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Sequential flow analysis coupled with ACSV for on-line monitoring of cobalt in the marine environment

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Abstract The development of a compact instrument for on-line measurement of trace metals in seawater is described. The system is based on adsorptive cathodic stripping voltammetry (ACSV), and on the concept of sequential flow analysis, to perform on-line measurements with controlled perturbation of natural equilibria of the element. The design combines a low volume flow cell with a miniature solenoid pump and valves to achieve low power consumption. The flow segmentation is time-controlled and the detection step takes place in a well-defined part of the flow stream where reagent and sample occur mixed. The system was tested on the determination of cobalt in seawater but it is likely that the same technique can be used to determine other metals detectable by CSV. The determination range was 6–1050 pmol/L cobalt with a detection limit (3σ) of 6 pmol/L. The measurement rate was about 60 h^{-1}. Comparative measurements were carried out using continuous flow analysis. The apparatus was used continuously on board a ship to determine the distribution pattern of cobalt in surface waters off the coast of California.

1 Introduction

Cathodic stripping voltammetry can be used to determine low levels of metals in seawater. Recent work has illustrated the advantage of combining electrochemical analysis with flow systems [1, 2]. Coupling this instrumentation with pumped seawater collection on-board of a ship has several advantages as it decreases the risk of contamination, avoids the collection and storage of samples, and provides data in real time. Voltammetric detectors based on mercury plated solid electrodes constructed from platinum, gold or carbon fibres, suffer from drawbacks due to poor reproducibility of the Hg film structure and due to fouling of the electrode surface.

An automated system based on ACSV using a mercury drop electrode was recently developed [3]: it combines continuous flow analysis and a flow cell with a volume of 3.8 μL. The aim of the present work was to integrate the flow cell into a simple and compact system, more suitable for automation and with the ability to run on battery power to allow unattended analysis in the field with a minimum of power use.

Novel components have recently appeared well suited to in-situ analysis. A solenoid micro-pump was recently used successfully for flow analysis in the field [4, 5]. This pump is small, light and has low power requirements. A drawback is that each channel of a manifold would require an individual pump and that the pump acts in one direction only. This deficiency leads us to look for a method different from the continuous flow which requires at least two channels, one for the reagent and the other one for the sample. Other common flow techniques are flow injection analysis (FIA) and sequential injection analysis (SIA). These are not well suited for the present work because they use a 6-way injection valve. This kind of valve is operated by stepper motors which require significant quantities of power. Furthermore, SIA requires the pump to change the flow direction.

The sequential flow analysis (SFA) procedure implemented here requires one, accurate and reproducible, single-channel pump and a three-way valve. The technique involves pumping a stream of sample and injecting a precise volume of reagent (a mixture of ligand and oxidant) before the pump as a discrete slug into the flowing stream. The reagent zone disperses and reacts with the sample, forming a complex with the analyte that is detected by a flow-through voltammetric cell and recorded. The perfor-

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Dedicated to Professor Dr. Günter Henze on the occasion of his 65th birthday

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mance of SFA coupled with ACSV is evaluated here: the method development is described, and the SFA method is compared with continuous flow analysis. Cobalt was selected as the analyte for validation of the sequential flow system, as it occurs at low (picomolar) levels in seawater but can be detected with good sensitivity by catalytic CSV; the high sensitivity is due a catalytic effect of Co(II) on the reduction of the oxidant (nitrate) which is added to a high concentration.

2 Experimental

2.1 Reagents and standards

All solutions were of analytical-reagent grade (AnalaR quality) and water was purified by reverse osmosis (Milli-RO, Millipore) followed by ion-exchange (Milli-Q system). Ammonia and HCl were purified by sub-boiling quartz-distillation.

An aqueous stock solution of 0.1 mol/L nioxime (1,2-cyclohexanedione dioxime) was prepared by dissolving the appropriate amount in 0.25 mol/L sodium hydroxide. A standard solution of 1 mmol/L nioxime was prepared daily by dilution of the stock solution in Milli-Q water. A 4 mol/L ammonium chloride solution, buffered at pH 9.2, was prepared using quartz-distilled ammonia and HCl. Sodium nitrite (5 mol/L $NaNO_2$) was electrolytically purified using a mercury pool electrode and an ESA potentiostat (Model 2014PM), as described before [6]. The reagents were combined, and diluted with MQ, to obtain a final reagent composition of 3.5 mol/L $NaNO_2$, 0.28 mol/L NH_4Cl, and 26 mmol/L nioxime. The cobalt concentration in the reagents was 6 pmol/L. A standard cobalt stock solution of 10^{-4} mol/L was prepared by dilution of Spectrosol standard solution (BDH) and acidified to pH 2. Working standards were prepared daily by dilution of the stock solution.

