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Prevention of Contamination and Other Accuracy Risks in Voltammetric Trace Metal Analysis of Natural Waters

Part III. Voltammetric Ultratrace Analysis with a Multicell System Designed for Clean Bench Working*

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Vermeidung von Kontamination und anderen die Richtigkeit beeinflussenden Einwirkungen bei der voltammetrischen Spurenanalyse in natürlichen Gewässern

Teil III. Voltammetrische Ultraspurenanalyse mit einem Multizellensystem zum Einsatz unter einer clean bench

Zusammenfassung. Für die Bestimmung und Untersuchung der Gehalte toxischer Metalle in natürlichen Gewässern stellt die geeignete Art der Voltammetrie eine außerordentlich zuverlässige Analysenmethode dar. Die Feststellung von Grundpegeln in den Ozeanen, nicht pollutierten Küsten- und Binnengewässern verlangt Bestimmungsmöglichkeiten bis zu 1 ng/kg. Dieser hohen Anforderung kann hinsichtlich der Simultanbestimmung von Cu, Bi, Pb, Cd und evtl. Zn zufriedenstellend entsprochen werden durch eine Version der differentiellen anodischen Pulsinversvoltammetrie (DPASV) an dem beschriebenen Typ der Quecksilberfilmelektrode (MFE). Die dargelegten erforderlichen Vorkehrungen zur Kontaminationsminimierung müssen berücksichtigt werden. Die erforderlichen instrumentellen Modifizierungen werden dargelegt und die Konstruktion und Behandlung der rotierenden Glaskohleelektrode wird detailliert beschrieben. Anschließend wird auf die Adaptierung dieser rotierenden Glaskohleelektrode für den kontaminationsfreien Einsatz in dem neuen Multizellensystem unter einer clean bench eingegangen. Weitere Abschnitte der Arbeit sind der Darlegung leistungsfähiger Probenvorbehandlungsmethoden mit ausgesprochen niedrigen Kontaminationsrisiken gewidmet. Hierbei handelt es sich einerseits um die UV-Bestrahlung unter verschiedenen Bedingungen zur photolytischen Zerlegung metallbindender Komponenten gelöster organischer Materie (DOM) und weiterhin um die Niedertemperaturveraschung im Sauerstoffplasma für den Aufschluß der abfiltrierten Schwebstoffe. Die anschließende Anwendung der im Detail beschriebenen voltammetrischen Bestimmung (DPASV) gewährt Bestimmungsgrenzen von 0,5 ng/kg für Pb und Cd und von 3 ng/kg für Cu und Bi bei einer RSD von 20%. Die Richtigkeit (*accuracy*) wurde im Ultraspurenbereich durch eine Vergleichsanalyse seitens verschiedener Laboratorien unter Einsatz völlig verschiedener instrumenteller Bestimmungsverfahren sichergestellt.

Summary. Suitable modes of voltammetry provide one of the most reliable analytical approaches for the determination of trace metal levels in natural waters. The establishment of base line values in the oceans, unpolluted coastal and inland waters requires determination potentialities down to 1 ng/kg. This substantial demand can be satisfactorily met for the simultaneous determination of Cu, Bi, Pb, Cd and eventually Zn by a version of differential pulse anodic stripping voltammetry (DPASV) at the described type of the mercury film electrode (MFE). Necessary provisions to minimize contamination risks have to be taken into account. The necessary optimalizing instrumental modifications are pointed out and the construction and treatment of a rotating glassy carbon mercury film electrode is described in detail. Subsequently the adaptation of this rotating electrode to contamination-free clean bench operation in a

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multicell system is pointed out. Further sections of the paper are devoted to the presentation of efficient pretreatment procedures with particularly low contamination risks, i.e. UV-irradiation under various conditions to decompose metal-binding components of dissolved organic matter (DOM) and the low temperature ashing (LTA) procedure to digest the filtered off suspended particulate matter. Applying the DPASV-procedure described in detail, determination limits of 0.5 ng/kg for Pb and Cd and 3 ng/kg for Cu and Bi are achieved with an RSD of 20%. The accuracy has been established at the ultratrace level by an interlaboratory comparison, applying completely different analytical procedures and instrumental determination methods.

Key words: Best. von Spurenmetallen in Wasser; Voltammetrie; differentielle Pulsinversvoltammetrie, Glaskohleelektrode, Quecksilberfilmelektrode, Multizellsystem, Kontaminationsausschluß

Introduction

Efficient and meaningful management of environmental pollution requires a sound knowledge on the levels, behaviour, fate and effects of hazardous substances in the considered ecosystems. A key prerequisite are sufficient data. Their validity and reliability depends strongly on the sensitivity, accuracy and precision of the analytical methods applied in research and control of environmental pollution. One group among the hazardous environmental chemicals of high priority and particular concern are with respect to their ecotoxicological actions and potential threads certain heavy metals, e.g. particularly Cd, Pb, Hg, but also a number of others, as Cu, Zn, etc., which have below their respective critical threshold levels essential actions on man and other organisms [23, 45]. Most heavy metals occur usually at relatively low concentration levels in the various types of ecosystems. This is particularly the case for the beforementioned most toxic metals. In natural waters the levels of the dissolved content of toxic metals and their amount bound to suspended particulate matter depend on the geographical and also seasonal origin of the sample and are typically for cases of pollution in the µg/kg-range (ppb), while they decrease for the base line values in the open ocean to the ultra trace range of ng/l (10^{-3} ppb).

Steadily expanding research has established over the last years that suitable advanced versions of voltammetry offer frequently the optimal approach for the determination of toxic heavy metal traces in the various types of natural waters, i.e. sea, lake, river, rain water and in processed natural water used as drinking water [1–4, 6, 8, 9, 11–13, 17–20, 24, 26, 27, 29, 31, 32, 40, 42, 43]. This is connected with the high sensitivity of suitable voltammetric modes, not surpassed for the before-mentioned particularly toxic metals by any other instrumental analytical method [23–25], as well as with the inherently high degree of accuracy and the satisfactory precision of voltammetric measurements. These basic advantageous properties of voltammetric analysis are related to its foundation on Faraday's law. Extended comparative studies with other analytical methods like electrothermal, flame and cold vapour AAS and isotopic dilution mass spectrometry, or utilizing standard reference materials, have emphasized the particular reliability of the voltammetric approach in toxic trace metal analysis for all types of environmental matrices [23, 25, 38] and in particular for natural water samples [13, 19, 23, 24, 42]. Moreover, the special property of voltammetry to be species sensitive makes this electroanalytical approach an efficient tool in studies on the speciation of toxic trace metals dissolved in natural waters at realistic concentration levels [23, 27, 31, 32].

