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Investigations on application of impregnated graphite electrode for the analysis of trace metals in sea water by anodic stripping voltammetry (ASV)*

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An increased influx of pollutants to seas and oceans results in a necessity of controlling the degree of contamination of sea water. Due to this, a rapid development of analytical methods enabling quantitative analysis of these pollutants is observed. Particular attention is paid to trace metals, due – among others – to the fact that accumulation of them in a trophic chain creates a serious hazard to human health. The presented paper aimed at examination of the suitability of anodic stripping voltammetry (ASV) method, as well as a working electrode and an electrochemical cell made in the Institute of Chemistry of the Maria Curie-Skłodowska University in Lublin, for the analysis of trace metal concentration in sea water.

Accomplishment of this aim required:

– determination of optimal analytical conditions,

– development of analytical procedure,

– determination of sensitivity of the method, both in laboratory and aboard a research vessel.

The applied apparatus consisted of the following elements:

– a UPE-1 type polarograph designed and constructed in the Institute of Inorganic Chemistry and Technology of the Technical University of Gdańsk, enabling linear potential scan with a maximum rate of 100 $mV\ s^{-1}$, with a sensitivity of electrolysis current determination equal to 50 $mV \cdot \mu A^{-1}$. The estimated minimal measureable current – 10 μA (depending on the recorder sensitivity);

– a Hewlett-Packard XY recorder of the sensitivity up to 5 $mV\ cm^{-1}$;

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– a gas supply system consisting of a cylinder with argon and a pressure valve, a gas washer, a flowmeter of the accuracy 1 $dm^3 h^{-1}$ and connections made of polyethylene tubes sealed with a PTFE tape;

– an electrochemical cell with electrodes (Fig. 1.).

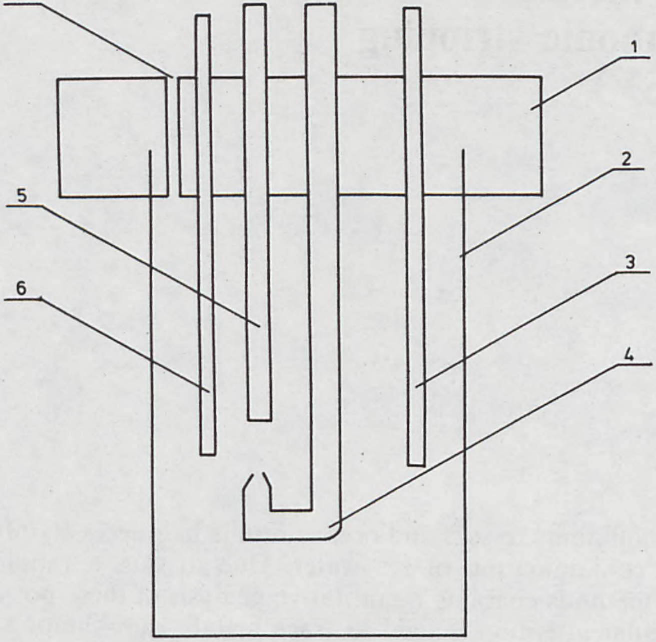

Fig. 1. Electrochemical cell with electrodes
1 – glass cell cover, 2 – glass cell, 3 – counterelectrode (platinum wire), 4 – capillary supplying deaerating gas, 5 – working electrode, 6 – reference electrode (saturated calomel electrode), 7 – gas outlet

A description of the working electrode and its characteristics has been given in papers by its designers (Sykut *et al*, 1980; Cukrowski *et al*, 1981).

The following reagents were used for the analysis:

– a $2 \cdot 10^{-5}$ mole solution of $HgNO_3$ (reagent grade) in 0.05 mole HNO_3 solution,

– 30% HCl Suprapur delivered by Merck (FRG),

– distilled water from an Elgastat Spectrum set.

Standard solutions of Cd, Pb, and Cu in 0.1 mole HCl were delivered by the Research Centre of Standards. Their initial concentration was equal to 1 ± 0.002 $g \cdot dm^{-3}$.

