Automated voltammetric system for shipboard determination of metal speciation in sea water

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Abstract

An automated and semi-intelligent voltammetric system is described for trace metal analysis. The system consists of a voltammeter interfaced with a personal computer, a sample changer, 2 peristaltic pumps, a motor burette and a hanging mercury drop electrode. The system carries out fully automatically approximately 5 metal determinations per hour (including at least 3 repetitive scans and calibration by standard addition) at trace levels encountered in clean sea water. The computer program decides what level of standard addition to use and evaluates the data prior to switching to the next sample. Alternatively, the system can be used to carry out complexing ligand titrations with copper whilst recording the labile copper concentration; in this mode up to 8 full titrations are carried out per day.

Depth profiles for chromium speciation in the Mediterranean Sea and a profile for copper complexing ligand concentrations in the North Atlantic Ocean measured on board-ship with the system are presented. The chromium speciation was determined using a new method to differentiate between Cr(III) and Cr(VI) utilizing adsorption of Cr(III) on silica particles.

Keywords: Voltammetry; Chromium; Copper; Metal speciation; Sea water; Shipboard determination; Waters

The redox and chemical speciation of trace metals in natural waters have important implications for the geochemical cycling and bioavailability of trace metals [1,2,3]. Electrochemical methods are very suitable for the study of speciation because of their high sensitivity and because the electrochemical response is species specific. Several studies on metal speciation, using electrochemical techniques, have been reported for estuarine [4,5], coastal [6] and oceanic environments [7,8].

Because of the low concentrations involved and the labour-intensity of the methods, the amount of data available on metal speciation is still limited. Furthermore, speciation measurements have to be performed quickly upon sampling, because of a possible change in the equilibria during storage and transport of the samples [9,10]. This requirement and the number of measurements involved in determining trace metal speciation necessitate automated on-board measurements. Automation of the electrochemical methods for accurate determination of trace metals in ocean waters has, however, been hampered for a long time because of the low levels involved. A number of examples of flow system for electrochemical determinations can be found in the literature [11-16]. However, the systems described are in most cases not suitable for the concentration levels encountered in unpolluted ocean waters. Furthermore, in the case of voltammetric flow systems, a suitable method for accurate low level addition of metal standard solution has yet to be found.

This article describes an automated voltammetric system for determination of trace metals at the levels encountered in unpolluted ocean
water, at a rate of approximately 5 and 7 determinations per hour, with and without calibration respectively. The system combines flow and batch operations and is applied here to determine the speciation of chromium and copper in sea water. Mixing of sample and reagent (for chromium measurements) takes place on-line; this mixture is pumped into a conventional voltammetric cell, which enables accurate determination of the metal concentration using a hanging mercury drop electrode (HMDE). The system was used onboard ship for speciation studies of copper and chromium using cathodic stripping voltammetry (CSV). Characterisation of the system and its field applications for trace metal determinations are explored in the following sections.

EXPERIMENTAL

Apparatus

A diagram of the automated electrochemical system is shown in Fig. 1. The system consisted of an HMDE (663 VA Stand, Metrohm; drop surface area: 0.38 mm²), a sample changer (PSA 20.020, Chemlab), a motor burette (665 Dosimat, Metrohm) and 2 peristaltic pumps (Minipuls 3, Gilson; four channels). These devices were connected to the digital input/output ports (DIO 1 and DIO 2) of the voltammetric analyser (Auto-

lab, Eco Chemie). An AT 80286 IBM compatible personal computer (Toshiba 3100) controlled the voltammetric analyser and the devices connected to this instrument.

The electrical connections are shown in more detail in Fig. 2. The personal computer (PC) was connected to the Autolab via a parallel interface card placed in an 8 bit slot of the computer. The HMDE was interfaced with the voltammetric analyser via an interface box (IME, Ecochemie). The pumps and sample changer were TTL controlled via port DIO 1 of the voltammetric analyser. The motor burette was controlled in a serial way via port DIO 2.

The original computer program (EAS 1.0, written in Quick Basic 3.0) provided by the manufacturer of the Autolab voltammetric analyser to control the electrode, potential scans and data treatment, was altered in order to control the pumps and sample changer. Further changes have been made to make the program self-decisive and intelligent (e.g. to reject failed scans and to perform additional scans when required). A dot matrix printer (IBM Proprinter) was used to print the results of the analysis.