The determination capabilities of suitably selected voltammetric modes have today reached a degree that usually other stages in the overall analytical procedure, i.e. the achievable elimination of contamination and avoidance of trace metal losses during sampling and the necessary sample preparation, have become of dominant influence for the determination limits attainable in practice. The general aspects of preventing contamination by the necessary improvements of the laboratory and the scrupulous cleaning procedures of all used labware have been described in detail together with the filtration and the storage of natural water samples in part I of this series [14]. Part II was concerned with the collection of samples being one of the most critical stages in the whole analytical procedure [15]. The present part III describes the necessary pretreatment steps which have been adapted in an optimal manner to the subsequently outlined voltammetric determination stage and the required prerequisites in terms of electrode construction and cell design. The experience gained during the last years in extended applications to over 2,000 sea water and several hundred inland water samples, culminated recently in the design and introduction of a multicell system, where 4 cells are operated at present. This system, specially adapted for operation under a clean bench with dust-free air is still operated manually, but automation now in progress will in future provide a rapid simultaneous voltammetric determination of the trace metals Cu, Bi, Pb, Cd and Zn from 4 samples simultaneously within 1 h.

General Aspects for the Choice of the Applied Voltammetric Method

The stringent requirements in aquatic trace metal chemistry with respect to determination limits, accuracy and precision render suitable only particular modes from the large variety of existing voltammetric methods [23, 25, 42]. Among the commercialized versions the most sensitive direct method is at present differential pulse polarography at the DME. This mode has a typical determination limit of 10^{-7} M, e.g. 10 µg/l for Cd, in water matrices. However, the signal suppression due to the presence of surface active organic traces frequently occuring in natural waters might even restrict the determination limit to somewhat higher concentrations.

Therefore, the ultra trace levels of toxic metals to be determined frequently in natural waters, decreasing to determination limits of 1 ng/l in open ocean samples, require the usage of *inverse* voltammetry, also termed *stripping* voltammetry. This is in principle an indirect approach, because a preconcentration step at a stationary electrode is involved before the actual measurement. As the heavy metals predominantly considered in this paper form amalgams with mercury, this preconcentration is achieved by plating an aliquot of the trace metals by adjusting a sufficiently negative potential at a stationary mercury electrode. Like this, a several 100-fold accumulation can be attained within several minutes of plating time. The intrinsic particular advantage of this electrochemical *in situ*-preconcentration is moreover that, compared with the common chemical preconcentration procedures, it is not connected with an increase of contamination risk, as it is performed at the working electrode in the voltammetric cell.

The extent of electrolytic preconcentration depends on the volume of the applied mercury electrode. If the conventional hanging mercury drop electrode (HMDE) is used, the determination limit in connection with differential pulse anodic stripping voltammetry (DPASV) is for Cd about 50 ng/l corresponding to 5×10^{-10} M. A considerably more efficient preconcentration is achieved with the rotating mercury film electrode (MFE) realized by plating a thin Hg-film of 200 – 1,000 Å thickness onto a specially polished glassy carbon support of about 0.3 cm^2 surface area. Due to the very small film volume of 0.6 to 3×10^{-6} cm^3 and the efficient and reproducible convective trace metal ion transfer towards the electrode rotating with 1,500 to 3,000 rpm, substantial preconcentration factors of 10^4 or more can be achieved within preelectrolysis times up to only 12 min. In this manner determination limits of 0.5 ng/l can be attained [13].

Similar limits can be achieved for the determination of Hg-traces carried out with usual DPASV at a common gold disc electrode [34] down to 100 ng/l and down to 1 ng/l with a twin gold electrode applying subtractive DPASV [37].

Precision and accuracy of the total analytical procedure in the trace and ultra trace range are affected mainly by the degree to which contamination can be restricted. In this respect, the simplification of sample pretreatment steps and the restriction of their number is a significant point. The possibility of *in situ* electrolytical preconcentration and the extraordinary sensitivity provided by differential pulse stripping voltammetry create a very favourable situation, compared with other non-voltammetric procedures. Thus, for instance AAS, rather popular in trace metal analysis, requires in most natural water matrices prior separation of the trace metals from interfering alkaline earth ions by solvent extraction or ion exchange. These chemical separation and pre-concentration procedures are inevitably connected with substantially increased risks of contamination or trace metal losses. The general features of stripping voltammetry have in addition the advantage that they allow in a convenient and easy way to work mainly with closed systems, flasks and cells, thus minimizing the contamination risks due to dust particles from the ambient atmosphere. These risks are further lowered substantially, as will be shown in detail later, by the good suitability of voltammetric measuring for clean bench working.

Voltammetric Equipment

Apparatus

Every commercial polarograph having the differential pulse mode and a sufficient current and voltage output of the incorporated potentiostat can be applied. The latter condition is important as for instance the surface area of the MFE can be 10 times larger than that of the HMDE.

In our work usually the polarograph 174 A from Princeton Applied Research has been applied after some modifications to achieve optimal performance. The oscillations of the incorporated potentiostat, appearing at the beginning of the pulse when analyzing highly conductive samples like sea water, were overcome by inserting a resistor of about 70 Ω in series with the rotating electrode. The potentiostatic action was somewhat degraded by this modification, but owing to the very low content of metal ions and the respective low current, the peak potentials during the stripping stage remained unchanged. In order to enhance sensitivity, as described in detail elsewhere [41], the time delay t_w (see Fig. 7) was shortened from originally 40 ms to 13 ms thus decreasing the pulse duration to 29 ms. The current sampling times t_{s1} and t_{s2} (see Fig. 7) remained 16 ms, as originally adjusted by the producer. A pulse modulation amplitude ΔE of 50 mV was applied. By shortening the pulse repetition period t_c ("clock") to 0.24 s a scan rate of 10 mV/s can be applied, thus reducing the duration of the recording of a voltammogram by a factor two. The mentioned modifications of the instrument are realized by

changing the respective time constants in the multivibrators controlling the time delay t_w and the clock time t_c. In the polarograph PAR 174 A these modifications are easily achieved, as the circuitry permits the necessary alterations of the respective resistors in the signal processing board. The resistor R 264 of 110 KΩ in the circuit "monostable II" was replaced by a variable resistor of 100 KΩ in series with a fixed resistor of 10 KΩ. The resistor R 63 in the circuit "clock" was substituted by a variable resistor of 50 KΩ and a fixed resistor of 10 KΩ in series [30].

To increase further the analysis number per working day, multicell operation has been introduced, working simultaneously with two polarographs connected to two cells while in further cells cleaning or deaeration procedures are going on. This multicell operation will be described in detail in a later section. The voltammograms from the respective two cells connected to the two polarographs are recorded simultaneously by a multichannel recorder, model 316, from W + W Electronic, Münchenstein, Basle, equipped with an X-Y-module.

Counter and Reference Electrodes

The *counter* electrode is a platinum wire. A silver wire covered with silver chloride serves as Ag/AgCl *reference* electrode. In the voltammetric cell both electrodes have to be separated from the sample solution to exclude contamination possibilities in the ultra trace range. Both electrodes are put into teflon tubes closed with a Vycor tip (Corning Glass Corp., Cleveland) of 4 mm diameter, by shrinking the teflon tube end over the tip. The Vycor glass tips have a porosity providing an ultralow leakage rate but nevertheless a low ohmic resistance. Both tubes are filled with saturated KCl-solution as electrolyte. The electric connections from the reference and counter electrodes to the shielded cables are made by soldering. These soldering points are completely enclosed by glue to avoid contamination of the electrolyte in the electrode compartments by corrosion products of the solder. A silicone tube covers the remaining small part from the shielded cable to the teflon tubes serving as electrode compartments, thus letting no bare wire in the clean area over the cell cover. Both teflon tubes containing the counter and the reference electrode are fitted into openings of the teflon cell cover (see Fig. 2a).