2.2 Instrument design

The manifold (Fig. 1) consisted of three lines: one for the sample inlet, a second for the reagent inlet and a third for the line to the flow cell where reagents mixed with sample during travel. All dead volumes were minimised as much as possible. The seawater was filtered (using an acid-cleaned, 0.45 μmol/L, cellulose nitrate membrane filter) at the inlet of the manifold to prevent scoring of the valve and pump. To measure UV-digested samples, the sample was passed through an on-line UV-digestion system [7] before the sample inlet. The UV-system consisted of a medium pressure mercury-vapour tube and a silica sample coil in an aluminium housing and cooled by a fan.

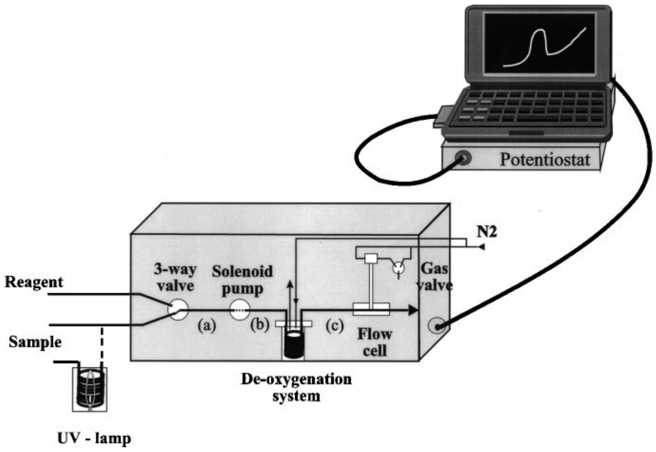


Fig. 1 Flow system for SFA of cobalt with detection by ACSV: (*a*) 10 cm, (*b*) 5 cm and (*c*) 5 cm

Sample flow and reagent flow were alternated using a low power three-way valve (Lee Co., model LFYA2418032H). A solenoid micro-pump (50 μL, Lee Co., model LPLA2410350L) was used to propel the solution through PTFE tubing (0.8 mm i.d.). An on-line de-oxygenating system (Colombo and van den Berg, in preparation) was made of silicone tubing (100 cm length and 0.5 mm i.d.) inserted in a 30 mL vial which was flushed with nitrogen gas at a rate of 50 mL min^{-1}. The flow time from the injection port to the detector was about 25 s.

The detector consisted of a flow cell constructed from extruded acrylic with a 2.5 cm path length and 0.7 mm i.d. [3]. The capillary of the working electrode (Metrohm 6.1246.020) was inserted through the top of the flow cell, perpendicular to the reference and counter electrode. Mercury drops were made by releasing the nitrogen pressure on one side of the Metrohm cartridge using a three way valve (Lee Co., model LFHA2400160H). The reference and counter electrodes were made of wires (1 cm length, 0.5 mm diameter) of silver and platinum, respectively. These electrodes were connected to the potentiostat (μ-Autolab, Eco Chemie, Netherlands) using soldered connections. The completed system was mounted on a polycarbonate box (30 cm length, 15 cm height, from Radio Spares Ltd.). The maximum power consumption of the system (when all the components are switched on) was 3.65 W without the UV-lamp. The actual power use was less as valves and pump used power intermittently. Using UV-digestion increased the power consumption by 100 W which was suitable for use onboard ship or in the laboratory, but not for battery use.

2.3 Hardware and software

The system was controlled by a portable PC-type computer connected to a potentiostat by a dedicated interface card. The proprietary software (EAS1 from Eco Chemie) was modified to allow pump and valve control commands to be sent via the input/output port of the potentiostat. The user can readily define an automated cycle for each experiment to establish operational parameters such as the size of the waste and active mercury drops at the working electrode, precise time control of the pump, injection of reagent into the sample stream, quiescence time prior to a scan and logging and saving data. Solution pumping rate was controlled by varying the frequency of pulses to the solenoid pump (1.0, 1.5 or 2.0 Hz, manually selected); pulses were produced in hardware. Each scan was evaluated and the peak height measured automatically.