The inner diameter of the tubing (Santoprene, Altec) used in the peristaltic pumps was 1.85 mm for sample delivery and 0.38 mm for chromium reagent delivery. PTFE tubing (1.0 mm, i.d.) was used for sample transport from pump to voltammetric cell. Ultraviolet irradiation was carried out for 4 h by using a 100-W high pressure mercury vapour lamp (Hanovia). The sample bottles (20
of the sample changer were replaced by 30-ml Teflon bottles to minimise adsorption effects.

Reagents
Water purified by reverse osmosis (Milli-RO, Millipore) followed by deionisation (Milli-Q, Millipore) was used for rinsing and to prepare reagents. All reagents were purchased from BDH (AnalaR quality), unless indicated differently.

An aqueous solution containing 0.025 M diethylenetriamine pentaacetic acid (DTPA, Sigma), 5 M NaNO₃ and 0.5 M CH₃COONa was prepared to determine chromium. Chromium contamination [comprising Cr(VI) and Cr(III)] was removed from a solution containing 5 M NaNO₃ and 0.5 M CH₃COONa by co-precipitation with hydrated iron(III) oxide by addition of iron (II) chloride (10⁻⁴ M) prior to the addition of the DTPA. The precipitate was removed from the solution by filtration using a 0.45 μm cellulose acetate membrane filter [10]. Addition of 0.625 ml of the chromium reagent to 10 ml sea water gave the required pH (pH 5.3 in sea water) and reagent concentration, whereas Cr(VI) contamination due to the addition was <0.01 nM. A suspension of 100 g l⁻¹ LiChrosorb Si 60 silica (particle size 5 μm, surface area 490 m² g⁻¹; Merck) was used to remove Cr(III) from sea water prior to the determination of Cr(VI). A quantity of 100 μl of this suspension was added to 25 ml of each sample at least 20 min before analysis. Cr(III) contamination was removed from the LiChrosorb silica by soaking overnight in 5 M HCl, followed by rinsing with deionised water and four-fold UV irradiation. The UV irradiation oxidised Cr(III) to Cr(VI), which in turn desorbed from the silica. Between the UV irradiation steps the LiChrosorb silica was centrifuged and subsequently rinsed with deionised water. Cr(VI) contamination due to the silica at a level of 0.4 g l⁻¹ was <0.01 nM.

Standard solutions of Cr(VI) were prepared by dissolving K₂CrO₄ in water. Standard solutions of Cr(III) were prepared by dilution of an atomic absorption standard solution and were acidified to pH 2.5 using 6 M HCl (quartz-distilled). A stock solution of 0.5 M tropolone (Aldrich) was prepared in methanol (quartz doubly-distilled). The pH buffer contained 1 M boric acid–0.35 M NH₄OH (both Arista grade), giving a pH of 8.35 upon 100-fold dilution with sea water. Standard solutions of copper were prepared by dilution of an atomic absorption standard solution and were acidified to pH 2.5 using 6 M HCl (quartz-distilled).

Sample collection and treatment
Chromium speciation was determined onboard ship (FS Valdivia) during a cruise on the Mediterranean Sea in February 1992 as part of the EROS 2000 program. The data presented here were obtained in samples collected at station 10 (36°N, 5°W).

Copper complexing ligand concentrations were measured on-board ship during RRS Challenger Cruise 76 (March 1991) on the North Atlantic Ocean. The data shown were obtained in samples collected at station 3 (48°N, 20°W).

Samples were collected using PTFE-coated Go-Flo bottles (General Oceanics). The samples were nitrogen-pressure filtered through 0.4-μm polycarbonate membrane filters (acid soaked, Nuclepore), immediately upon collection. A 30 ml aliquot of the filtrate coming out of the Go-Flo bottle was sub sampled directly into a silica tube (30 ml) and subjected to UV digestion prior to the determination of total chromium. This procedure prevented loss of the Cr(III) fraction by adsorption on the walls of intermediate sample bottles [10]. All sample handling took place in a laminar flow hood.

