($E_{\text{pulse}} = 80$ mV, $E_{\text{step}} = 10$ mV, $T = 640$ ms) and recording the WE current difference.
- (5) Stripping both WE for 30 s at -100 mV in a stirred solution.

RESULTS AND DISCUSSION

Typical normal mode DPASV voltammograms at the thin film mercury electrode (TFME) obtained with stored seawater samples and employing relatively short deposition times (2 min) are shown in Fig. 4. A notable feature of these voltammograms is the curved base line which is a result of relatively high background currents at the cathodic and anodic extremes of the analysis. The background current is apparently due to the hydrogen reduction at the cathodic end and mercury oxidation at the anodic end. These relatively high background currents completely mask the Cu(II) peak and could interfere with the determination of Zn(II) and Pb(II) if the concentration levels of these are low. Most disturbing, however, is the disappearance of the Cu(II) peak. The peak is completely masked in the analysis of the original seawater sample (Fig. 4a), is barely detectable after standard addition of 1.25 ppb Cu(II) (Fig. 4b) and is well formed only after an additional standard addition of 1.25 ppb Cu(II) (Fig. 4c). It is thus evident that in DPASV at the TFME the detection level of Cu(II) is about 1 ppb. Interference of high Cl^- concentration in the determination of Cu(II) was previously also reported for linear sweep ASV at the hanging drop mercury electrode [14].

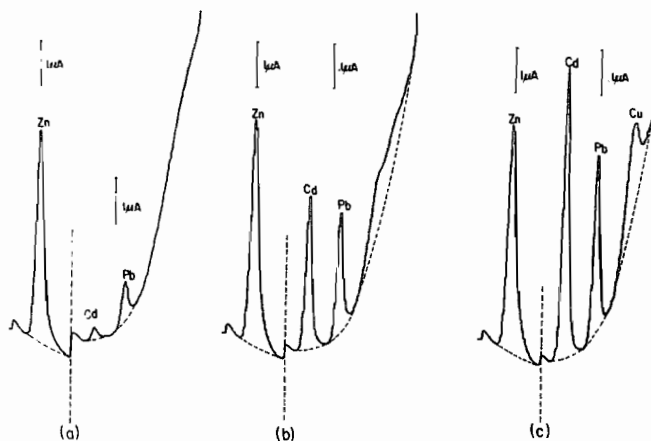


Fig. 4. Normal mode DPASV voltammograms (a) on stored Gulf of Eilat seawater, (b) and (c) after successive standard additions of 1.25 ppb Zn(II), Cd(II), Pb(II) and Cu(II). Plating potential -1400 mV vs. Ag/AgCl; plating time 2 min.