2.4 Voltammetric settings

ACSV measurements were performed using square-wave modulation, with a step potential of 3.66 mV and a frequency of 10 Hz. The deposition and equilibration potentials were –0.75 V and

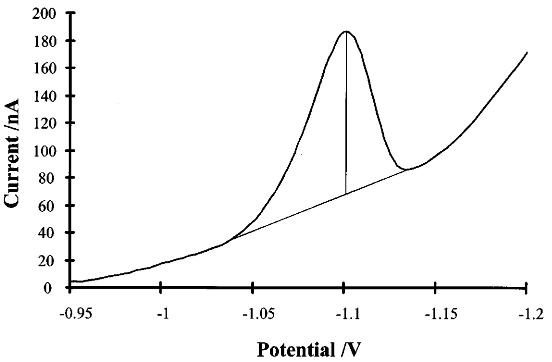


Fig. 2 ACSV scan for 126 pmol/L cobalt in seawater

–0.95 V, respectively. The deposition and equilibration times were typically 15 s and 10 s. A peak corresponding with the reduction of cobalt appeared at –1.1 V (Fig. 2).

3 Results and discussion

3.1 Operating principle

An accurately timed sequential flow procedure was adopted because it has the advantage to require a single-channel pump with a three-way valve instead of the two-channel pump and the six-way valve commonly used in conventional flow-injection analysis equipment [8], which are more expensive and use more power. A similar strategy has been used before [9], and was then termed "controlled-dispersion flow analysis". We decided to base the method on injection of the reagent into the sample flow stream because this approach is well suited to on-line measurements where the sample material is abundant and the reagent supply is limited. In many applications, this "reversed injection" mode is known to increase the sensitivity of the measurement which is an important feature in trace analysis [8]. An added advantage is that the tubing is flushed with sample in between measurements. The reagent volume injected is metered as a function of time and the injection is executed by switching from the sample input to the reagent input and back, programmable via the software.

The system (Fig. 1) comprised a single line manifold, through which the sample was propelled by the pump under conditions of laminar flow through narrow-bore tubing. The timing sequence of the system is presented in Table 1. The valve was normally set to its rest position in the sample line. Injection of the reagent was achieved by switching the valve to the reagent line for 10 s, without stopping the pump, thus aspirating a well-defined volume of reagent. The valve then returned to the sample line and the slug of reagent passed through the pump and onwards along the reactor tubing for a second period of 10 s (termed travel time). As it proceeds along the tubing, the slug begins to disperse into sample and adopts a hollow, bullet-shaped form. The boundary layer of sample mixes rapidly with the slug by diffusion, and the Co-nioxime complexation reaction takes place along the tubing. The mixture was flushed through the in-line de-oxygenating system. A new mercury drop was extruded, and the deposition potential set to –0.75 V. Complex adsorption on the electrode occurred as the mixture passed through the voltammetric detector. The pump was stopped and the potential set to –0.95 V followed by a 10 s equilibration period, whereafter the potential was scanned towards more negative potentials (to –1.20 V). Before the next sequence, the electrode surface was cleaned by releasing a large mercury drop (in three smaller aliquots of standard drop size) which filled the channel bore and which was flushed with the flow stream when the flow was restarted.

3.1.1 Advantages of the solenoid pump. An inescapable aspect of SFA is that the injection occurs before the pump. The pump is therefore a key unit of the system, because the slug has to pass through the pump with minimal dispersion. In this configuration, a peristaltic pump has an important drawback: the use of pump tubing makes it difficult to minimise the dispersion which leads to poor reproducibility of the mixing in the pump tubing. Peristaltic pumps, generally used in typical FIA and SIA systems, have three main drawbacks related to their large size and weight, their relatively high power consumption and the use of pump tubing which may need to be changed daily for some reagents. Solenoid pumps are known to be well-suited to in-situ applications [4, 5]. This type of pump is light and small (average volume 20 mL with a weight of 45 g) and uses considerably less power than a peristaltic pump (about 1/80). It functions by a solenoid-driven piston pressing or releasing a diaphragm that is integrated with a dual check valve. The fluid is then exposed to wetted surfaces of Peek® and Viton® within the pump. The flow rate of the pump is proportional to the frequency of the voltage pulses generated by the microprocessor.