Automated CSV determination of chromium speciation sea water
The speciation of chromium was determined by CSV using a new method to differentiate between Cr(VI) and Cr(III). Separation was achieved by utilising the known adsorption of Cr(III) onto silica particles [17], to remove Cr(III) from sea water prior to determination of Cr(VI). Cr(VI) was determined after addition of 100 μl of a suspension containing 100 g l⁻¹ LiChrosorb silica into PTFE sample bottles placed in the sample changer, followed by 25 ml sea water giving a final silica concentration of 0.4 g l⁻¹. The automated measurements were initiated after a reaction time of at least 20 min.
Total chromium was determined as Cr(VI) after UV irradiation (4 h) of the untreated samples to convert all Cr(III) to Cr(VI) [10]. The Cr(III) fraction was then calculated from the difference between total chromium and Cr(VI). The samples to be analysed for total and labile chromium on-board ship were placed on the same sample tray, thus minimising day to day variability of the measurements.

The procedure to determine Cr(VI) automatically was as follows: from a sample bottle 10 ml of sea water was pumped into the voltammetric cell by peristaltic pump 1 at a rate of ca. 8.5 ml min⁻¹ (0.6% R.S.D., n = 10). The sample flow was mixed with that of the chromium reagent at a ratio of 16:1 (sample–reagent) giving a DTPA concentration of 20 μM. The pumping time of the peristaltic pump was calibrated three times a day to give precisely 10.0 ml, and the difference in pumping efficiency was normally less than 0.3%. A 10-ml aliquot of each sample was used to rinse the tubing, voltammetric cell and the electrode, whereas a second aliquot was used for analysis. The voltammetric cell was deaerated for 3 min using water-saturated N₂, 2 new mercury drops were made and after the extrusion of a third drop the potential of the HMDE was set to -1 V whilst the solution was stirred. Adsorption of the Cr(III)–DTPA₂ complex on the HMDE was carried out for a period of 30 s, the stirrer was stopped and a quiescence period of 8 s was allowed. Then a potential scan was carried out using the square wave modulation at a frequency of 100 Hz, a modulation amplitude of 25 mV, and a step height of 2.4 mV. The scan direction was towards more negative potentials, and the reduction peak corresponding with chromium appeared at -1.2 V.

Fig. 3 shows a flow diagram of the subsequent steps made by the program. After a series of scans the relative standard deviation (R.S.D.) of the peak heights of 3 consecutive chromium determinations was calculated; a fourth determination (loop 1) was carried out if the R.S.D. was greater than a pre-set value (5%). In case the requirement of R.S.D. < 5% was still not met, determinations differing by more than 5% from the mean value were discarded and another scan was carried out (loop 2). Loop 3 was executed in case after the second additional scan the value of the R.S.D. still exceeded 5%. During loop 3 only scan rejection took place.

After 3 (or maximally 5) scans, a standard chromium addition as Cr(VI) was made using the motor burette and the chromium signal was determined as before. Subsequently, the ratio of the peak height of the sample with and without added chromium standard was evaluated to verify whether the standard addition was sufficiently large. More chromium was added if the ratio was below 2, the added amount being estimated from the ratio. This test was carried out once more, and the sensitivity (nA nM⁻¹) was then calculated from the increase in the peak height. Subsequently, the chromium concentration in the sample was calculated from the mean peak height of the sample without standard addition and the sensitivity. The scans were then stored digitally for further data handling and the results of the analysis, together with the standard deviation, were printed. A printed message was given stating that the chromium determination was imprecise in case the R.S.D. had exceeded 5% in any series of scans. The voltammetric cell was then emptied by pump 2 and the next sample was pumped into the cell by pump 1.
The procedure to determine copper complexing ligand concentrations

The concentration of copper complexing ligands was determined onboard ship using CSV with tropolone as the copper binding ligand [18]. The following procedure was used for determining the complexed ligand titrations with copper: sea water (25 ml) to which 0.01 M borate buffer and 0.4 mM tropolone was added was pipetted into PTFE bottles. Copper was added to give an added concentration range between 0 and 20 nM in 10 steps. The sample aliquots were allowed to equilibrate for 8–10 h with the added metal and tropolone. Then the PTFE bottles were placed in the tray of the sample changer (in order of increasing copper addition) and the automated analysis was started. Labile copper concentrations of 2 sample titrations could be measured in a single run, as the tray held 20 bottles.