All the vessels contacting with samples and reagents have been prepared according to procedures described in the literature (Batley, Matousek, 1977; Mart *et al*, 1979).

The following operating parameters have been checked during testing of the cell:

– mutual alignment of the working electrode and the capillary supplying deaerating gas,

– distance between the working electrode and the capillary,
– gas flow rate.

The measurements have been carried out on sea water spiked with $1 \cdot 10^{-6}$ g·dm^{-3} of the analysed metal ions. Deposition potential was equal to -0.9 V, and the deposition time – to 5 min.

Figure 2 illustrates the effect of gas flow rate and the distance between the

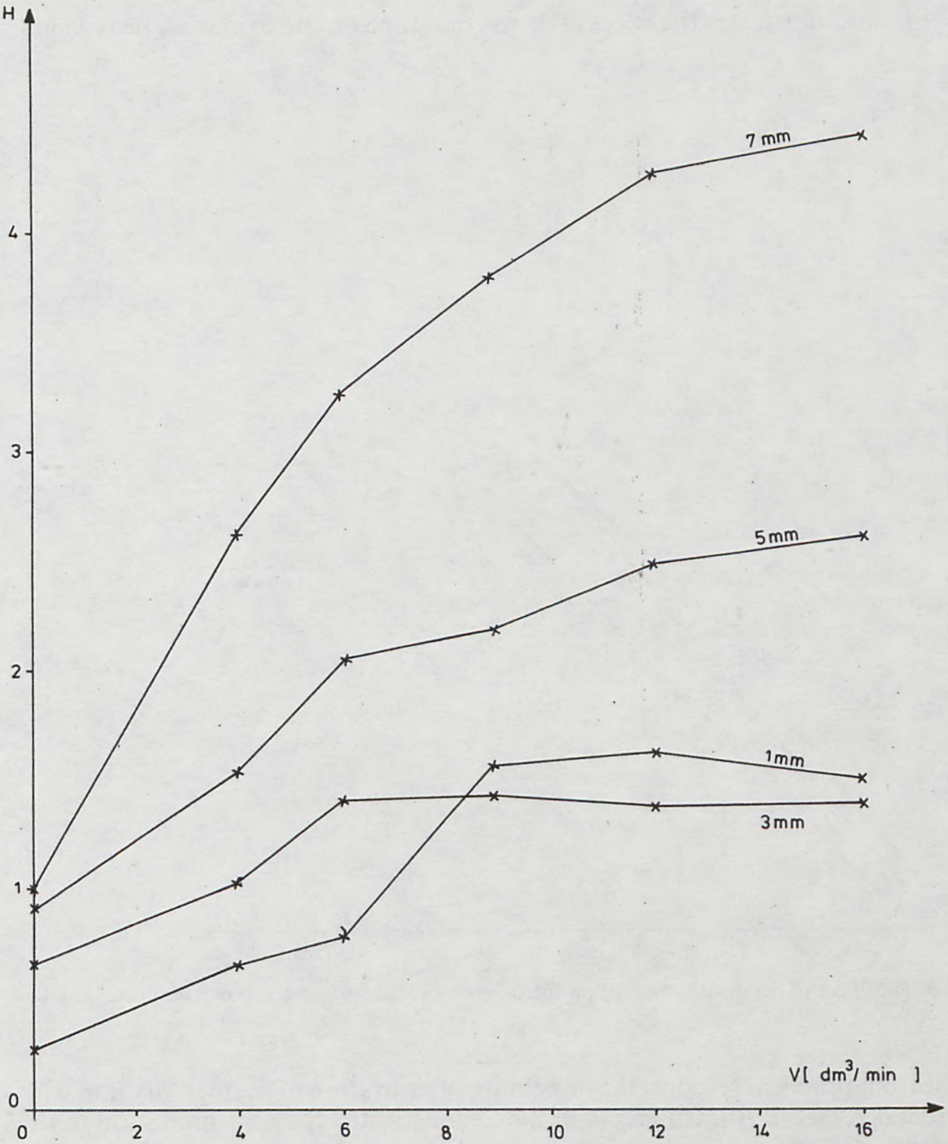

Fig. 2. The effect of gas flow rate (V) and distance between the working electrode and gas inlet on the copper oxidation peak height (H)