The pump is designed to dispense a 50 µL pulse of fluid per stroke. However, the pump flow rate was found to be influenced by the length and internal diameter of the tubing attached to the pump (Fig. 3). A length of 3 m (0.5 i.d.) tubing in front of the pump did not affect the flow

Table 1 Operating sequence of the sequential flow procedure

Valve position	Pump	Hg Drop	Time (s)	Comments
Sample	on	none	30	fill the manifold
Reagent	on	none	10	inject the reagent
Sample	on	none	10	travel time
Sample	on	one	0.3	measurement drop
Sample	on	one	15	potential set to –0.75 V, deposition time
Sample	off	one	10	potential set to –0.95 V, equilibration time
Sample	off	one	5	potential scan from –1.0 V to –1.2 V
Sample	off	two	0.3	waste Hg drop 1
Sample	off	three	0.3	waste Hg drop 2
Sample	off	four	0.3	waste Hg drop 3 completes mercury flush
Total cycle time			51.2	

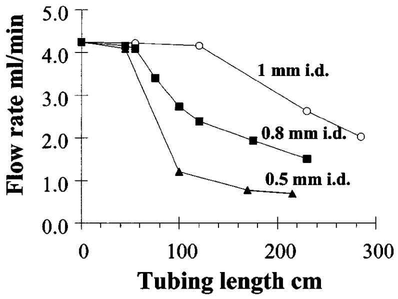


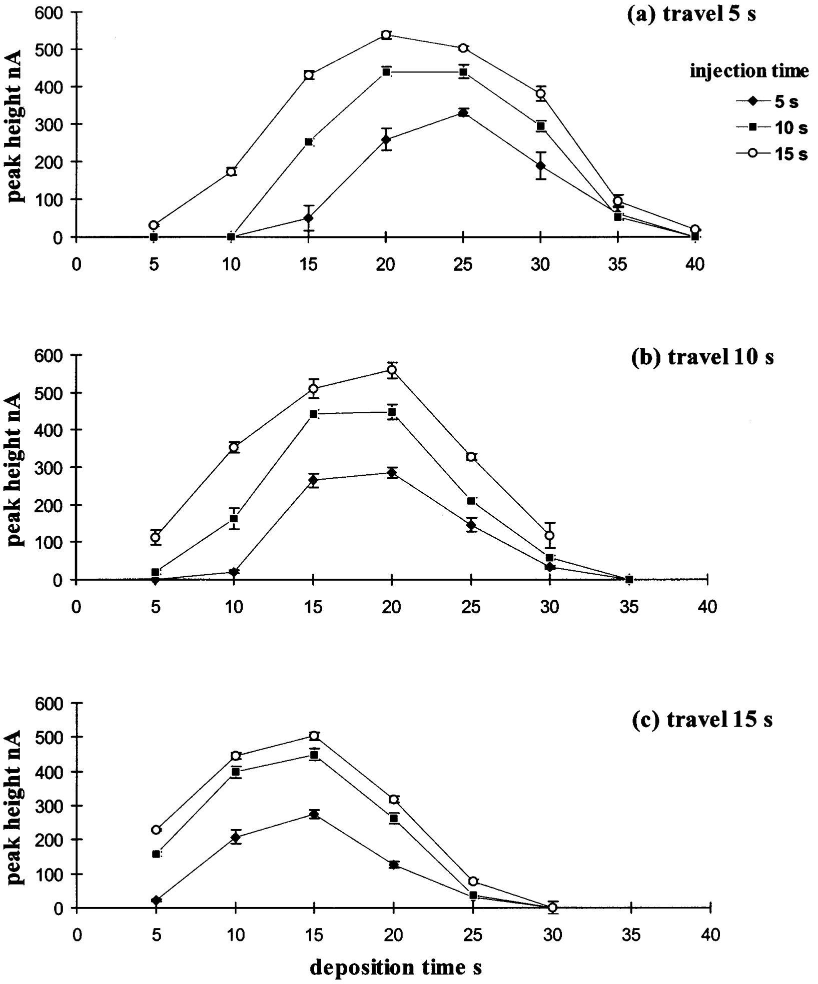
Fig. 3 Influence of the length of the tubing attached to the outlet of the solenoid pump on the pump flow rate. Tested internal diameters: ○ 1 mm, ■ 0.8 mm, and ▲ 0.5 mm, at a pump frequency of 1.5 Hz

rate of the system significantly, but the tubing after the solenoid pump was found to influence the flow rate, especially when it had a narrow-bore: the flow rate obtained with tubing of 45 cm was decreased by 3.3% when the internal diameter was 0.5 mm, and only by 0.45% with an internal diameter of 1 mm. To obtain a flow rate of 0.8 mL min^{-1} with the tubing length and internal diameter used here, a pump frequency of 1.5 Hz (equivalent to one stroke every 0.66 s) was applied.