Working Electrode

The working electrode material used in trace metal analysis is usually mercury. Only for the determination of Hg, as well as the simultaneous determination of Cu and Hg [34], gold electrodes are most recommendable according to our experiences. Production of gold electrodes and procedures for voltammetric trace analysis of Hg and Cu by DPASV and ultra trace analysis of ng/l-concentrations of Hg by subtractive DPASV at the twin gold electrode have been already described previously [37]. The determination of Cu, Cd, Pb and Zn at the HMDE in DPASV at trace metal levels above 200 ng/l, levels usually encountered e.g. in rain water, snow, drinking water or in the analyte solutions of digested biological materials, has been described elsewhere [10, 11, 19, 23, 28, 42–44].

In this paper the mercury electrode type usually applied as working electrode in the ultra trace range, typically between 500 and 1 ng/l, will be considered in detail. Such low toxic trace metal concentrations are usually encountered in water samples from the sea, from estuaries and also from certain inland waters with low or negligible heavy metal pollution [1–4, 6, 13, 21, 23, 33, 40].

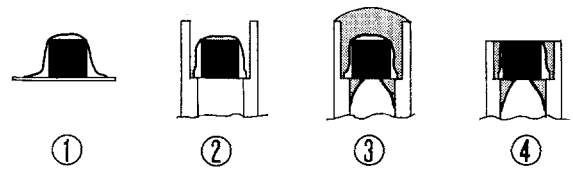

Fig. 1. Steps of glassy carbon support production. *1* Glassy carbon rod after hardening of two-component glue; *2* Insertion of machined rod into the electrode holder; *3* Glassy carbon rod embedded into UV-hardening glue; *4* Glassy carbon electrode after grinding

The working electrode to be utilized is the mercury film electrode, MFE, that has been first introduced by Florence [7] in connection with conventional inverse voltammetry (ASV). Yet one of the first successful MFE for ultratrace analysis by application of DPASV has been produced by us [27]. The working electrode is formed freshly for each analysis in the first stage of the voltammetric measurement by depositing electrolytically a thin mercury film on a specially polished glassy carbon surface. The sample solution has been spiked before with Hg(II) to establish a concentration of about 10^{-5} M. The plating of the mercury film is performed under rotation of the electrode with 1,500 to 3,000 rpm to speed up mass transfer from the bulk of the solution towards the interface.

The properties of the glassy carbon support and particularly its surface are critical for the performance of the MFE. Therefore in this section the production of a reliable glassy carbon support will be described in detail.

Most commercially available glassy carbon electrodes offer not completely satisfactory performance with respect to the fitting of the glassy carbon rod into the holder material and also concerning the properties of the glassy carbon surface. Fissures resulting from unsatisfactory fitting are inevitably filled with grains from abrasive powder during the polishing procedure. This can create a long lasting source of contamination during analysis. Thus, it has been felt necessary to use home-made electrodes. The subsequently described production procedure [13] constitutes a considerable improvement as it provides glassy carbon supports behaving perfectly for years if treated or stored appropriately as described below.

According to our experience a most suitable glassy carbon material for constructing a MFE-support is the quality EB-6-GC-A produced by Tokai Carbon Ltd., Tokyo, represented in Europe by COC-Luxembourg, Luxembourg. Figure 1 shows the stages of the fitting of the glassy carbon rod to the plexiglass electrode holder. The two-component glue Araldit B plus hardener HT 903, having a

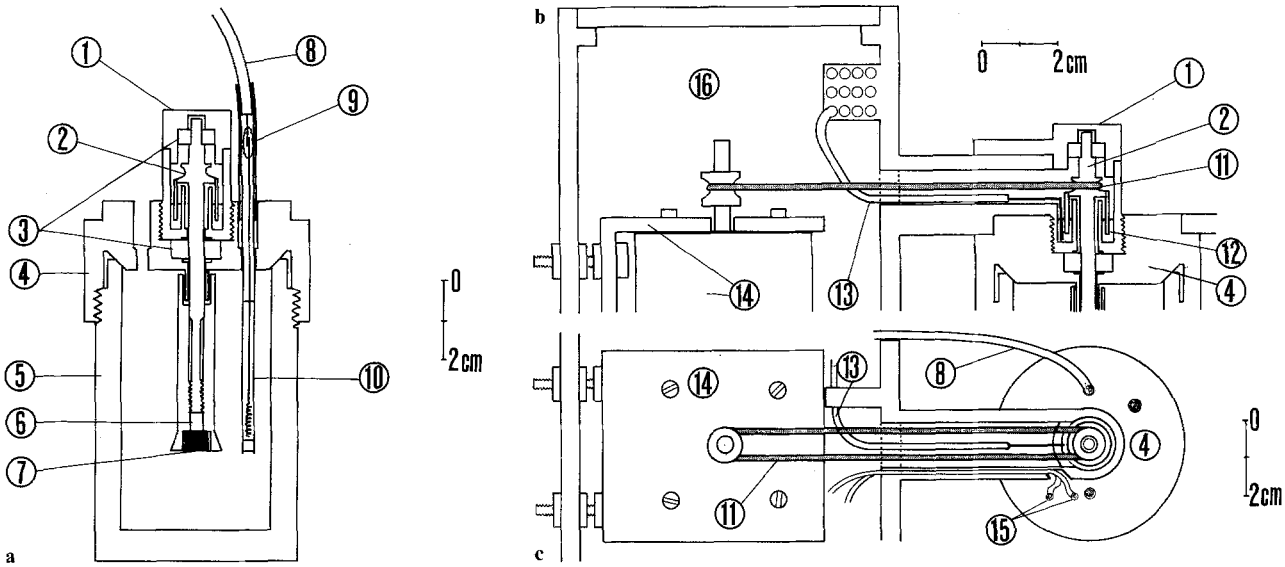

Fig. 2. Left: rotating electrode assembly and voltammetric cell. Right: rotating electrode: side and top view. *1* Axle cover removable for change of driving belt; *2* Stainless steel axle with driving wheel; *3* Ball bearings; *4* Cell cover, machined teflon; *5* Voltammetric cell, machined teflon; *6* Mercury for electric contact of *7* glassy carbon rod and *2* axle; *8* Shielded electric connection to counter electrode; *9* Soldered connection enclosed with glue for avoidance of pollution of electrolyte in counter electrode tubing; *10* Heat-shrinking teflon tubing with inserted Vycor frit; *11* O-ring made of Perbunan N used as driving belt; *12* Electric connection for rotating electrode by immersion bell from steel; *13* Shielded electric connection to rotating electrode plunging into mercury; *14* Driving motor at holder; *15* Nitrogen supply tubings for bubbling through and blanketing; *16* Motor compartment made from plexiglas. The openings in the cover (*4*) serve for the insertion of the reference electrode and counter electrode