The sequence of events of the automated determination of labile copper was initiated by pumping a 10-ml sample aliquot into the voltammetric cell. Similar to the chromium determination this aliquot was used for rinsing, whereas a second aliquot was used for the analysis. The voltammetric cell was deaerated for 5 min using \( N_2 \), subsequently 2 mercury drops were discarded and 3 s after the extrusion of the third mercury drop the adsorption period was initiated. Adsorption of the Cu–tropolone complex on the HMDE was carried out for 40 s, whilst stirring the solution with the potential set at \(-0.755 \) V. Then the stirrer was stopped and a quiescence period of 8 s was allowed, followed by the potential scan carried out using the square wave modulation at a frequency of 200 Hz, a modulation amplitude of 25 mV and a step height of 2.4 mV. The scan direction was towards more negative potentials, and the reduction peak corresponding with copper appeared at \(-0.225 \) V. The potential was set briefly (1 s) to \(-0.6 \) V between the accumulation and quiescence period in order to desorb interfering organic compounds.

The computer program performed three repetitive scans and checked the standard deviation of the peak height. A tangent along a plot of the peak height versus the copper concentration in the equilibrated aliquots (see Fig. 6a) was used to determine the sensitivity. Furthermore, a standard addition of copper was made to an aliquot with a high concentration of added copper to corroborate the sensitivity obtained from the tangent, and to verify that the endpoint of the titration had been reached. The initial copper concentration in the sample was measured after UV irradiation of 30 ml of an acidified aliquot of the sample (pH 2.5).

RESULTS AND DISCUSSION

Reproducibility and accuracy of the automated system

The accuracy of the automated electrochemical system was tested by determination of total dissolved nickel in certified sea water [BCR reference Southern North Sea water (CRM 403)] using in-line UV irradiation [19]. Acidified sea water sample aliquots (pH \( \sim 2.5 \)) were pumped at a speed of ca. 0.7 ml min\(^{-1}\) through a silica coil (3 m \( \times \) 0.5 mm i.d.) placed in the aluminium housing (home-built) of an UV irradiation unit (100 W Hanovia high pressure mercury vapour lamp). Mixing of the sea water and nickel reagent (aqueous mixture of 3.2 mM DMG and 0.15 M \( \text{NH}_3 \)) flows at a ratio of 16:1 (sample–reagent) took place beyond the UV lamp to give a final concentration of 0.2 mM DMG and pH 9.0. All other sample transport procedures and program routines used were similar as described for the Cr(VI) determination. Electrochemical procedures used were: adsorption for 60 s at a potential of \(-0.8 \) V; potential scan using square wave at a frequency of 300 Hz, a modulation amplitude of 25 mV, and a step height of 2.4 mV. The scan direction was towards more negative potentials, and the reduction peak corresponding with nickel appeared at \(-1.0 \) V.

A total nickel concentration of 3.90 \( \pm \) 0.03 nM \((n = 4)\) was found in the certified sea water (BCR CRM 403) using the automatic voltammetric system. A concentration of 4.03 \( \pm \) 0.17 nM \((n = 2)\) was found by fully manual determinations of total nickel (i.e. batch-wise UV irradiation and manual sample handling). These concentrations compare
well with the certified nickel concentration in the BCR sea water of 4.23 ± 0.34 nM [20].

Additional experiments were carried out to compare automated and manual determinations of chromium. Sea water aliquots originating from the Menai Straits were analysed in order to verify the precision and reproducibility. An R.S.D. of 3.4% was obtained from a series of 8 automated total dissolved chromium determinations (in different aliquots of the same sample), whereas the standard deviation of 10 manual determinations was 4.7%. The mean concentrations determined by the 2 techniques were in very good agreement (Automated: [Cr] = 20.6 nM (n = 8); Manual: [Cr] = 20.5 nM (n = 10)). Using the automated determination of chromium, the calculated standard deviation of the Cr(III) concentration is ±0.15 nM in the presence of 2.0 nM Cr(VI) and 2.5 nM of total chromium, as the Cr(III) concentration is obtained by difference. Determination by CSV of chromium in sea water in which the metal concentration had been verified by other techniques has previously been shown to produce accurate results [10].