A functional drawback of these pumps is the pulsating flow generated by each stroke. This could disturb the measurement, which is based on even mixing of sample and reagent, if the reaction is not taken to its end point. This deficiency was not a drawback with detection with ACSV because this relies on an adsorption preconcentration step during which there is an integration of many (usually 27) pump strokes. The pulse wave generated at the detector was not strong enough to dislodge the mercury drop hanging from the capillary.

3.1.2 Deposition time. In the SFA procedure followed here, deposition on the electrode took place when the sample/reagent mixture flowed through the detector. Conventional ACSV of cobalt is characterised by peak heights proportional to the deposition period [6]. Variation of the deposition period at a constant reagent injection time showed that the peak height increased until a deposition time of 20 s whereafter it decreased and approached zero (Fig. 4). The limited dependence of the peak height on the deposition period is due to the reagent/sample mixture being flushed by new sample without reagent, and is an interesting feature of the new SFA method. It is necessary to distinguish between an apparent deposition time (i.e. the period of applying the deposition potential) and an effec-

Fig. 4 Effect of varying the deposition time at fixed travel and injection periods on the peak height for cobalt in seawater. The travel periods were (*a*) 5 s, (*b*) 10 s and (*c*) 15 s, and the injection periods (volumes) of ◆ 5 s (65 μL), ■ 10 s (130 μL) and ○ 15 s (195 μL)



tive deposition time (i.e. the period of actual deposition during the passage of the reagent/sample mixture). The apparent deposition time should be carefully chosen. If the deposition potential is applied before the reagent/sample mixture reaches the flow cell, it is possible that the mercury drop is covered with surface active organic matter from the seawater which can lower the sensitivity. On the other hand, the sensitivity is very low if the scan is undertaken after the reagent/sample mixture has passed through the detector as the catalytic effect occurs only at high ambient levels of nitrite.

The effective deposition time was determined by the time required for the reagent slug to flow from the injection valve to the flow cell, and by the volume of reagent injected. The overall tubing length of the manifold was largely determined by the de-oxygenation system. A minimum silicon tubing length of 1 m was used for optimal de-aeration of the sample (Colombo and van den Berg, in preparation). This, including the tubing linking the pump and the valve (7 cm), led to a transport time of 25 s from the injection port to the detector. This period was long enough to obtain considerable reagent dispersion into the seawater. To allow the reagent/sample mixture to reach the flow cell, a travel time of 10 s was introduced between the end of the injection and the beginning of the deposition step which was marked by extrusion of a new mercury drop. An advantage of this travel time was to minimise errors caused by any impurities in the carrier stream as the mercury drop was absent during this time.

The timing was optimised by comparative tests: using an injection time of 10 s (equivalent to 130 µL reagent) and a travel time of 5 s, the optimal deposition time was 25 s (Fig. 4a); with a travel time of 10 s the optimal deposition time was 20 s (Fig. 4b); and with a travel time of 15 s, it was 15 s (Fig. 4c). Apparently, the reagent/sample mixture had completely passed the electrode after a combined period of 30 s after the end of the reagent pumping period. The sensitivity was increased with the reagent volume injected, causing an increase in peak height, but not proportional to the reagent volume injected (range 65–195 µL). To allow a maximised deposition time with minimised reagent consumption, a compromise injection volume of 130 µL (10 s of injection) was chosen for subsequent experiments.