particularly good adherence to glassy carbon, is prepared by heating Araldit B to 120° C. After melting, the hardener HT 903 is added and the well mixed melt is kept at 120° C until the glue becomes clear and free of air bubbles. Glassy carbon rods of about 8 mm length, which had been cut from a bar with 6 mm diameter, are added to the glue. After some minutes the rods are taken out with a clean pincer and placed on a teflon sheet. Hardening of the glue is carried out at 120° C over at least 24 h. In this manner the glassy carbon rods are adapted for later interaction with a plexiglass glue. Overlapping pieces of the glue are cut off and the rod is inserted into the plexiglass holder which had been machined before (see Fig. 1). The gaps are carefully filled with a plexiglass glue, Acrifix 92, Röhm and Haas, Darmstadt, avoiding air inclusions. A large excess of this glue adhering well to the Araldit B-covered surface of the glassy carbon rod is required, as it shrinks considerably during the subsequent hardening induced by UV-irradiation from sun light or an UV-lamp. During the first hours of hardening, the top of the holder has to be protected from too strong UV-irradiation, inducing in this manner first a hardening in the bulk, proceeding progressively to the top zone. The completion of hardening is followed by a grinding procedure at medium rotation speeds of 500 to 1,000 rpm beginning with rough glass paper and gradually proceeding to glass paper with finer grains. This grinding is continued until all the excessive glue has been eliminated and the bare glassy carbon surface appears. The following final polishing is performed manually, using wet filter paper onto which aluminium oxide first of 1 μm grain size and subsequently of 0.3 μm has been dispersed. The polishing is carried out until a mirror-like glassy carbon surface has been produced. Remaining aluminium oxide particles, which would constitute a serious contamination, are removed by careful rinsing with distilled water acidified to pH 1 with HCl, Merck, Suprapur. The machined plexiglass holder of the glassy carbon rod is fixed to a stainless steel axle (see Fig. 2). To achieve a well conducting electric connection, necessary for a low noise performance, the axle is contacted by mercury to the glassy carbon rod. For the same reason the electrical contact to the polarograph is made via a steel immersion bell plunging into mercury. Further details of the working electrode design are given in Fig. 2.

Commercial rotating glassy carbon electrodes generally have some construction principles unfavourable from the contamination aspect. Motor and electrical connections are placed above the voltammetric cell. Our first version of home-made rotating electrodes, based on the concept of Sipos et al. [35], was constructed in the same way [21, 27]. It turned out, however, that this design is not very favourable for ultra trace analysis, because it enhances significantly the contamination risk during cell change or when the cell cover has to be opened, e.g. for standard additions. The contaminants are dust, corrosion and abrasion products from the motor and the electrical connections. Only a quite different design separating motor, drive and electrical connections of the working electrode with the polarograph, will render meaningful the utilization of a clean bench.

Therefore in the new design (see Fig. 2) described here, the rotating glassy carbon electrodes have been reduced in length to 9 cm, using a belt drive which works reliably for rotation speeds of 1,500 to 3,000 rpm, depending on the pully size upon the motor axle. A most suitable rotation speed is 2,000 rpm.

The belt drive concept permitted to place the motor at parallel height with the cell. The very reliable synchronous motor from Dunker, type SY 52 × 60-4,

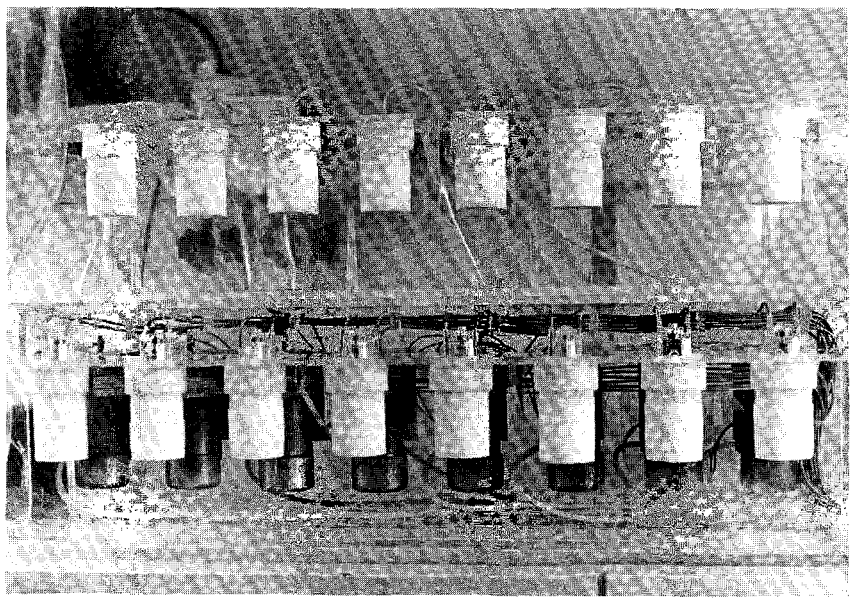

Fig. 3
Multicell system under clean bench. Upper rack: cells fitted for outgassing. Lower rack: voltammetric cells with rotating electrodes. The motors and electric connections are housed in a separate closed compartment

1,500 rpm, is used, although it is rather overdimensioned for the task and can be replaced by suitable other types. The motor and electrical connections compartment is usually kept hermetically closed. If necessary it is accessible by removing its top cover. In this way the driving belts, consisting of O-rings from Perbunan N, can be replaced after several 100 h of operation. Contamination by particles coming through chinks in the motor compartment or driving tunnel is eliminated by keeping them under slight underpressure with the aid of a fan sucking cooling air through the motor compartment. This air is, of course, exhausted outside the clean bench.

The Multicell System

In the new multicell system (see Fig. 3) used now to improve further the analysis rate, usually four cells are operated. Two or more cells are placed for outgassing into an upper rack, while for the at present still manual measurements two cells in the lower measurement rack are connected to two polarographs for simultaneous voltammetric measurement. These cells are fitted by screwing to their covers (see Fig. 2a). The multicell system is placed under a clean bench with laminar filtered air flow to prevent contamination by dust particles from the laboratory atmosphere. Nevertheless the whole laboratory room should have the trace chemical layout and maintenance according to the aspects outlined in part I [14]. The whole multicell set-up is already designed for future semiautomated operation, which will permit simultaneous voltammetric measurements in eight cells while further eight samples are deaerated.

