In-line deoxygenation for flow analysis with voltammetric detection

Carlo Colombo[1], Constant M.G. van den Berg[*]

Oceanography Laboratories, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

Abstract

Voltammetric detection of metals in natural waters suffers from interference by dissolved oxygen. We describe here a deoxygenation method suitable for flow analysis with detection by cathodic stripping voltammetry (FIA-CSV). The apparatus is based on the permeation of oxygen through semi-permeable tubing (silicone, Poreflon and others) into an oxygen-free chamber. Two methods of oxygen removal are proposed: in the first oxygen is removed physically from the chamber by flushing with nitrogen at a rate of 50 ml min^{-1}; in the second oxygen is removed chemically by filling the chamber with an aqueous solution of a reducing agent (Na_2SO_3 or other compounds). At a fixed sample flow rate of 1 ml min^{-1}, the length of the tubing is the main parameter which affects the deoxygenation efficiency, as it determines the residence time of the sample. 98% oxygen removal is achieved using 3 m tubing (36 s residence time). A removal of 90% of oxygen (1 m tubing and 12 s residence time) is sufficient to obtain a background current similar to conventional (batch) voltammetric systems and reproducible metal (copper and cobalt) peak heights are obtained at low metal concentrations. This enables the determination of trace metals by flow analysis with voltammetric detection at concentration levels encountered in uncontaminated seawater. © 1998 Elsevier Science B.V. All rights reserved.
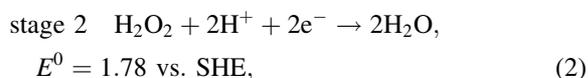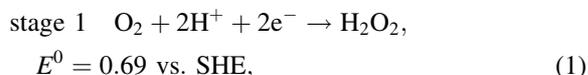
1. Introduction

Trace metals in natural waters are determined to understand their biogeochemistry. This can be carried out in the field by flow analysis using detection by cathodic stripping voltammetry (CSV) [1,2] or anodic stripping 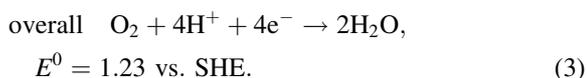voltammetry. Prior to the voltammetric detection oxygen has to be removed as it interferes. Oxygen is present in air-saturated aqueous solution at a concentration of about 0.3 mM [3,4]. Dissolved oxygen is reduced in two steps at potentials more negative than 0 V [5].

The standard reduction potentials of interest are, in acidic media

stage 1 $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$,
$$E^0 = 0.69 \text{ vs. SHE}, \tag{1}$$

stage 2 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$,
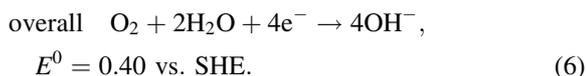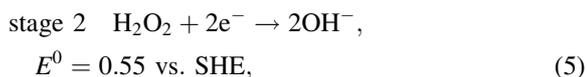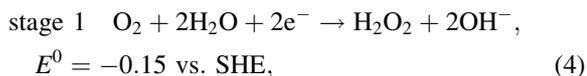$$E^0 = 1.78 \text{ vs. SHE}, \tag{2}$$

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*Corresponding author. Tel.: +44-151-794-4090; fax: +44-151-794-4099.

[1]Present address: Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland.

overall $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$,

$\quad E^0 = 1.23$ vs. SHE. $\hfill (3)$

In neutral or basic media

stage 1 $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$,

$\quad E^0 = -0.15$ vs. SHE, $\hfill (4)$

stage 2 $H_2O_2 + 2e^- \rightarrow 2OH^-$,

$\quad E^0 = 0.55$ vs. SHE, $\hfill (5)$

overall $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$,

$\quad E^0 = 0.40$ vs. SHE. $\hfill (6)$

With increasing pH the waves due to oxygen are shifted to more negative potentials; in practice at the mercury electrode the reduction of oxygen to OH^- is electrochemically poorly reversible, and proceeds in two steps occurring at $E_{1/2}=0$ V and $E_{1/2}=-0.9$ V at neutral pH values due to the shifts in the equilibria and the electrochemical irreversibility of the reduction steps. The oxygen reduction generates a large background current, greater than that of the trace metals, and dissolved oxygen therefore tends to interfere with voltammetric analysis. In a conventional (batch) voltammetric cell oxygen is removed by purging with an inert gas (usually nitrogen) for ∼5 min prior to analysis. This procedure is time consuming and not suitable for flow analysis.