Table 2 Sensitivity of the measurement with a single and multiple successive reagent injections (the time before the deposition step was fixed at 17 s)

Measurement	Sequence
10 s injection + 7 s travel + 20 s deposition	1610 nA nmol^{-1} L
5 s injection + 5 s travel + 5 s injection + 2 s travel + 20 s deposition	1160 nA nmol^{-1} L
2 s injection + 2 s travel + 2 s injection + 2 s travel + 2 s injection + 2 s travel + 2 s injection + 2 s travel + 2 s injection + 20 s deposition	760 nA nmol^{-1} L

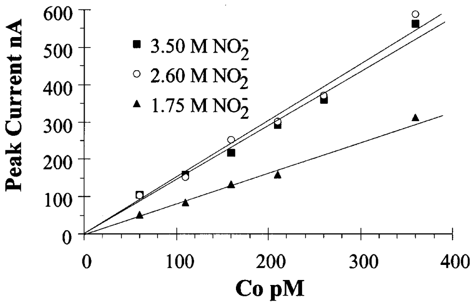


Fig. 5 Influence of the nitrite concentration on the sensitivity of the measurement. The sensitivities were: (■) 1512 ± 101 nA nmol^{-1} L, (○) 1595 ± 108 nA nmol^{-1} L, (▲) 877 ± 47 nA nmol^{-1} L

The characteristics of the concentration gradients formed by several successive injections were evaluated in comparative experiments. With such a procedure, each reagent zone chases a previous one during the flow through the system, successive zones gradually penetrating into each other. The interest in this procedure is that the mixing rate of the reaction should be improved. Unexpectedly, greatest sensitivity was obtained when the reagent was added in a single injection (Table 2). This can be explained by the influence of nitrite on the reaction: the reagent was apparently diluted more when it was injected in several injections than in a single injection, causing the peak height to drop due to the reduced level of nitrite. Separate experiments in which the nitrite concentration was varied showed that the sensitivity of the measurement was reduced with a decrease in the nitrite concentration (Fig. 5).