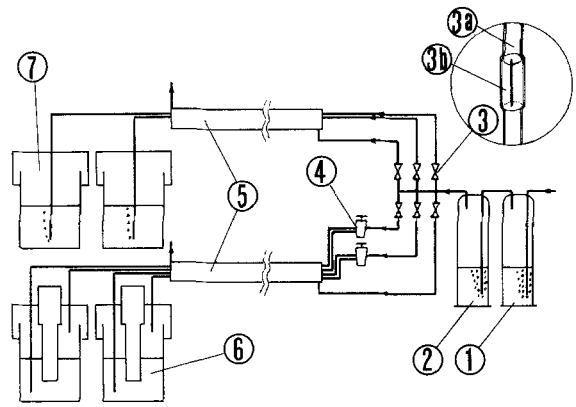

Fig. 4. Nitrogen supply system for deaeration. *1* Oxygen scrubbing system, vanadium(II) solution and zinc amalgam for V(II) regeneration, it is not to be used during Zn determination because of measurable Zn blanks. *2* Scrubbing bottle, filled with acidified water (pH 1). *3* Pressure reduction from 1 bar in main connection to low pressure for bubbling through. *3a* Silicone tubing with *3b* inserted piece of glass capillary; the inner diameter of about 0.08 mm determines gas flow for outgassing. *4* 2-way-stopcock for adjusting either N_2-bubbling through or a N_2-blanket above the sample in the cell, (to be replaced by electric valve in the projected automated system). *5* Outer polyethylene tubing, covering the N_2 supply tubings over longer distances and flushed with N_2. *6* Cell in measurement rack. *7* Cell in outgassing rack

The cells in the upper rack are connected to the nitrogen supply system shown in Fig. 4. This rack can be moved back to attain access to the motors situated below. Of course, also the cells in the lower rack, being in different stages of the voltammetric measurement, have to remain connected to the deaeration system in order to keep an inert atmosphere over the sample solution. Numerous nitrogen supply lines are therefore required, two for each cell on the measuring rack and one for each cell on the upper rack where the prior deaeration is performed by bubbling 99.999% pure nitrogen through the sample solution. The nitrogen supply lines are flexible silicone tubes con-

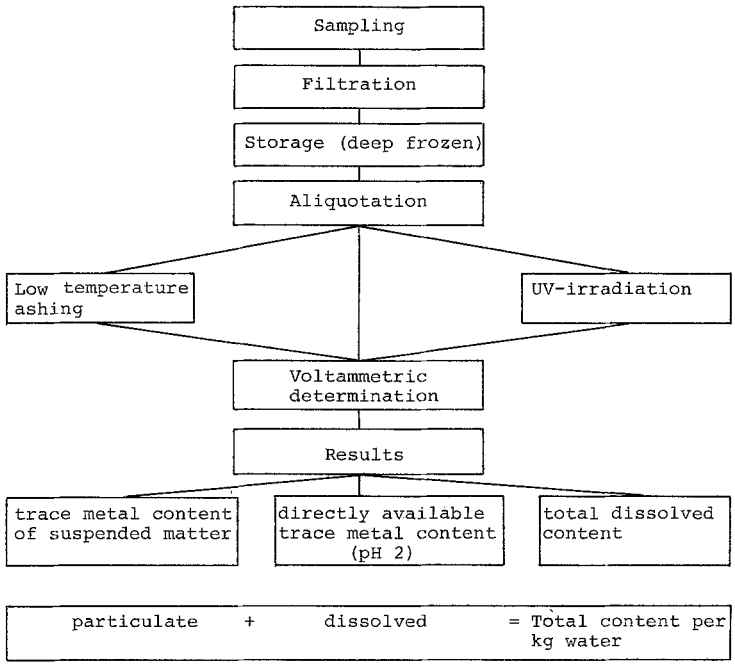

Fig. 5
Flow chart of analytical procedure

nected to the teflon inlets of the cells. An obvious disadvantage of lengthy silicone tubing is its permeability to oxygen from the ambient air. To compensate this effect, the flexible silicone tubes are bundled and put into a wider polyethylene tube flushed with nitrogen.

The voltammetric cells are machined from conventional TFE teflon bars. The inner diameter of the cell is 40 mm and it has a volume of 85 ml. Usually the cell is half filled, the sample amount being determined by weighing. This relatively large volume facilitates considerably standard additions, as small volumes of rather concentrated standard solutions can be added. As pointed out later, samples have to be subjected to UV-irradiation. This pretreatment of the samples is performed within the voltammetric cells, thus avoiding the transfer of the sample from a particular irradiation flask of different material into the measuring cell. During irradiation, the top of the cell is exposed to temperatures of 220° C. Therefore the thread of the machined teflon cell is cut after having heated it up to 240° C for at least 24 h. In this manner the tensions inherent to the teflon disappear. The cells have to be finally subjected to the scrupulous cleaning procedures described in part I of this series [14].

Contamination Minimization in Clean Bench Operations

Measurements of the air flow pattern in the clean bench showed that the laminar flow is altered into turbulent motion in the vicinity of the cells in the deaeration and measurement rack. Therefore, contamination aspects during the critical phase of cell changing were investigated in detail, although previous voltammetric analyses with blanks handled in the same way had reflected no noticeable contamination after this manipulation. A Kratel particle counting system, Partoscope, model R, was applied and usually for a sucked-through air volume of 281 min^{-1}, 1 to 2 particles were counted within the laminar and also turbulent air flow. However, a manipulation like screwing off simultaneously cells in the upper and lower rack and interchanging them, is followed by a sharp increase of the particle number to several hundred (sampling interval: 10 s) in the vicinity of the measuring electrodes being bare during this change. Dust from the hand, although covered by a polyethylene glove and the arm of the operator was carried down to the lower rack during manipulation in the deaeration rack. By altering the sequence of manipulations, this potential contamination source could be eliminated. First, a cell in the deaeration rack is screwed off and taken down to the measurement rack, always remaining distinctly in the laminar air flow. After about 10 s the particles from this manipulation in the deaeration rack have been carried out of the vicinity of the measuring cells. Now only the measuring cell is screwed off and replaced by the new one. The risk of contaminating the bare electrodes or the sample in the open cell is negligible, as only about 40 particles (sampling interval 10 s) can be counted during this cell exchange in the turbulent zone.

It must be emphasized that even such apparently minor details constitute a contribution to the overall contamination control, thus enabling reliable voltammetric ultra trace metal analysis.

The Analytical Procedure

The flow chart in Fig. 5 summarizes the stages of a simultaneous voltammetric analysis of several trace metals, being present dissolved or bound to suspended particulate matter in natural water samples. In the

determination stage, the application of differential pulse anodic stripping voltammetry (DPASV) at a mercury film electrode (MFE) is presumed. The procedure outlined below permits the simultaneous determination of Cu, Bi, Pb and Cd down to ultra trace determination limits of 0.5 – 3 ng/kg. By adjusting the pH to 4, the determination of Zn traces can be included as well.

Procedures for sampling in surface waters [15] and in deep waters [16], as well as pretreatment steps like filtration and storage of samples have been treated in part I [14]. Thus, the following chapters will deal with the further stages of the analytical procedure to which appropriately stored samples of suspended particulate matter and filtrated water have to be subjected.

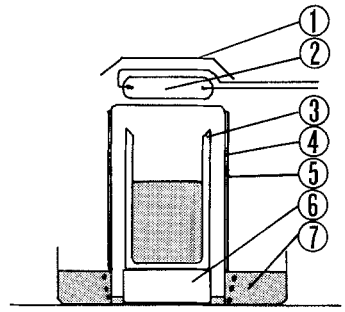

Fig. 6. UV-irradiation device. *1* Reflector; *2* UV-lamp; *3* Voltammetric cell filled with sample; *4* Quartz beaker; *5* Aluminium foil, the area of the foil determines temperature under the beaker; *6* Distance block from teflon; *7* Glas dish with water for separating the cell from the outer atmosphere

Low Temperature Ashing of Particulate Matter

During missions, filters loaded with particulate matter had been stored deep frozen (−20° C) in cleaned glass dishes protected from dust by enveloping polyethylene bags. The filters and the particulate material are digested by low temperature ashing (LTA) at 150° C in an oxygen plasma induced by micro waves. This method is suitable for trace metals as Cu, Bi, Pb, Cd and Zn and avoids volatilization losses. Hg, however, requires a suitable wet digestion procedure.