In flow analysis with detection by CSV (FIA-CSV) it is necessary to deoxygenate the sample stream before it reaches the electrode. Equipment for continuous deaeration and deoxygenation exists since the 1950s [6]. During the past 20 years, chemical, electrolytic, photochemical and physical methods have been proposed for oxygen removal in flow systems. Chemical methods are based on the reduction of dissolved oxygen by adding a reducing agent to the solution (e.g. sulphite for alkaline solutions) [7], or immobilised in a reactor (e.g. zinc containing oxygen-scrubber column) [8]. These methods are not suitable for trace metal analysis since they may introduce contamination and interferences in the voltammetric analysis. Electrolytic methods have also been proposed for deoxygenation [9], but they are not suitable for metal determinations since the metals themselves will be removed when a negative potential is applied. More recently, photochemical processing based on the

reaction of oxygen with organic acids, such as citric, formic and oxalic acids under UV irradiation have been used [10]. Although the application of these methods coupled with the breakdown of dissolved organic matter by UV irradiation [11] could be of interest in the on-line determination of trace metals, the likelihood of contamination due to the high (1 M) concentration of acid added, and the difficulty of pH neutralisation prior to analysis by CSV, are unacceptable for the analysis of natural waters containing trace metals at nM levels.

Oxygen removal using diffusion through a semi-permeable membrane would be suitable for flow analysis. On-line deoxygenation methods include pumping the sample along a semi-permeable membrane [12], a chromatomembrane [13], or silicone [14] or Poreflon [15] tubing, surrounded by inert gas at reduced pressure. These methods are well suited for application in a laboratory, and can be adapted to be used in field or in-situ measurements where simple and compact instrumentation is necessary.

This paper describes the use of a gas permeation unit for the on-line deoxygenation of water prior to FIA-CSV of trace metals (cobalt and copper) in natural waters. Copper and cobalt were chosen to evaluate this method, since their peak potentials are near those of oxygen. Tests using tubing of several materials (silicone, Poreflon, polyvinylchloride (PVC), polythene and Teflon) and of different lengths and diameters are carried out showing that silicone and Poreflon tubing are most effective in the oxygen removal. Shipboard determination of cobalt at a frequency of 60 samples per hour was achieved using silicone tubing and nitrogen as deoxygenator medium [1]. The possibility of minimising gas use by coupling the permeation with chemical scavenging solutions (sodium sulphite (Na_2SO_3), ascorbic acid ($C_6H_8O_6$), sodium borohydride ($NaBH_4$) and manganese hydroxide ($Mn(OH)_2$) is also investigated.

2. Instrumentation and reagents

2.1. Equipment

A standard voltammetric system was used for preliminary, batch, experiments, consisting of an Autolab voltammeter (Eco Chemie), connected to a HMDE

Table 1
Type of tubing used during the experiments

Tubing	i.d. (mm)	o.d. (mm)	Wall thickness (mm)	i.v. (ml) (1 m tubing)	Permeability[a]	Supplier	Part no.
PVC	0.5	1.0	0.25	0.2	0.13–36	Altec	01-94-1598
Polythene	0.5	1.0	0.25	0.2	–	Fisher	800/100/160/100
Teflon	0.5	1.0	0.25	0.2	–	Cole Parmer	6417-21-24 TW
Silicone	0.5	1.0	0.25	0.2	7961	Altec	01-94-1403
Silicone	0.5	1.5	0.5	0.2	7961	Altec	01-94-1450
Silicone	1.0	2.0	0.5	0.8	7961	Altec	01-94-1407
Silicone	2.0	3.0	0.5	3.1	7961	Altec	01-94-1456
Poreflon	1.0	2.0	0.5	0.8	–	Sumitomo	

Internal diameter (i.d.), outer diameter (o.d.), and internal volumes (i.v.) are shown together with wall thickness and permeability data (when available).