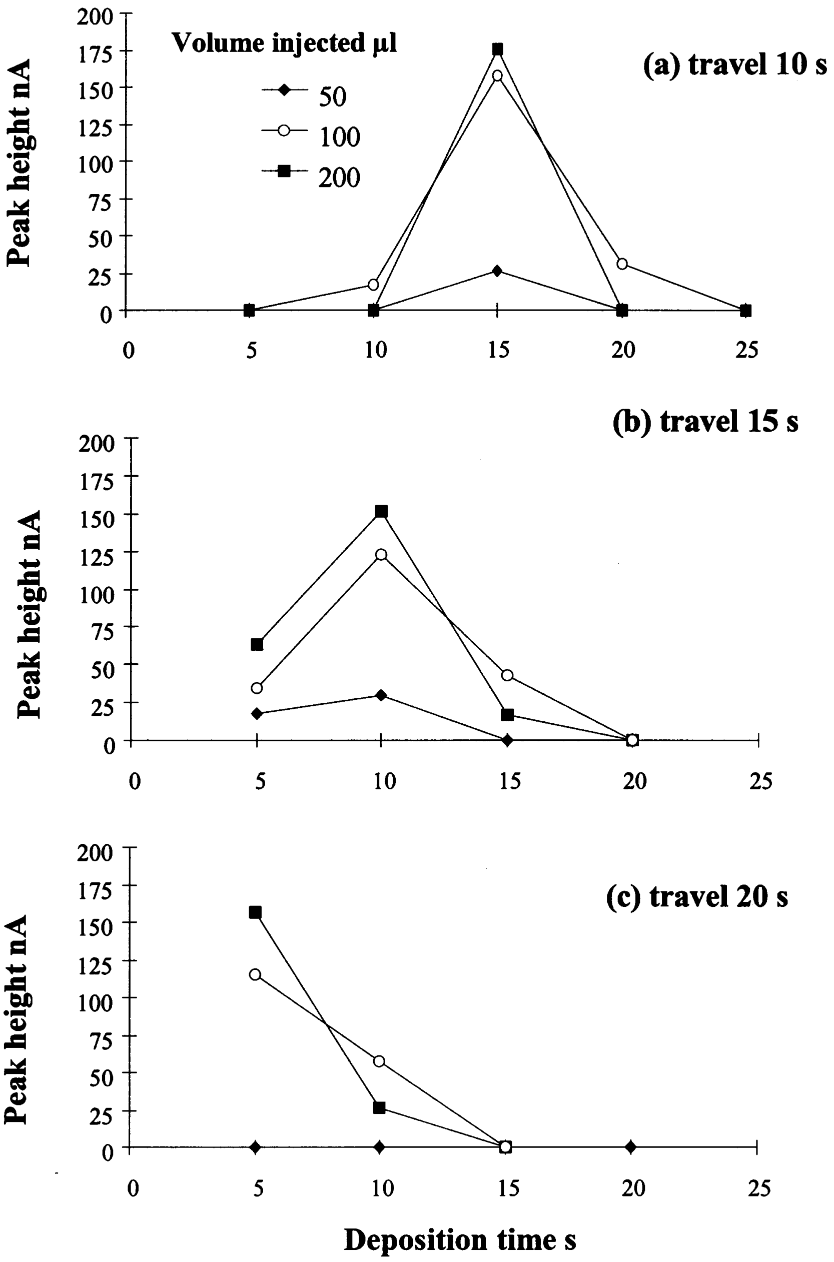
3.2 Characteristics of the system

3.2.1 Linear range, detection limit, reproducibility. The sensitivity was calibrated by pumping seawater to which a cobalt addition had been made in the sample line. A second three-way valve was installed in front of the injection port to allow self-calibration of the system for a field version. The linear range was evaluated by increasing the concentration of cobalt in UV-digested seawater. The peak height was found to increase linearly with the cobalt concentration over a tested concentration range up to 1050 pmol/L, and had a sensitivity of 1519 ± 88 nA nmol^{-1} L. This concentration range is greater than cobalt levels occurring in unpolluted waters, so it is not likely that high cobalt levels will cause non-linearity. The sensitivity was higher than that obtained with the batch system (225 nA nmol^{-1} L for 15 s deposition) [6], which is due to the smaller degree of dilution of the nitrite in SFA.

The cobalt concentration was determined in purified seawater using the optimised conditions to establish the limit of detection of this method. The sensitivity was calibrated by cobalt standard additions to the seawater. The residual cobalt concentration in the purified seawater was 17.5 pmol/L and the detection limit (3σ) was 6.2 pmol/L. The accuracy of the method was verified by replicate analysis of certified seawater (NASS-2, National Research Council Canada). This sample is supplied acidified to pH 1.65 with nitric acid and is certified to contain 68 ± 17 pmol/L Co. Aliquots of this reference material were UV-irradiated and buffered with distilled NH_3 (6.5 mol/L). We found a cobalt concentration of 65 ± 5 pmol/L (n = 15) which is in good agreement with the certified value. Repeated voltammograms (n = 49) for 126 pmol/L cobalt in seawater produced a relative standard deviation of 3.9% demonstrating the high reproducibility of the system.

3.2.2 Interferences. Nioxime has high selectivity for Co and Ni [6]. Because the peak potentials are well separated by ~0.2 V, the peak of nickel at –0.9 V does not interfere with that of cobalt at normal seawater concentrations. Interference by high levels of nickel can be eliminated by selecting a lower deposition potential (–1.0 V). This step also eliminates the reduction peak of free nioxime. The effect of other metals is negligible [6]. Interference by surface active organic matter in seawater, causing competitive adsorption on the electrode surface and lowering the sensitivity of ACSV, is eliminated by UV-digestion of the seawater. Its effect was not further investigated here as it presumably is similar to that in the conventional, batch method for cobalt where it was shown to reduce the sensitivity by 12% in seawater from the Atlantic without UV-digestion [6].

Fig. 6 Flow system based on the FIA procedure. Effect of varying the deposition on the peak current, using a travel time of (*a*) 10 s, (*b*) 15 s, (*c*) 20 s. This test was performed for three different volumes of the injection loop: ◆ 50 µL, ○ 100 µL, ■ 200 µL



3.2.3 Comparison of sequential flow analysis with different flow analysis configurations. The SFA procedure was compared with more established flow techniques such as continuous flow and flow injection analysis (FIA), all in turn connected to the same voltammetric flow cell detector. The FIA system consisted of a peristaltic pump (Ismatec, model CA-4E/8/24) and a 6-way injection valve (Rheodyne, model 5020). The sample flow rate was the same as that for the SFA system (0.8 mL/min) and the reagent flow rate was 0.14 mL/min. The manifold after the injection valve was the same as that used with the SFA experiments. Three different loop lengths of 50 μL, 100 μL and 200 μL were used. The operational sequence consisted of injection of the reagent volume by rotation of the injection valve, pumping of the seawater/reagent to the flow cell, formation of a new mercury drop, deposition of cobalt complexes, and stopping of the pump, followed by a potential scan. The injection valve was then returned to the load position and a waste drop was formed prior to the next measurement.