**Determination of Cr(VI)**

The optimum addition of silica particles for removal of Cr(III) was determined using UV irradiated Atlantic Sea water [sampled at station 8 (30°N, 24°W) during the RRS Challenger cruise in 1991]. Cr(III) was added to give a concentration of 1.0 nM, in the presence of 2.00 ± 0.05 nM (n = 10; manual determination) chromium as Cr(VI). According to Fig. 4a, a concentration of 0.4 g l⁻¹ LiChrosorb silica was sufficient for the removal of the added Cr(III). Concentration levels of silica below 0.2 g l⁻¹ did not take out all the added Cr(III), whereas levels over 1.2 g l⁻¹ were found to interfere with the electrochemical Cr(VI) determination.

The reaction time was varied to investigate the kinetics of the removal of Cr(III) by the LiChrosorb silica at a concentration of 0.4 g l⁻¹ in UV treated Atlantic Sea water (see Fig. 4b). The time on the x-axis of Fig. 4b refers to the reaction time between the silica particles and added Cr(III) prior to addition of chromium reagent. Most of the Cr(III) (ca. 80%) was re-

![Fig. 4. (a) Chromium versus added silica particle concentrations for sea water aliquots with 1.0 nM added Cr(III). Initial chromium concentration [Cr(VI)] in UV treated sea water sample, originating from the North Atlantic Ocean, was 2.00 ± 0.05 nM (n = 10). Reaction time of at least 20 min was applied. (b) Chromium concentration in UV treated sea water aliquots plotted against reaction time between 0.4 g l⁻¹ silica particles and 1.0 nM Cr(III). Initial chromium concentration [Cr(VI)] was 2.00 ± 0.05 nM (n = 10). Reaction time is taken from the moment of addition of silica and Cr(III) and addition of chromium reagent.

moved from the solution within a reaction time of 5 min with the silica, but a reaction time >20 min was used to ensure complete removal of Cr(III).

**The speciation of chromium in the Mediterranean**

The automated system was tested by determination of the redox speciation of chromium in the Mediterranean. Figuration of the difference in concentration between Cr(total) and Cr(VI) (after addition of reagent) was measured for Cr(total), Cr(VI), and Cr(III). The Cr(total) was estimated to ∼ 0.07 nM and ∼ 0.07 nM for Cr(total), Cr(VI), and Cr(III).
[Fig. 5. Vertical depth profile of Cr(III), Cr(VI), Cr(total) and salinity for station 10 (36°N, 5°W) in the Mediterranean. Cr(total) was measured after UV treatment of the samples, Cr(VI) after addition of 0.4 g l⁻¹ silica particles prior to a reaction time of minimally 20 min, and Cr(III) as the difference between Cr(total) and Cr(VI). The standard deviations for Cr(total), Cr(VI) and Cr(III) are, respectively, ~0.08 nM, ~0.07 nM and ~0.15 nM.]

Mediterranean, Fig. 5 shows the vertical distribution of the different species of chromium in the water column of the Mediterranean Sea at station 10. The Cr(VI) concentration was found to increase slightly with depth from ~2 nM at the surface to ~2.8 nM below 200 m. The deeper water mass, with its higher salinity, represents the Mediterranean Sea water (salinity between ca. 37–39 p.s.u.). The upper water mass has a lower salinity and originates from the North Atlantic Ocean. The Cr(VI) concentrations determined in the deeper water mass during this EROS 2000 cruise are in very good agreement with other data on the Mediterranean [21]. The Cr(VI) concentrations in the upper part of the profile in Fig. 5 are similar to the concentrations in the North Atlantic Ocean reported elsewhere [17].

The concentration of Cr(III) is much lower than that of Cr(VI). Few data are available on Cr(III) in unpolluted sea water. However, concentrations of Cr(III) similar to those shown in Fig. 5 have been reported for the North Atlantic Ocean [17], the Mediterranean [21] and the Eastern Pacific Ocean [22].