[a]Permeability: $\dfrac{cc \times mm}{cm^2 \times s \times cmHg} \times 10^{-10}$[19].

(hanging mercury drop electrode, Metrohm 663 VA, drop surface area=0.38 mm^2). The voltammetric cell was made of glass and solutions in the cell were stirred using a rotating PTFE rod (Metrohm electrode). Potentials are given with respect to a double junction, Ag/AgCl reference electrode (saturated AgCl in 3 M KCl), with the salt bridge filled with 3 M KCl, and with a graphite rod as a counter electrode. The system was controlled by an IBM-compatible personal computer, using a compiled Basic program (GPES32 from Eco Chemie).

The flow-cell and instrumental set-up used for the in-line voltammetric system is described in detail elsewhere [1]. It consisted of an Autolab voltammeter (Eco Chemie) connected via a home-built interface to a peristaltic pump (Gilson 3), two valves and a cartridge of the HMDE (Metrohm), and was controlled by an IBM-compatible personal computer, using a modified compiled Basic program (EAS from Eco Chemie).

2.2. Deoxygenation chamber

Tubing was coiled ($\sim$2 cm diameter) around a cylindrical home-made support (length $\sim$5 cm) and inserted in a 30 ml vial (polystyrene, from Sterilin). When coiling was impracticable due to long length or wide outer diameter (o.d.) of the tubing, the tubing was simply "stuffed" in the deoxygenating chamber. No differences were observed in the deoxygenation efficiency due to this. The Sterilin had four holes drilled in the cap, two for the inlet and outlet of the

silicone FIA tubing, and two (short lengths of Teflon tubing) for the nitrogen gas inlet and outlet. When different tubing materials were compared solutions were pumped at a rate of 1 ml min^{-1} through the tubing, and the nitrogen flow was maintained at about 50 ml min^{-1} using a home-made flow-limiter. The gas flow limiter consisted of a silica needle for chromatographic syringes (11 mm length, 0.23 mm o.d.) placed inside two pipette tips for reinforcement, and inserted in the gas line; a short length (5 cm) of Teflon tubing of 0.1 mm i.d. can be used with similar effect.

2.3. Deoxygenating tubing

Types of tubing used are listed in Table 1 along with inner (i.d.) and outer (o.d.) diameters, wall thickness, internal volumes for 1 m length and permeability data (when available). Several lengths (0.1, 0.5, 1.0, 2.0, 3.0, and 5.0 m) of silicone tubing (i.d. 0.5 mm, o.d. 1.0 mm) and several lengths (0.5, 1.0, 2.0, and 2.5 m) of microporous Teflon tubing (i.d. 1.0 mm, o.d. 2.0 mm) (Poreflon TB21, kindly provided by Sumitomo, UK Plc, London EC 4V 3BJ) were used to compare the effect of the tubing length on the deoxygenation efficiency.

2.4. Experimental parameters and reagents for on-line metal determinations and for chemical deoxygenation

Reagents and voltammetric parameters used in the determination of copper and cobalt are listed in

Table 2
Voltammetric and FIA parameters used in the determination of copper and cobalt

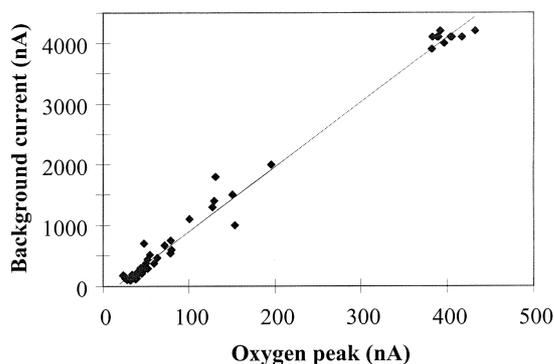| Metal	Copper	Cobalt
pH buffer	HEPES	NH$_3$/NH$_4$Cl
Buffer concentration (mM)	10	25
Complexing ligand (μM)	10 μM oxine	4.5 μM nioxime
Oxidant (catalytic CSV)	–	0.45 M NaNO$_2$
Wave modulation	Square-wave	Square-wave
Frequency (Hz)	200	10
Modulation amplitude (V)	0.025	0.025
Step potential (mV)	3.66	3.66
Deposition time (s)	40	30
Deposition potential (V)	−1.0	−0.75
Equilibration time (s)	10	10
Equilibration potential (V)	−0.25	−0.85
Initial potential (V)	−0.25	−0.85
Final potential (V)	−1.0	−1.25
Sample flow rate (ml min^{-1})	1.0	1.0
Reagents flow rate (ml min^{-1})	0.15	0.15
Total flow rate (ml min^{-1})	1.15	1.15