The filters are put with a plastic pincer into marked quartz dishes. Four of those quartz dishes can be loaded in each of the four compartments of the LTA-device from Internat. Plasma Corp., Hayward, Calif. Adjusting a vacuum of 1 – 5 torr, an oxygen supply flow of 300 cm^3 min^{-1} and a microwave power of 150 W, the digestion is completed within 4 h. The residues are taken up in 1 ml water. Depending on the ash quantity 50 – 200 µl HCl, Merck, Suprapur are added. After 5 min the quartz dish is emptied into a voltammetric cell and rinsed with about 40 ml water.

The blank values can be kept low, provided appropriately cleaned filters [14] are used, and amount to 1 ng Cd, 3 ng Pb and 5 ng Cu per filter.

The LTA-procedure decomposes all biological and organic components of the particulate matter, i.e. algae and detritus, including the organic films on silica or clay particles which remain themselves unaffected. Inorganic carbonates are dissolved by the subsequent acidification. Thus, a determination includes the trace metal amount in the water samples which might become remobilized to the dissolved state and which can enter at least partially the aquatic food chain due to immediate uptake by filter feeders as e.g. mussels.

Treatment of the Filtrate

The required procedure depends on the water sample. For certain natural water types some steps of the analysis scheme can be omitted and the analytical procedure is simplified. Acidified samples with very low amounts of dissolved organic matter (DOM), e.g. from the open oceans, certain unpolluted coastal water areas, drinking water or rain water, require usually no further pretreatment, provided they have not been stored longer than one month.

Samples stored for longer periods, even if they have been acidified and deep frozen, may show immobilization of a certain trace metal amount due to binding by macromolecular substances. This will cause serious disturbances in the voltammograms and the analytical results will be too low. The same problem arises with water samples from rivers, lakes, estuaries and polluted coastal water areas.

A further adversive effect in samples with more substantial levels of dissolved organic matter are interferences in the voltammetric determination of the nonchelated amount of dissolved trace metals. Particularly surface active components tend to be adsorbed at the mercury film surface of the working electrode. Such adsorbed layers cause inhibition of the electrode processes and lead consequently to sensitivity losses due to signal suppression and to base line sloping.

All these interferences can be overcome by introducing a pretreatment step. The samples are irradiated by UV at elevated temperatures in order to destroy organic matter and to leach the fraction of immobilized trace metals.

The UV-irradiation is performed in the same teflon flask used later as voltammetric cell. The cell is half filled with sample water and its weight is determined on an electrical balance, whose pan is covered by a clean polyethylene sheet. According to Fig. 6 the cell is covered with a clean quartz beaker and isolated from the outer atmosphere by the water bath. All these manipulations are carried out under a clean bench with hands covered by cleaned polyethylene gloves.

The subsequent UV-irradiation in the quasi-closed device (see Fig. 6) must be performed outside the clean bench. The irradiation of a 150 W mercury vapour lamp, Hanau, is focused with the aid of a reflector through the quartz cover onto the sample solution. Depending on the origin, the sample is irradiated for 1 to 4 h. During irradiation the temperature rises to about 100° C; the solution simmers down to one half or one third of the original volume.

Samples with more elevated DOM-levels, e.g. frequently encountered in near shore waters due to the effect of waste water inlets

Table 1. Effect of UV-irradiation on determinable dissolved trace metal concentration

Cd (µg/kg)		Pb (µg/kg)	
without UV	after UV	without UV	after UV
0.019	0.022	0.072	0.094
0.009	0.015	0.049	0.054
0.031	0.043	0.058	0.105
0.012	0.014	0.047	0.048
–	–	0.043	0.051
0.011	0.014	0.048	0.052
0.008	0.011	0.078	0.080
0.036	0.041	0.072	0.090
0.013	0.024	0.106	0.145
0.022	0.027	0.032	0.048

or polluted rivers, are stronger acidified by addition of 1 ml conc. HCl, Merck, Suprapur, to support the photolytic decomposition of organics and leaching of chelated trace metals.

Usually the additional amount of trace metals released by this treatment is on average 20 % of the total dissolved trace metal level, but may go up in certain samples to even 60 % (see Table 1).

To samples from estuaries and polluted rivers or lakes with relatively high levels of dissolved organic matter, furthermore 1 ml perhydrol, Merck, Suprapur, is added to achieve efficient oxidative decomposition. The resulting somewhat higher blank is well compatible with the usually higher trace metal levels in this sample type. A similar pretreatment has been applied successfully in the trace metal analysis of wines [10] and domestic waste water [42].

Voltammetric Determination Stage

In the following, a manual operation of the multicell system with two cells connected to two polarographs (Fig. 3) will be presumed. It is, however, emphasized that the voltammetric determination proceeds similarly if only a single system and one polarograph is applied, as in our earlier investigations [27, 40].

Two or more cells with samples pretreated as outlined in the previous section, are spiked with 50 µl of a 2.5×10^{-2} M $Hg(NO_3)_2$-solution, Merck, Suprapur, adjusting a mercury concentration of about 10^{-5} M for film formation in the later cathodic deposition stage. The cells are fitted to covers in the deaeration rack and are deaerated with oxygen-free nitrogen for 10 – 20 min. At the same time the below outlined stages of voltammetric measurement may go on with already outgassed samples in two other cells in the measurement rack.

After outgassing, the cells are transfered to the measurement rack and positioned under prepared working electrodes. Precautions described previously should be taken into consideration.

After a final outgassing of 3 min the voltammetric measurement begins with the *cathodic deposition* step by applying a potential of −1.0 V to the working electrode rotating with 2,000 rpm, in order to speed up mass transfer from the bulk of the solution towards its surface. This rather negative deposition potential is important to attain a homogeneous mercury film of closely packed Hg-microdroplets of rather equal size.

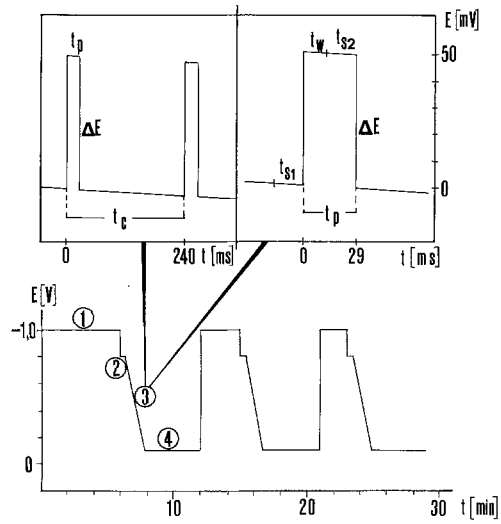

Fig. 7. Voltage sequence during voltammetric determination. *1* Cathodic deposition period t_d. *2* Rest time. *3* Linear voltage ramp with pulses of height ΔE; pulse duration t_p; current sampling intervals t_{s1} and t_{s2} and clock time t_c. *4* Standard addition followed by voltage patterns after 1st and 2nd standard addition with systematically reduced t_d

If more positive potentials would be applied to the bare glassy carbon electrode, the distribution of the active deposition sites on the glassy carbon surface will become inhomogeneous [39] and a mercury film of unsatisfactory performance will be the consequence. Once a thin mercury film has been built up, e.g. after 3 – 5 min plating time, less negative deposition potentials can be applied for further plating.