Even though the difference between Cr(VI) and total chromium for individual samples is small (and sometimes within the standard deviation of the analysis), the fact that there is a systematic positive difference between the total dissolved chromium and Cr(VI) concentrations for all the samples indicates that the Cr(III) concentrations found can be treated with confidence.

Natural surface active organic material in the sea water affected the sensitivity of the Cr(VI) determinations, causing the sensitivity to vary between 9 and 13 nA nM⁻¹ in samples from different origin at a constant 30 s adsorption period. This variation in the sensitivity illustrates the necessity to use the standard addition technique for calibration of the CSV sensitivity for each sample.

Copper complexation in the Atlantic Ocean

The result of a typical complexing ligand titration is shown in Fig. 6a.; a plot of the CSV label copper concentration as a function of the total copper concentration in a sample originating from a depth of 100 m in the North Atlantic Ocean. Curvature indicates that not all ligands were saturated by the copper initially present in the sample and that some of the added copper was bound by the complexing matter. The Van den Berg–Ruzic plot [1] is straight (Fig. 6b), indicating that only one competing ligand is predominant in the present conditions, as was the case for all samples determined. Fig. 7 shows a depth profile for station 3 of the copper complexing ligand concentration. The ligand concentration was ca. 7 nM in the surface waters, a maximum of ca. 12 nM was reached at 200 m and the concentration decreased to ca. 5 nM towards greater depth. The higher ligand concentration in the upper water column is probably attributable to metal complexation by soluble exudates of phytoplankton [23] or residues of algal cells damaged by predation. The conditional stability constants of the copper–natural ligand complexes range between 12.0 and 13.0 (log values) at the detection window (log $a_{Cu^{2+}} = 3.29$) used. This means that relatively weak copper binding ligands have been
reproducibility. Accurate delivery of sample by peristaltic pump and metal standard by burette, and furthermore precise timing of the subsequent electrochemical analysis steps greatly increase the reliability of the data obtained. The good reproducibility of the titrations shown in Fig. 6a and b is hard to achieve by manual sample handling. This good reproducibility of the data is necessary for accurate calculation of ligand concentrations and binding constants in the case of complexing ligand titrations. Furthermore, precise determination of Cr(VI) and total dissolved chromium are necessary to calculate Cr(III) from the difference.

The accuracy of metal determinations using the automated system was shown by measurements of total dissolved nickel in certified sea water. The use of in-line UV irradiation for the determination of total nickel further reduced the risk of contamination caused by sample handling.

The described automated system has proved to be reliable in the field. The system has enabled us to measure metal speciation onboard ship. The full stand-alone system is very convenient, with human operators doing only quality scans, cleaning, and engine ventilation. The average number of scans performed per day at 15 depth profiles was obtained (and has improved). On the Atlantic, copper speciation was compared to at most five depth profiles of copper determined by wet chemical copper determination.

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Fig. 6. (a) Complexing capacity titrations: plot of the peak height of the CSV labile copper as a function of the total dissolved copper concentration for a sample from station 3 (48°N, 20°W) in the North Atlantic Ocean. (b) Linear transformation of titration curve data of (a), showing a plot of [CSV labile Cu]/[CuL] as a function of CSV labile copper. CuL is the concentration of Cu(II) complexed by natural organic ligand L.

Fig. 7. Vertical depth profile of the concentration of natural ligands for station 3 (48°N, 20°W) in the North Atlantic Ocean.

...to measure metal speciation automatically onboard ship. The built-in intelligence has assured full stand-alone performance of the system which is very convenient in case of sea sickness of the human operator. The automatic rejections of low quality scans, such as caused by ship movement and engine vibrations, appeared to be very convenient. The automated system increased greatly the number of measurements that could be performed per day. During the Mediterranean cruise 65 depth profiles for chromium speciation were obtained (among other metals) within 10 days. On the Atlantic Ocean, up to 80 aliquots for copper speciation were measured per day, compared to at most 30 manually. This way, 16 depth profiles of copper complexing capacity were determined comprising approximately 1600 labile copper determinations, in a period of 4 weeks.

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