Fig. 1. Relation between the background current during deposition and the height of the oxygen peak (r^2=0.995, n=60).

could therefore be used as a convenient indicator for the interference of oxygen with metal determinations and its removal by on-line permeation.

Table 2. The background current was monitored by chronoamperometry at −0.8 V using a sampling frequency of 2 Hz.

Several sodium sulphite (Na$_2$SO$_3$) concentrations (0.01, 0.1, 0.25, 0.5, 0.75, 1, and 2 M), 0.01 M ascorbic acid (C$_6$H$_8$O$_6$), 0.01 M sodium borohydride (NaBH$_4$) and 0.015 M manganese hydroxide (Mn(OH)$_2$) were used to study the effect of chemical deoxygenation. The 0.015 M Mn(OH)$_2$ solution was prepared by dilution of 0.2 ml of 2 M MnSO$_4$ with 25 ml of 10 M sodium hydroxide (NaOH), whilst the other solutions were prepared in MilliQ.

3. Results and discussion

Measurements of the background current during deposition whilst pumping the water-reagent mixture through 1 m silicone tubing in a nitrogen flushed container (residence time 12 s) showed that the background current at −0.8 V dropped from 2.5 mA to less than 500 nA, indicating that oxygen was removed. Preliminary experiments showed that the background current in the presence of oxygen during the deposition step at −0.8 V was directly related to the oxygen peak height (Fig. 1). Amperometric detection of the diffusion current (i–t curves) of oxygen at −0.8 V

3.1. Tests using chronoamperometry

Current–time (i–t) curves are produced by the diffusion of reducible and oxidisable substances to the electrode [16]. Diffusion at a large spherical electrode like the HMDE is planar and the equation for the instantaneous current consists of two terms, one constant and one time-dependent:

$$I_t = 4\pi r n FDC_b + \frac{nFAD^{1/2}C_b}{\pi^{1/2}t^{1/2}}, \qquad (7)$$

where i_t is the instantaneous current, r the radius of the electrode formed by the area surrounding the electrode depleted the diffusing species, n the number of electrons exchanged between the species and the electrode, D the diffusion coefficient, C_b the concentration of the bulk solution, A the surface area of the electrode in cm^2, and t the time of electrolysis in seconds.