Simultaneously with the formation of the mercury film also an aliquot of the trace metal ions like Cu, Bi, Pb and Cd is discharged and deposited as amalgams. This electrochemical preconcentration is achieved *in situ* and therefore without any additional contamination risk. The deposition time t_d is adjusted to values between 3 and 12 min, according to the respective order of the trace metal bulk concentration. A deposition period t_d of 3 min can be regarded as a practical minimum with respect to the later outlined mode of standard additions. At the end of the plating step the motor is switched off and the solution is allowed to come to a rest within an interval of 30 s. During this step and the subsequent stripping, the sample is blanketed with nitrogen.

The anodic stripping is performed in the differential pulse mode (DPASV). Optimal instrumental settings are: scan rate 10 mV s^{-1}; pulse amplitude ΔE 50 mV; pulse duration t_p 29 ms; current sampling times t_{s1} and t_{s2} 16 ms; pulse repetition period t_c 0.24 s. The whole polarisation sequence during the various DPASV-stages is summarized in Fig. 7.

At the appropriate potentials an aliquot of the trace metals concentrated as amalgams is reoxidized to their respective ions. The current corresponding to this electrode reaction is sampled twice during each pulse repetition period. The difference between these measurements is obtained electronically and represents the y-signal

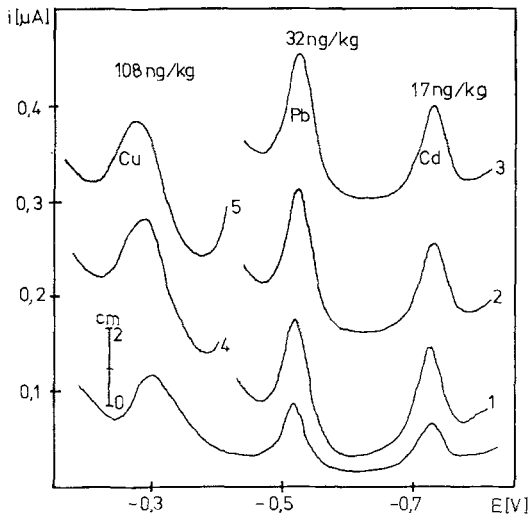

Fig. 8. Voltammogram of a sea water sample from the German Bight (1978); deposition times for Cd and Pb: $t_{ds} = 6$ min, $t_{d1} = 3$ min, $t_{d2} = 2$ min; deposition times for Cu: $t_{ds} = 6$ min, $t_{d1} = 3$ min. Standard additions: Cd = 0.8 ng, Pb = 2 ng, Cu = 6 ng, sample weight 51.1 g

displayed on the recorder. A voltammogram is shown in Fig. 8. Peak heights are proportional to the trace metal concentrations in the bulk of the solution.

Usually an unknown sample requires first an exploratory run made with a cathodic deposition time of 5 min, yielding an approximate estimate of the different trace metal levels. From this run the appropriate deposition time t_{ds} from 3 – 12 min can be deduced. In the following actual determination run the appropriate instrumental sensitivity for the trace metal with the most negative reoxidation potential, usually Cd, is adjusted and the Cd-peak is recorded. If necessary, the scan can be stopped in the valley after this first peak. The instrumental sensitivity is readjusted, according to the results of the exploratory run, in order to record the next peak in suitable height. During this instrumental setting effectuated within 10 s, the deposition current is negligible due to lack of convection. The scan is started again and the next peak is recorded. At the end of the potential scan, usually at −0.1 V, the motor is switched on again and during 3 min remaining amounts of all trace metals in the mercury film are reoxidized (see stage 4 in Fig. 7). Two standard additions are carried out for later evaluation of the trace metal concentrations. After each standard addition a similar voltammetric procedure is carried out. However, as pointed out in the next section, the cathodic deposition times are appropriately reduced.

Standard Addition and Adapted Deposition Times

Making a correct standard addition is a matter of experience. From the first voltammogram a skilled operator can deduce the approximative amount of trace metals necessary to double roughly the bulk concentration by the first standard addition. This same amount is also applied in the second addition.

After the first addition, the deposition time is halved ($t_{d1} = t_{ds}/2$) and after the second addition, t_{d2} is reduced to one third of t_{ds}. Besides the advantage of reducing the overall analysis time, this practice eliminates slight deviations from the linear relation of peak height to trace metal concentration in DPASV [13] at film electrodes. Each stripping step starts with approximately the same trace metal amount concentrated in the mercury film and the recorded peaks are all of the same order of magnitude. It must be emphasized that this method works reliably in analysis of Cd, Pb and Bi, even if the primary aim of doubling approximately the bulk concentration has not been attained, e.g. by making a too high or too low standard addition.

According to our experiences this described practice offers the only convenient way to cope with problems of Cu-analysis at a thin mercury film electrode. Compared to Cd and Pb, the solubility of Cu in Hg is very low: 0.002 %. Depending on the bulk concentration, the film thickness and the plating time, only a part of the Cu deposited will be soluble as amalgam. Problems arise during anodic stripping, as the peak-concentration relation of both plated Cu species is different. This is reflected by constantly decreasing Cu peaks in repetitive analysis, as the Hg amount grows with each plating, thus amalgamating an increasing amount of Cu [13]. Usual standard addition followed by constant plating times will alter seriously the proportion of both deposited Cu species, leading to a completely non-linear bulk concentration-peak height relation.

In order to avoid these problems, the determination of Cu is performed after the complete procedure for Cd and Pb, including their two standard additions. As the approximative amount of Cu is known from the exploratory run, an appropriate plating time can be choosen. For the determination of high Cu concentrations a medium or large (!) plating time and a low instrumental gain is set up. Thus, the non-amalgamated portion of plated Cu is predominant. For low and ultratrace Cu levels, the shortest (!) possible deposition time and high instrumental sensitivity will be choosen. The deposited small amount of Cu is totally amalgamated and gives a defined anodic stripping response. The procedure of standard addition, reducing plating times as outlined above, is applied. If the resulting peaks differ for more than about 30 % in height, e.g. the standard addition has not been well adjusted, the plating step should be repeated, increasing or decreasing the deposition time according to requirement.