The results obtained with the FIA configuration were quite similar to the SFA data (Fig. 6). At varying travel and deposition times, maximum peak height was observed for a combined time of 25 s. A characteristic of the FIA system was that the maximum peak height measured was lower than with the SFA, and that the length of the reagent/sample mixture was less important. This indicated that the solenoid pump induced some dispersion of the reagent/seawater mixture. An advantage of the dispersion was that it led to a better mixing of the reagent slug which increased the sensitivity of the measurement (800 nA nmol^{-1} L for FIA compared to 1500 nA/nM for SFA). An extended mixing zone was required in the FIA manifold to reach the sensitivity obtained with the SFA system.

In the continuous flow mode, the injection valve used for the FIA injection was replaced by a T-junction, and the reagent was pumped continuously into the sample flow stream. There were no injection and travel steps as the seawater/reagent mixture arrived continuously at the detector, and the sequence of the measurement consisted of successive deposition and measurement steps [3]. The results were similar to those obtained by SFA when the same reagent volume was injected in several steps. A dilution of the reagent occurred which led to a decrease in the sensitivity (300 nA nmol^{-1} L) due to a lower nitrite concentration around the mercury drop during the scan.

An important drawback caused by the reagent-introduction procedure in continuous flow analysis is the possibility of cross-contamination between successive samples. Thus, if measurement of discrete samples is needed with the continuous flow technique, it is necessary to flush the system between successive samples to remove cross-contamination. An added advantage of the SFA procedure is that the manifold tubing is flushed by seawater between measurements as part of the normal procedure.

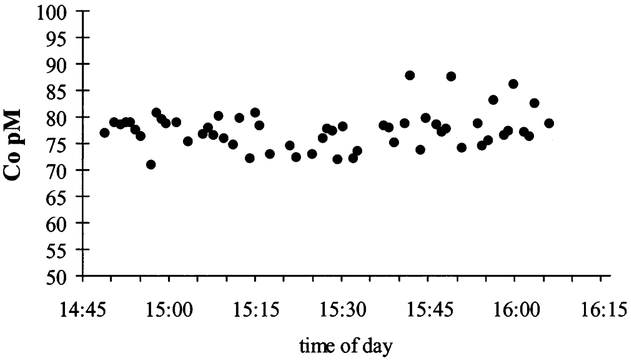


Fig. 7 Ship-board determination of labile cobalt in surface waters of the eastern North Pacific, July 1996

3.3 Field application

The suitability of the sequential flow analyser to shipboard analysis was evaluated during a cruise in the North East Pacific in July 1996. The analyser was used to determine labile cobalt. Surface seawater was continuously pumped on-board ship, and the seawater for the on-line system was sub-sampled before the main flow entered the pump. A small part of the data acquired is shown in Fig. 7: the labile cobalt concentration varied between 75 and 80 pmol/L in these data. This concentration is in reasonable agreement with other data for cobalt in surface seawater determined using conventional techniques [10, 11]. The sensitivity was calibrated at 6 h intervals, and was found to remain stable over a period of several days. The results clearly showed the main advantages of using SFA coupled with ACSV for analysis of trace metals in seawater: sample handling and contamination were minimised, and a rapid and precise determination of parameters important to calculate trace metal speciation (labile and total metal concentrations) was obtained. A very high data frequency (60 h^{-1}) allows a precise mapping of the distribution of metals in waters with a high variability in metal concentrations such as estuarine and coastal waters.

4 Conclusions

Sequential flow analysis was coupled successfully with ACSV for the detection of metals in natural waters. Advantages over conventional batch-wise analyses are automation of reagent additions, and the requirement of only small sample volumes (0.45 mL per measurement). A very high data frequency of 60 samples per hour was obtained in the monitoring mode. Comparison showed that the sequential flow method was more sensitive than either batch-wise or continuous flow measurements, but a drawback was that the effective deposition time could not be extended beyond 20 s without including additional mixing reservoirs. Nevertheless, very low cobalt levels (6 pmol/L) could be determined with this short deposition time. The method will be extended to other metals in further work.

A low power consumption (3.5 W during peak use, at 24 V) of the main components (micro-pump and valve) of the system (excluding the microcomputer and the potentiostat which have separate battery power) means that the system is suitable to run on batteries.

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