Using long periods (>10 s) of electrolysis from stationary solutions the second term diminishes and the current approaches a constant value at which comparison of deoxygenation efficiency can be carried out. The diffusion layer thickness is much reduced in flow conditions, and mass transport is therefore kept high and constant by maintaining the second term large and constant.
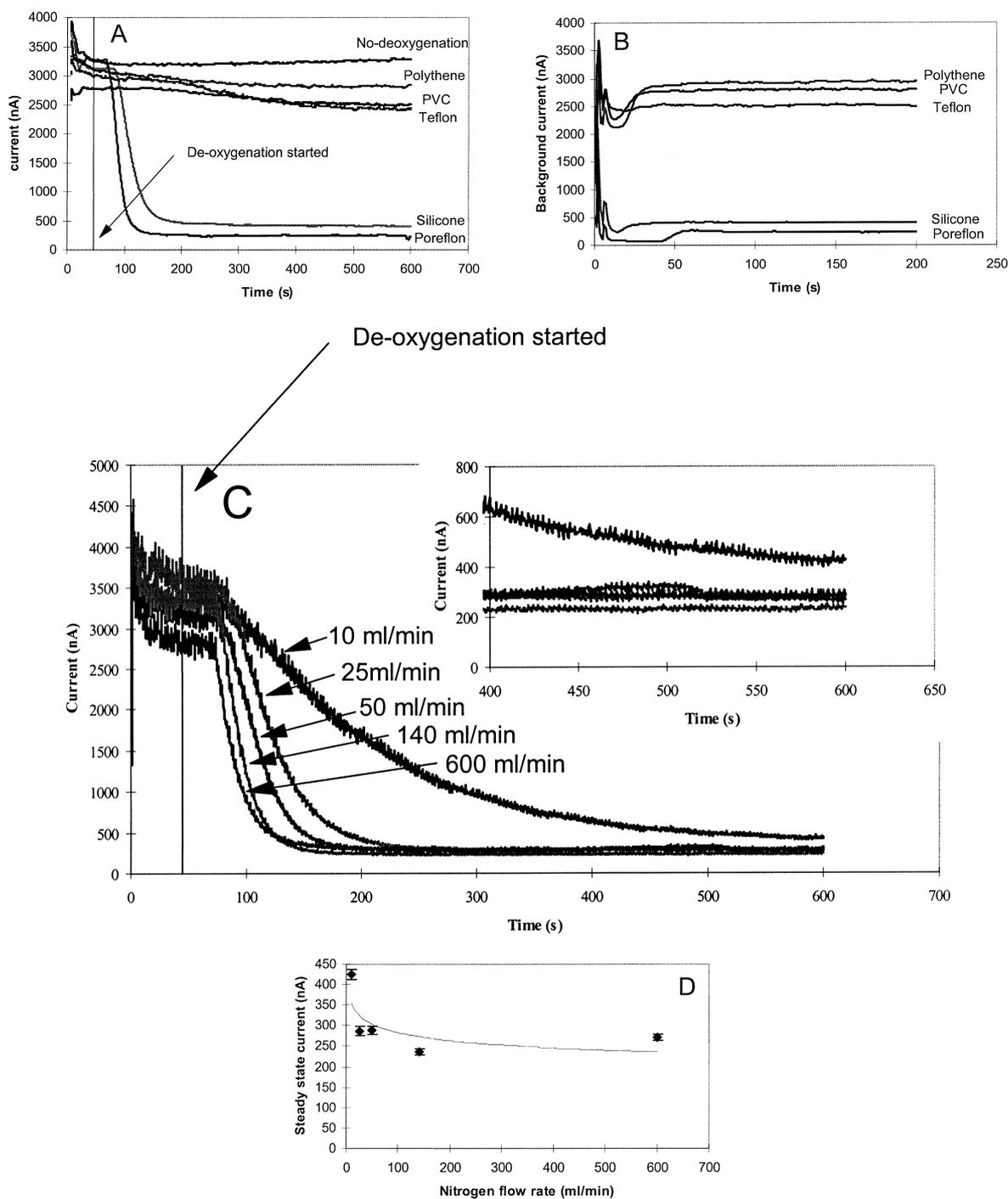
Fig. 2. Effect of deoxygenation on the background current as detected by chronoamperometry: (A) Comparison of the deoxygenation efficiency of various tubing inserted in the deoxygenating reservoir; (B) as (A) but starting from a deoxygenated reservoir; (C) effect of the nitrogen flow rate on the time required to reach steady state oxygen removal; (D) effect of increasing the nitrogen flow rate on the steady state oxygen concentration using silicone tubing (0.5 mm i.d., 1 mm o.d.).
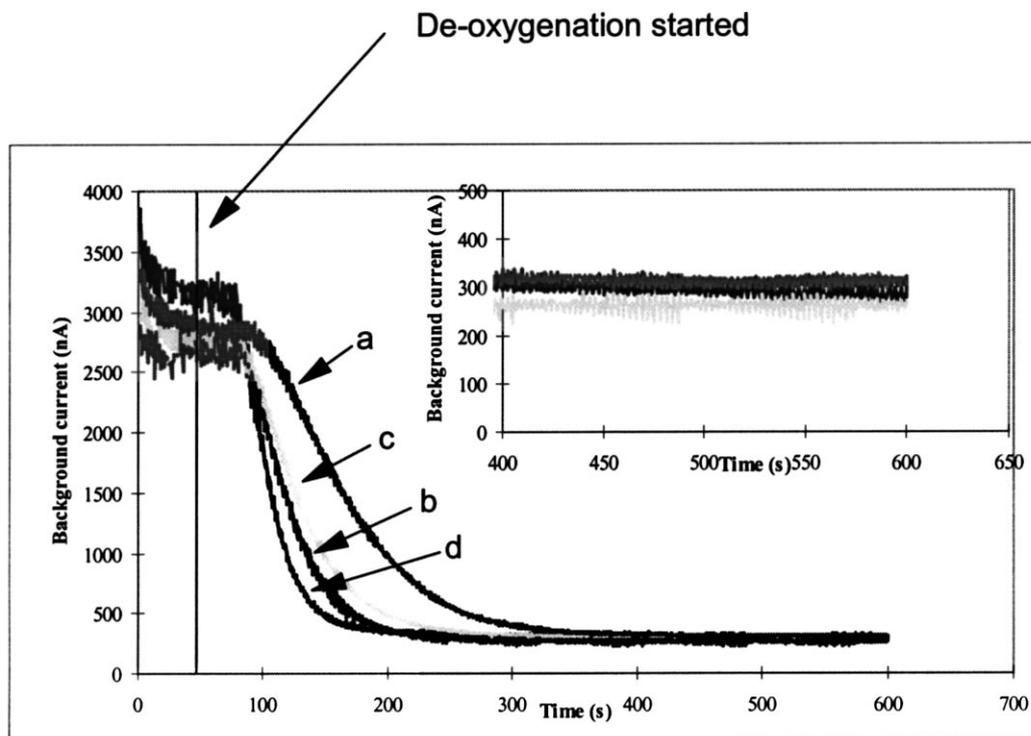
Fig. 3. The chronoamperometric response showing the time required to achieve a steady state in the removal of dissolved oxygen from water after switching on the gas flow. Different diameters of silicone tubing are compared: (A) 2.0 mm i.d. and 3.0 mm o.d.; (B) 1.0 mm i.d. and 2.0 mm o.d.; (C) 0.5 mm i.d. and 1.5 mm o.d.; and (D) 0.5 mm i.d. and 1.0 mm o.d.