The evaluation of the trace metal content is conveniently performed with a programmable pocket calculator. First the peak heights i'_s and i'_1 for one common plating time t_{d2} have to be calculated:

$$i'_s = \frac{i_s \cdot t_{d2}}{t_{ds}} \text{ and } i'_1 = \frac{i_1 \cdot t_{d2}}{t_{d1}} \text{ and } i'_2 = i_2$$

with the respective plating times of the original sample (t_{ds}), after the first (t_{d1}) and the second standard

addition ($t_{d,2}$) and the peak currents of the sample (i_s), after the first addition (i_1) and the original peak current (i_2) after the second standard addition.

Now, a relation valid for conventional standard addition can be applied to the corrected peak currents i'_s, i'_1 and to i_2. The average value Δi of the increase in (corrected) peak height after the first standard addition (Δi_1) and after the second addition (Δi_2) is calculated:

$$\Delta i = \frac{\Delta i_1 + \Delta i_2}{2} \text{ with:}$$

$$\Delta i_1 = i'_1 - i'_s \text{ and } \Delta i_2 = i_2 - i'_1 .$$

The original trace metal concentration (c) in µg/kg is calculated after the following equation:

$$c = \frac{m \cdot i'_s}{w \cdot \Delta i} (\mu g/kg)$$

where m is the standard addition in ng and w the weight of the sample in the cell in g.

Working Electrode Maintenance and Storage

Usually the working electrode is in continuous use during an analysis series. The first step in each analysis has to be devoted to the regeneration of the working electrode. The voltammetric determination of a fresh sample is preferably carried out with a freshly formed MFE. Therefore the old mercury film used in the previous analysis has to be removed. When working in acidified (pH 2 – 3) samples, it is not sufficient to wipe it just off with wet filter paper. This leaves the glassy carbon surface in an unsuitable state reflected by a progressively decreasing hydrogen overvoltage. The resulting slope of the base line in the voltammogram would impede soon the precise determination of trace metals, particularly of those with rather negative reoxidation potentials like Cd. Most severe are the consequences of this inadequate maintenance of the working electrode in the ultra trace range, when high instrumental gain has to be used.

A recommended adequate maintenance procedure of the working electrode is as follows.

A wet folded filter paper on which some aluminium oxide (0.3 µm grain size) has been spread, is brought for about 20 s into contact with the electrode rotating at reduced speed in order to avoid spilling of the abrasive material by centrifugal forces. The reduced speed is achieved by switching a resistor in series with the motor. The old mercury film is removed and the appearing glassy carbon surface is subjected to a brief polishing. Subsequently the reestablished glassy carbon electrode is rinsed carefully with deionized water, removing completely all traces of the aluminium oxide which would act as a serious contaminant. A final rinsing step is performed by rotating the electrode for some minutes in deionized water acidified to maximal pH 1. Higher acidity might have adversive effects on the glassy carbon surface [5]. The working electrode is now ready for the fresh formation of a mercury film in a subsequent analysis.

Alternatively, the glassy carbon electrode can be stored. Before storage a small flask filled with mercury is put into the centre of a cell and the remaining volume is filled up with acidified water. By fitting the cell to its cover, the working electrode is plunged into mercury. Storage in water or worse, in acidified water will deteriorate the glassy carbon surface soon. The Vycor tips of the counter and reference electrode compartments are protected from drying out by their immersion in the acidified water. The cell with its electrodes can be stored for longer periods without any deterioration in electrode performance.

According to the outlined maintenance procedure, properly treated glassy carbon working electrodes will keep their high performance qualities for years.

Ultra Trace Range Modifications

For precision measurements in the ultra trace range at levels between 50 and 1 ng/kg, the following additional contamination control and conditioning step of the working electrode should be introduced before the actual voltammetric determination.

The cells are filled with ultrapure water blanks acidified to pH 2 and spiked with mercury. They are subjected to the described outgassing and DPASV procedure. The blank value of Pb, most critical with respect to contamination, is roughly evaluated with a calibration curve. According to the requirements of the following analysis, it should be below 1 – 5 ng/kg. The mercury film plated during this test is not removed from the glassy carbon support and is used for the following ultra trace analysis. To avoid deterioration of the film, the electrode rotation has to be stopped during the exchange of the test cells versus the cells with the samples.

Determination Limits, Precision and Accuracy

The determination limit with an acceptable precision for the voltammetric determination stage depends on the length of the cathodic deposition time t_d. Yet in practice the determination limit is given by the attainable minimization of contamination. At present, determination limits of 0.5 ng/kg for Cd, Pb, and 3 ng/kg for Cu and Bi with an RSD of ±20 % are attainable with a rather reasonable t_d of 12 min (see Fig. 9). This corresponds incidentally for Cd in a sample volume of 40 ml to an absolute amount of only 20 pg. These determination limits have proved hitherto fully sufficient to determine even the lowest levels of the mentioned trace metals in natural waters encountered in certain areas of the open ocean. As can be seen from Fig. 9, the precision decreases again at elevated concentrations, because now the mercury film tends to become more and more overloaded.

An obvious conclusion is that the MFE should not be applied at trace metal levels above several 100 µg/kg. In this higher concentration range the MFE has to be substituted by the HMDE which is certainly easier to apply and operate, bearing in mind that it is not suitable

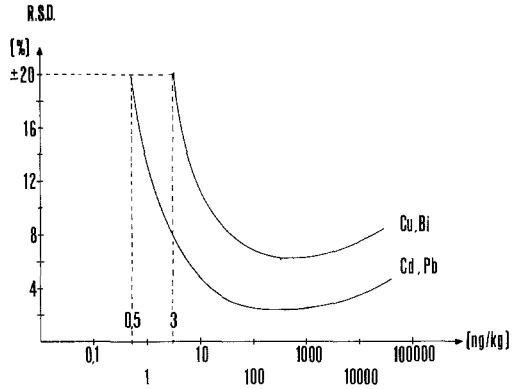

Fig. 9. Precision and actual determination limits. Relative standard deviation of 20 % at determination limits of 0.5 ng/kg for Cd and Pb, 3 ng/kg for Cu

Table 2. Accuracy test by interlaboratory comparison of a deep sea water sample. Sample taken 120 km off the Californian coast from 1,000 m depth with CIT sampler (B. Schaule and C. C. Patterson)

(ng/kg)	(1)	(2)	(3)
Cd		105	101
Pb	3.3		2.9
Cu		115	110

(1) C. C. Patterson, California Institute of Technology, Pasadena. CH_3Cl-dithizone extraction and isotopic dilution mass-spectroscopy
(2) K. Bruland, University of California, Santa Cruz. APDC-DDDC extraction and electrothermal AAS
(3) L. Mart, Nuclear Research Center, Jülich, DPASV

for concentrations below typically 100 ng/kg. In the concentration range between 0.1 – 500 µg/kg the application range of both electrode types overlaps [22, 26].

In modern trace analysis the common approach to test accuracy is the comparative analysis of the same sample by two or more completely independent analytical methods [38].

An example for the accuracy confirmation in ultra trace metal analysis of sea water is given in Table 2. The agreement of this interlaboratory comparison is good and the results emphasize the high reliability of the presented approach by DPASV at the MFE. In this context it has to be stressed, moreover, that the voltammetric analysis was the by far most rapid procedure, an aspect of substantial practical significance in the analytical investigation of numerous samples from extended field missions in environmental research or chemical oceanography.

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