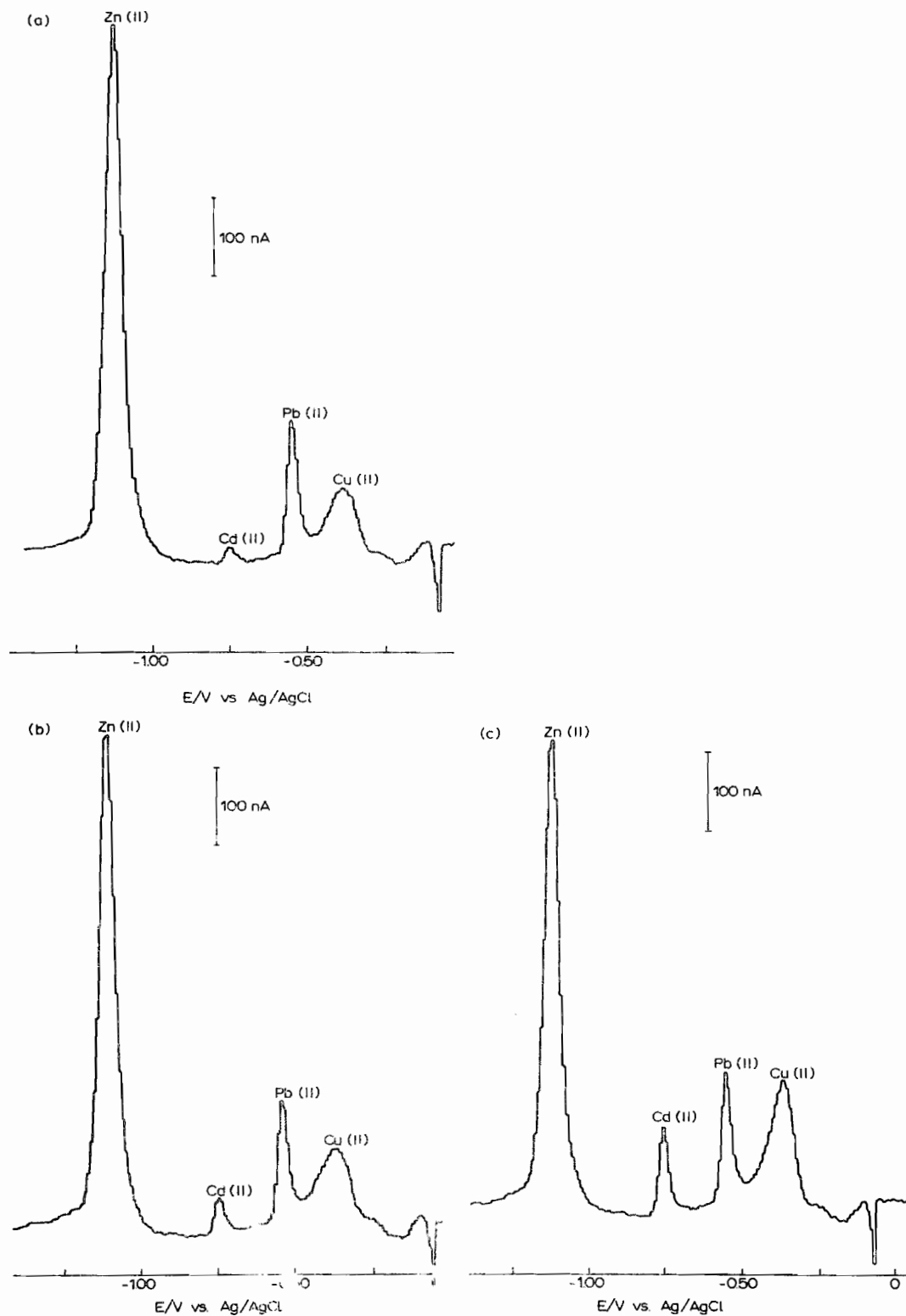


Fig. 5. SDPASV voltammogram (a) on stored seawater, (b) after standard addition of 0.375 ppb Cd(II) and (c) after standard additions of 0.375 ppb Cd(II) and 1.25 ppb Cu(II).

Typical subtractive mode DPASV (SDPASV) voltammograms obtained during this study are shown in Fig. 5. The main difference between these and the normal mode DPASV voltammograms is the relatively straight base line which resulted from the differential operation. The improvement is particularly evident for Cu(II) which is clearly detected without interference, even for the original seawater run (Fig. 5a). It should be mentioned in this connection, that the two runs (Figs. 4 and 5) were obtained with different batches of stored Gulf of Eilat seawater. One should expect, therefore, to detect different concentrations of the analyzed trace heavy metals, even though the sampling point was the same. This difference is especially evident for Zn(II) which exhibits a much larger peak in the analysis of Fig. 4 as compared to that of Fig. 5. The large difference is expected, considering the fact that the seawater used in the normal mode analysis (Fig. 4) was stored for a long time (two months) before analysis. The increase in Zn(II) concentration could be a result of contamination from the container or due to decomposition of organic matter.

The voltammograms of Fig. 5 represent three analyses, one on the original seawater (Fig. 5a), after standard addition of $0.375 \mu\text{g l}^{-1}$ Cd(II) (Fig. 5b) and after standard addition of $1 \mu\text{g/l}$ Cd(II) and $1.25 \mu\text{g/l}$ Cu(II) (Fig. 5c). These voltammograms are samples of a series of runs that were used to obtain calibration curves for Cd(II) and Cu(II). By using extrapolation on the Cu(II) calibration curve (Fig. 6) the original concentration of Cu(II) in the sample is estimated to be 0.35 ppb which is well below the detection limit of the normal mode DPASV at the TFME (Fig. 4). Linearity over a relatively large concentration range was determined for Cd(II) (Fig. 7). The calibration curve clearly demonstrates the good linearity obtained with this analytical method.

The repeatability of the analysis for Cu(II) determination was tested by repeating SDPASV runs on the original seawater. The Cu(II) peak-height range for nine runs was between 0.8 and $0.92 \mu\text{A}$ with a standard deviation of $0.048 \mu\text{A}$ which is about 5.6% of the mean value $0.85 \mu\text{A}$. The slope of the calibration curves for Cu(II) and Cd(II) (Figs. 6 and 7) is found to be about 0.15 and $0.8 \mu\text{A/ppb}$ respectively. As the noise level is estimated to be about 10 nA (Fig. 5), the sensitivity limits of SDPASV are estimated to be 0.067 ppb for Cu(II) and 0.025 ppb for Cd(II) when using a deposition time of 2 min. These sensitivity levels are about ten times more sensitive than those reported for the differential ASV in which a linear sweep rather than a differential pulse technique was employed [10]. However, higher sensitivities were reported for the subtractive ASV at the rotating split disc glassy carbon electrode [11] in which a linear sweep was used. This is expected considering the much higher deposition efficiency at the rotating disc electrode.