3.1.1. Comparison of tubing and effect of varying the nitrogen flow rate

Several experiments were carried out to optimise the deoxygenating conditions for the determination of copper and cobalt. Water was pumped through semi-permeable tubing and the background current was monitored by amperometry. Two types of tests were carried out to compare the various tubing: in the first the deoxygenation was started ∼60 s after starting of the pump (indicated by an S in Fig. 3); in the second the chamber was continuously flushed with nitrogen prior to the start of the pump.

Starting from high background currents (water saturated with air) the current dropped rapidly when the flushing was initiated. The oxygen level in the pumped solution (1 ml min^{-1}) levelled off 2 min after initiation of the purging (the residence time in this experiment was 12 s) (Fig. 2(A)). Starting from a deoxygenated reservoir, the background current of

the pumped solution first dropped for a period of 12 s (silicone) or 48 s (Poreflon) related to the residence time of the equilibrated water out of the deoxygenator, and then rose slightly to a constant level (Fig. 2(B)).

Several types of tubing, made of different materials, were compared. The comparative experiments showed that best deoxygenation was achieved using silicone and Poreflon tubing (Fig. 3(A) and (B)), whilst much poorer deoxygenation was achieved using PVC, Teflon and polythene, presumably due to poor oxygen permeability of these materials. The lowest residual oxygen levels were obtained using Poreflon but some of its greater efficiency could be due to the greater internal diameter (1 mm for Poreflon, 0.5 mm for silicone) of the Poreflon tubing, and therefore a longer residence time in the deoxygenating chamber.