working electrode and the capillary on the height of copper oxidation peak (the height of a peak in Figures presenting the peak height *vs* the examined parameter is expressed in relative units, *viz* the unit is the biggest height peak obtained for the first value of the examined parameter). An increase of the oxidation peak height was observed with an increase of the distance between the capillary and the electrode (limited by the level of liquid in the cell). Beginning from a certain value of gas flow rate, a further increase did not influence the results, which indicates that the maximum efficiency of stirring of the sample with deaerating gas was achieved.

Figure 3 illustrates the effect of deposition time on the oxidation peak height.

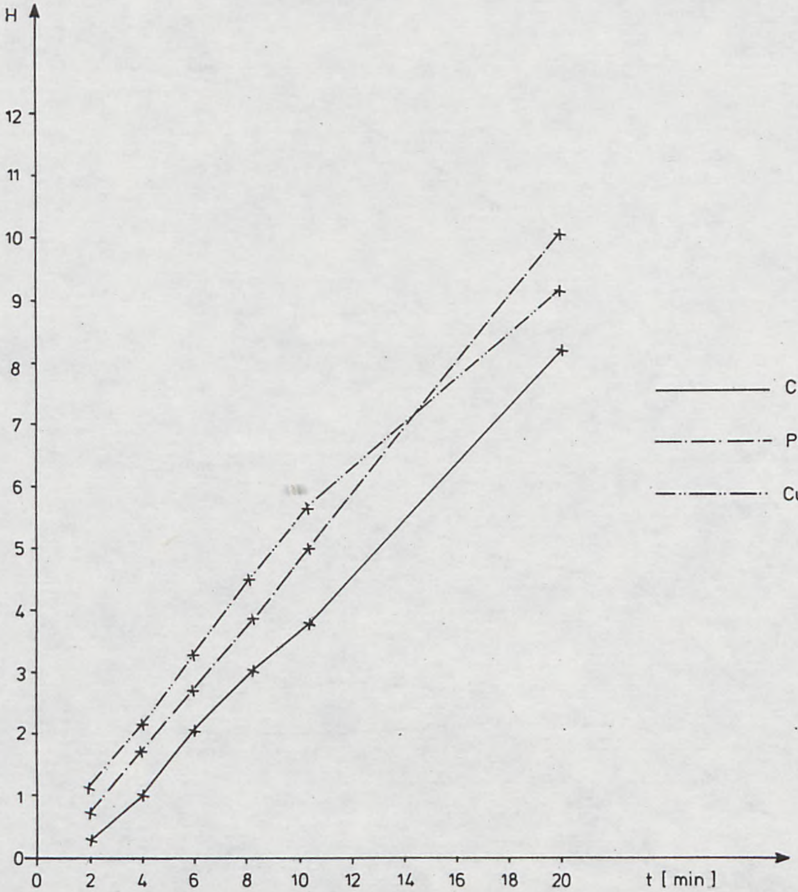

Fig. 3. The effect of deposition time (t) on the height of oxidation peak (H) of cadmium, lead, and copper

Aside from practical reasons, the possibility of saturation of the mercury film with the reduced metals (Piotrowicz *et al*, 1982) constituted the only limitation to the deposition time. Saturation results in non-linearity of the dicussed relationship. At short deposition times (2 and 4 min) a decreased precision of determination was observed, which was probably due to fluctuations of argon flow rate.

Figure 4 presents the effect of potential scan rate on the height of oxidation peak of cadmium, lead, and copper. Scan rate is limited by the possibilities of the polarograph and recorder response time. Polarograms unsuitable for quantitative interpretation were obtained in a majority of analyses carried at the 1 V · min^{-1} and 2 V · min^{-1} scan rate. This was due to evolution of gas bubbles at the electrode surface from a solution saturated with argon during a relatively long scan period.