Comparison between the present results and previously reported data reveal that the detection limits of this method are comparable to those reported earlier for seawater analysis by normal DPASV at the rotating TFME. The data of Nürnberg et al. [15] suggest that the detection limit of that method is about 0.0002 ppb for Cd(II) when using a -60 min deposition time. Comparison between these reported results and our data, which were obtained with a -2 min deposition time, is possible by applying the fact that the sensitivity is linearly dependent on deposition time [15]. Hence, the present detection limit of $0.025 \mu\text{g l}^{-1}$ for Cd(II) is translated to $\sim 0.001 \mu\text{g l}^{-1}$ for a 60 min deposition

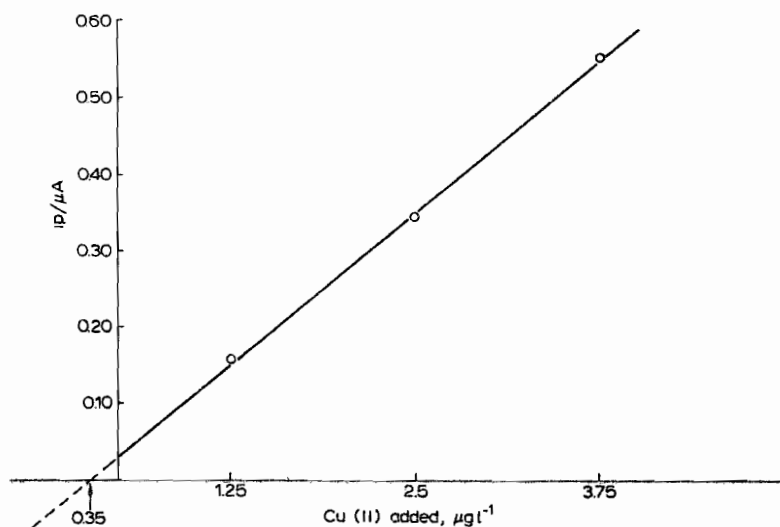


Fig. 6. Calibration curve for Cu(II) determined by SDPASV on stored seawater.

time. This compares favorably with the detection limit reported by Nürnberg [15] considering the fact that we have applied a stationary electrode which has a much lower deposition efficiency than the rotating electrode used earlier.

The twin electrode was recently incorporated in a flow-through cell similar in design to that described by Wang and Ariel [10] and is being used aboard R/V *Arnona* for studying the geochemistry of trace heavy metals at the Gulf of Eilat. Preliminary results of this study suggest that the SDPASV technique at the stationary electrode offers a significant advantage over the normal DPASV at the stationary electrode.

The data presented here demonstrate the improvement in sensitivity that is

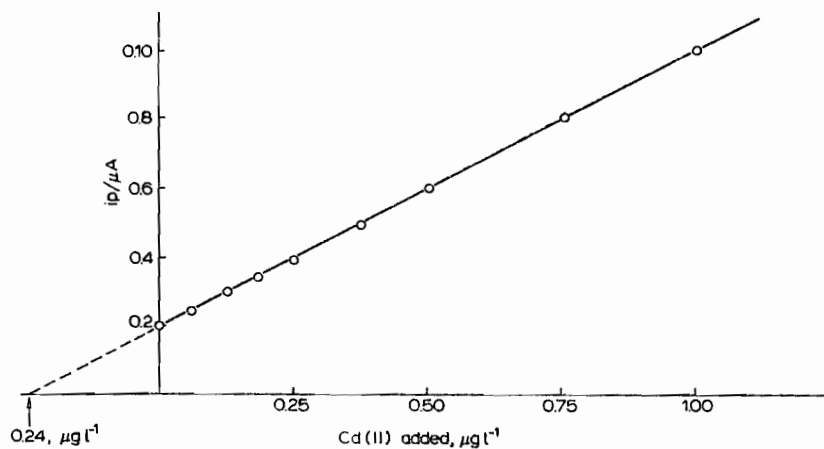


Fig. 7. Extended calibration curve for Cd(II) determined by SDPASV on stored seawater.

gained by SDPASV. Using a more sophisticated sampling strategy [7] the sensitivity could probably be improved. The high sensitivity of the method coupled to the relative simplicity of the stationary electrodes could also be an advantage in other survey and monitoring systems for natural water and environmental studies.

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