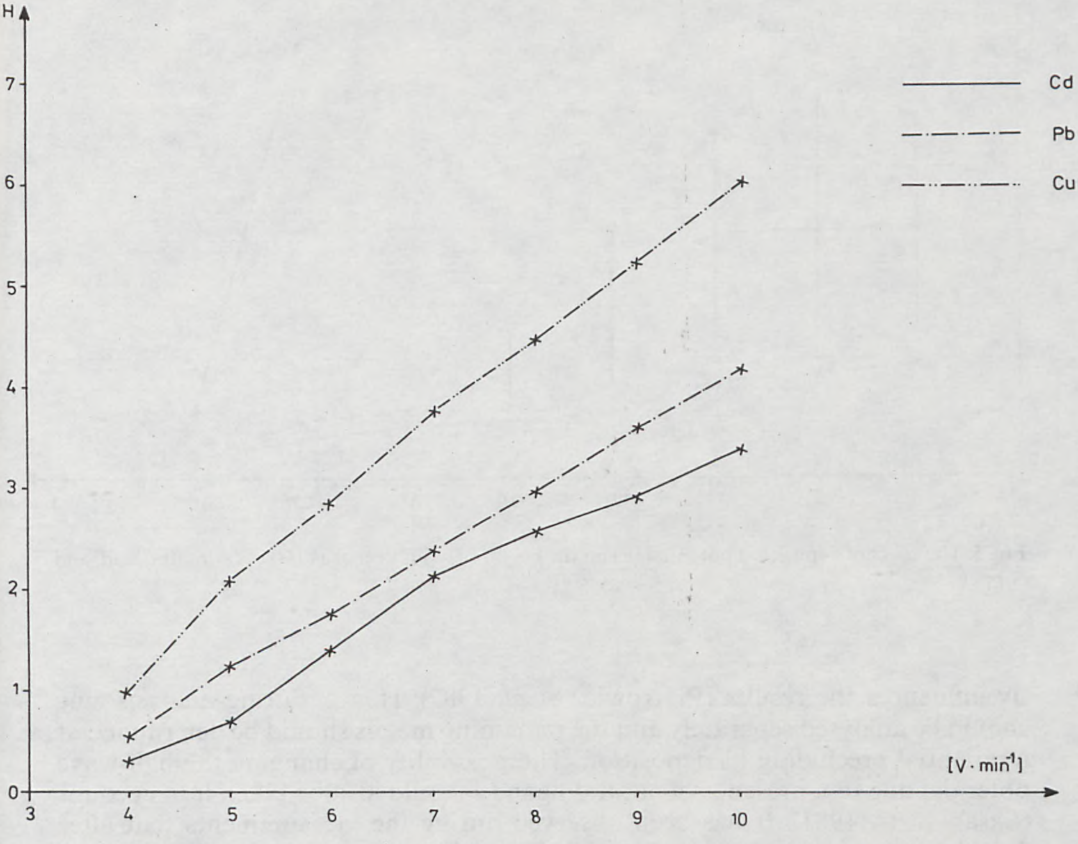

Fig. 4. The effect of scan rate on the height of oxidation peak (H) of cadmium, lead, and copper

Figure 5 illustrates the effect of deposition potential on the height of oxidation peaks. This dependence is also called a pseudo-polarographic wave (Copeland, Skogerboe, 1974; Sipos *et al*, 1980). Vertical segments in the diagram of copper represent a standard deviation (marked in cases when the relative standard deviation exceeded 0.15%). Successive measurements carried out under similar conditions revealed an increase of copper peak heights and a decrease of zinc peak heights. This was probably due to a formation of intermetallic copper and zinc compounds, undergoing oxidation at a potential of copper oxidation (Birhaye *et al*, 1983). This phenomenon can be neglected in a case of application of mercury drop electrode, yet in a case of application of a mercury film it significant-

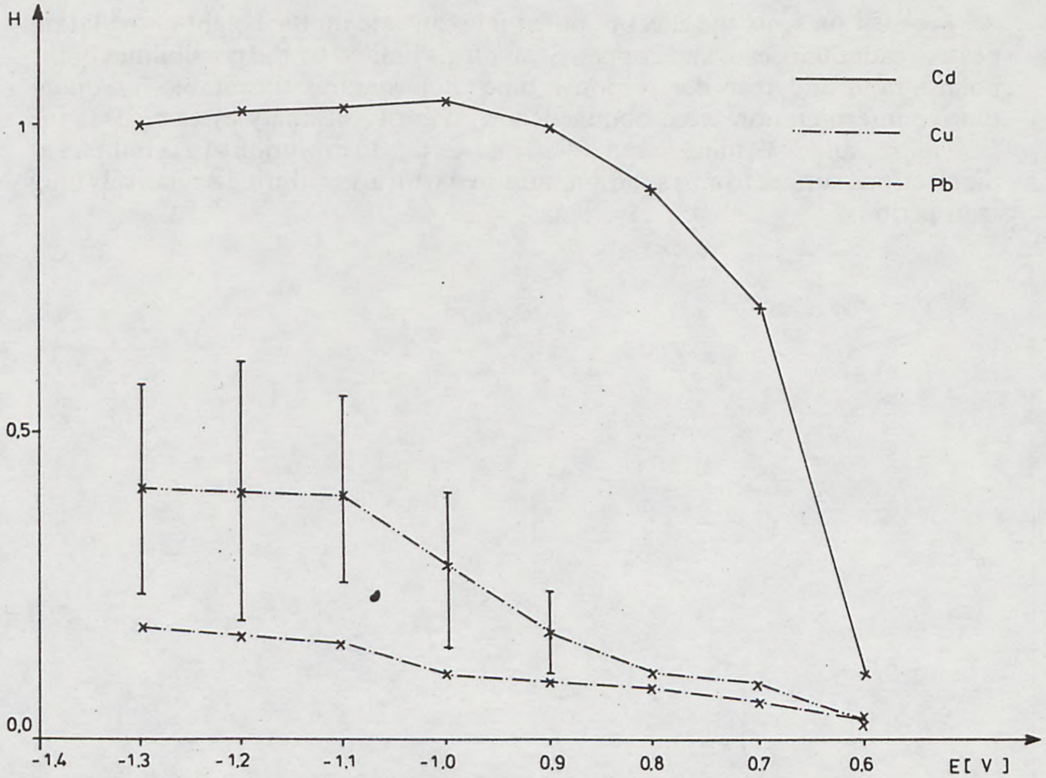

Fig. 5. The effect of deposition potential (E) on the height of oxidation peak (H) of cadmium, lead, and copper

tly influences the results (Piotrowicz *et al*, 1982). Hence, during analysis zinc should be analysed separately and the remaining metals should be determined at a potential precluding its deposition. The possibility of changing the half-wave potential due to a presence of natural ligands should also be taken into account (Lasar, Katz, 1981). It has been observed during the measurements that after finishing the scan cycle (and theoretical transfer of the metals to the solution) a repeated scan, not preceded by a deposition step, indicates the presence of a certain amount of metal remaining in the film. This is known as the "memory effect" and is due either to incomplete dissolution of metal from the mercury film, or to a repeated transfer of the metal to the film resulting from a high concentration of ions in a thin stratum of solution in the vicinity of the electrode (Lund, Salberg, 1975). Figure 6 presents peak heights on polarograms recorded without previous deposition after 1, 2, 3, and 4 min from recording of the polarogram "I". Between the successive recordings the solution has not been stirred, and the potential was kept at 0.0 V.

The following analytical procedure has been developed on the basis of the obtained results: 13 cm^3 of the analysed sea water should be poured into a cell containing an electrode with the formed mercury film. The surface of the elec-

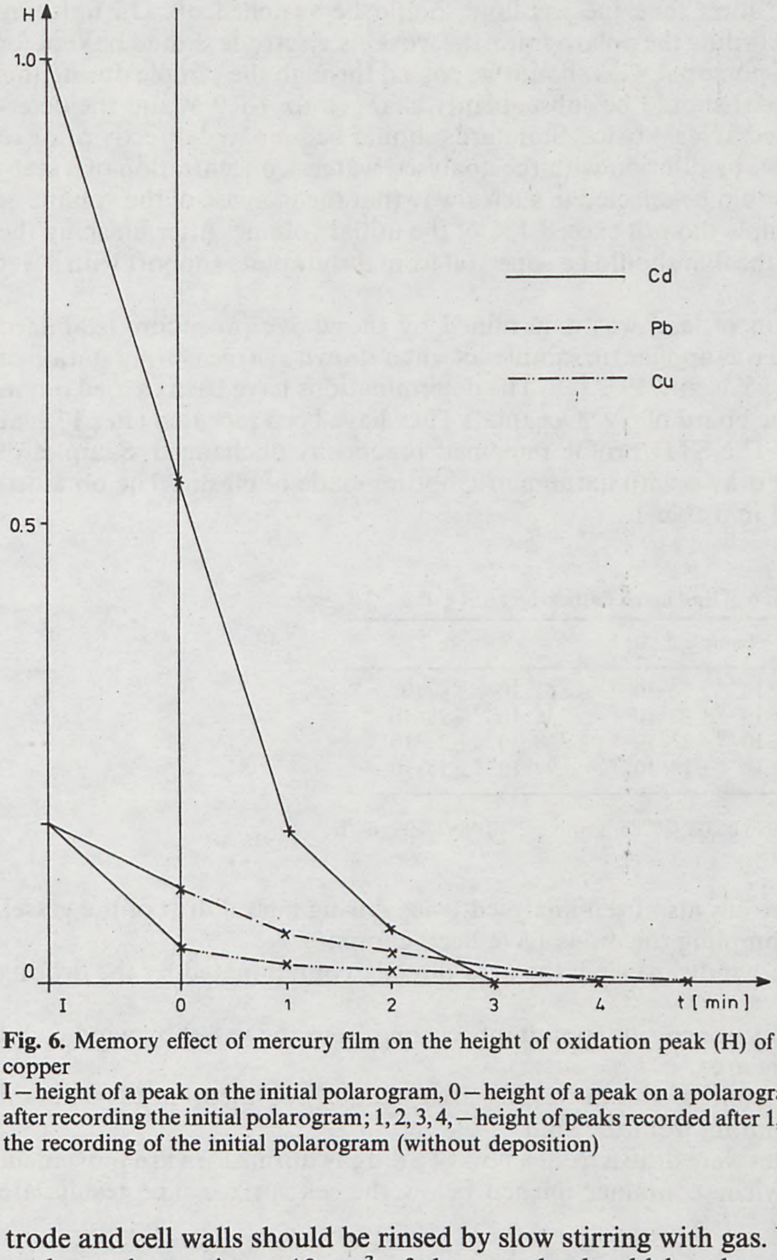

Fig. 6. Memory effect of mercury film on the height of oxidation peak (H) of cadmium, lead, and copper
I – height of a peak on the initial polarogram, 0 – height of a peak on a polarogram recorded directly after recording the initial polarogram; 1, 2, 3, 4, – height of peaks recorded after 1, 2, 3, and 4 min from the recording of the initial polarogram (without deposition)

trode and cell walls should be rinsed by slow stirring with gas. Water should be exchanged two times. 10 cm^3 of the sample should be placed in the cell and acidified to pH 2 with Suprapur hydrochloric acid (determination of pH in the cell accomplished by an electrode rinsed with the examined water). The sample should be deaerated by passing a stream of argon at a rate of 14 dm$^3 \cdot$ h^{-1} for 10 min. During deaeration the deposition potential of −0.9 V and the scan rate of 10 V min^{-1} should be set on a polarograph. After deaeration the preset potential should be applied to the working electrode and kept constant for at least 10 min (exact time determined with a stopwatch). A few seconds before the end of the deposition time the gas flow should be switched off. On finishing scanning and recording the polarogram, the working electrode should be kept for 1.5 min at 0.0 V potential. Gas should be passed through the sample during this time. The potential should be subsequently changed to −0.9 V and the determination repeated at least twice. Standards should be prepared directly prior to the determination by dilution with the analysed water. Concentration of a standard solution should be selected in such a way that the increase of the volume of the analysed sample did not exceed 1% of the initial volume. After finishing the determinations, the film should be wiped off from the graphite support with a wet filter paper.

Concentration of lead was determined by the above procedure (standard addition method was applied) in samples of water drawn at a measuring station of co-ordinates 54°55′ N and 19°22′ E. The determinations have been carried out in laboratory on the board of r/v "Oceania". They have been repeated after 13 h at the same point. The STD profile remained practically unchanged. Samples of water have been drawn with bathometric bottles made of plastic. The obtained results are listed in Table 1.

Table 1. Concentration of lead in the Baltic water (in $[g \cdot dm^{-3}]$)*

Depth [m]	Sample 1	Sample 2
10	$280 \cdot 10^{-9} \pm 50 \cdot 10^{-9}$	$41 \cdot 10^{-9} \pm 6 \cdot 10^{-9}$
25	$140 \cdot 10^{-9} \pm 20 \cdot 10^{-9}$	$148 \cdot 10^{-9} \pm 28 \cdot 10^{-9}$
60	$123 \cdot 10^{-9} \pm 22 \cdot 10^{-9}$	$118 \cdot 10^{-9} \pm 26 \cdot 10^{-9}$
90	$105 \cdot 10^{-9} \pm 19 \cdot 10^{-9}$	$99 \cdot 10^{-9} \pm 18 \cdot 10^{-9}$

* Sample 1 – 1986.06.08, 17^{00}h, sample 2 – 1986.06.09, 6^{00}h

Surface water has also been analysed twice during lateral drift of the vessel. The following sampling locations have been chosen:

– 50 m from windward side; the area directly contaminated by the drifting vessel,

– 50 m from leeward side; pollutants carried from the vessel by wind could have been in this area,

– 100 m in front of the bow; this area should not theoretically contain pollutants originating from the ship.

Water samples were drawn from a bow of a dinghy during forward movement using a polyethylene container opened below the sea surface. The results are listed in Table 2.

Table 2. Concentration of lead in the Baltic water in surface layer (in $[g \cdot dm^{-3}]$)*

Sample	Leeward side	Windward side	In front of bow
1	$66 \cdot 10^{-9} \pm 8 \cdot 10^{-9}$	$83 \cdot 10^{-9} \pm 18 \cdot 10^{-9}$	$43 \cdot 10^{-9} \pm 4 \cdot 10^{-9}$
2	$42 \cdot 10^{-9} \pm 9 \cdot 10^{-9}$	$48 \cdot 10^{-9} \pm 8 \cdot 10^{-9}$	$12 \cdot 10^{-9} \pm 4 \cdot 10^{-9}$

*Sample 1 – 1986. 06. 04, sample 2 – 1986. 06. 07

The obtained results indicate that the examined apparatus is well suited for analyses under marine conditions. It reveals low susceptibility to swaying (due to a replacement of a magnetic stirrer with gas stirring). The polarograph is electrically stable, even under the conditions of ship electrical supply. The working electrode did not require additional polishing after 6 months and was found to be chemically resistant during operation in an acidic medium.

The basic limitation of the method is long analysis time, reaching 1 h at the concentrations of hundredths of microgram, encountered in the Baltic water. This problem can be solved by application of a number of instrumental sets. However, this would require automation of the analysis control. It should also be remembered that metals occur in sea water not as simple ions, but in various physico-chemical forms (Batley, 1983). The above method allows determination of a concentration of metals that can be defined as the concentration of metal ions electroactive at pH 2, contained in unfiltered sea water.

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