Variation of nitrogen flow rate in the deoxygenating chamber (Fig. 3(C) and (D)) showed that the oxygen

removal efficiency was directly related to the nitrogen flow rate (Fig. 2(C)) at flow rates up to 50 ml min^{-1}; the efficiency was not improved significantly at greater flow rates. However, the gas flow rate influenced the time necessary to reach a constant level of deoxygenation (Fig. 2(D)): the apparatus required a purging time of 600 s (10 min) to become operational at the slowest flow rate (10 ml min^{-1}), whereas it required only 180 s (3 min) at a flow rate of 50 ml min^{-1}. The residual background current was ~450 nA using 10 ml min^{-1}, and it dropped to 280 nA at 25 ml min^{-1}. There was little improvement in the performance of the deoxygenation at flow rates >50 ml min^{-1}, so this was selected for further work.

3.1.2. Effect of varying the residence time in the deoxygenator

The amperometric detection of the in-line flushing solution showed the importance of the residence time of the solution in the container before reaching the electrode. The residence time is a function of the internal volume of the tubing and of the flow rate of the solution in the tubing. The residence time of the solutions in the deoxygenator can be varied by using tubing of several internal diameters (Table 1) or different length. The deoxygenation efficiency could also be affected by changes in permeability due to variations in the tubing wall thickness. For this reason we compared tubing with the same wall thickness but with different internal diameters to vary the residence time. Tests on silicone tubing (Fig. 3 and Table 3) with various i.d. and o.d. showed no significant difference in the steady state back-

ground current: the steady state background current was 335 nA (i.d. 0.5 mm, o.d. 1.5 mm), 285 nA (i.d. 1.0 mm, o.d. 2.0 mm), and 305 nA (i.d. 2.0 mm, o.d. 3.0 mm) (Table 3). This indicates that the oxygen permeation was independent from the i.d. of the tubing at a solution flow rate of 1 ml min^{-1}. The efficiency of oxygen removal decreased when tubing with a greater wall thickness was used: the steady state background current increased from 285 nA (i.d. 0.5 mm, o.d. 1.0 mm) to 335 nA (i.d. 0.5 mm, o.d. 1.5 mm) (Table 3). However, the i.d., which controls the residence time of the solution in the tubing has an influence on the time necessary to reach a constant value of the background current and therefore a stable level of oxygen removal (Fig. 3). A stable level was obtained in a shorter period of time (ca. 2 min) using the silicone tubing with the smallest i.d. and o.d. The time necessary to reach a stable background current using tubing with a thicker wall was similar to that using a wider bore Fig. 3. This can be explained by the increased residence time of the solution in the deoxygenating chamber, which compensated for the increased wall thickness.

Variation of the length of the silicone tubing (10, 50, 1, 2, 3, and 5 m) showed that the deoxygenation efficiency improved with increasing tubing length up to a length of 3 m (residence time 48 s) (Fig. 4(A)). The steady state background current dropped to 60 nA at tubing length of 3 and 5 m, whereas it was 80 nA using 2 m, 270 nA using 1 m, 1500 nA using 0.5 m, and 2500 nA using 0.1 m silicone tubing. A tube length of 1 m (residence time 12 s) was sufficient for the voltammetric measurements.

Tests on different Poreflon tubing lengths (50, 1, 2, and 2.5 m) showed a variation in the deoxygenation efficiency similar to that of the silicone tubing. It is evident that the deoxygenation was almost complete (Fig. 4(B)) using 2.5 m.

The effect of varying the solution flow rate (0.25, 0.5, 1, and 2 ml min^{-1}) was also tested (the mercury drop was dislodged by higher flow rates). The background current (oxygen level) increased when the flow rate was increased from 1 to 2 ml min^{-1} due to the shorter residence time of the water in the deoxygenator; similarly the background current decreased when the pumping rate was decreased from 1 to 0.25 ml min^{-1} (Fig. 4(C)).

Table 3
Effect of the i.d. and o.d. of silicone tubing on the steady state background current

i.d. (mm)	o.d. (mm)	Steady state current (nA)	SD (%)
0.5	1.0	286	3.9
0.5	1.5	310	2.0
1.0	2.0	262	2.9
2.0	3.0	314	2.1

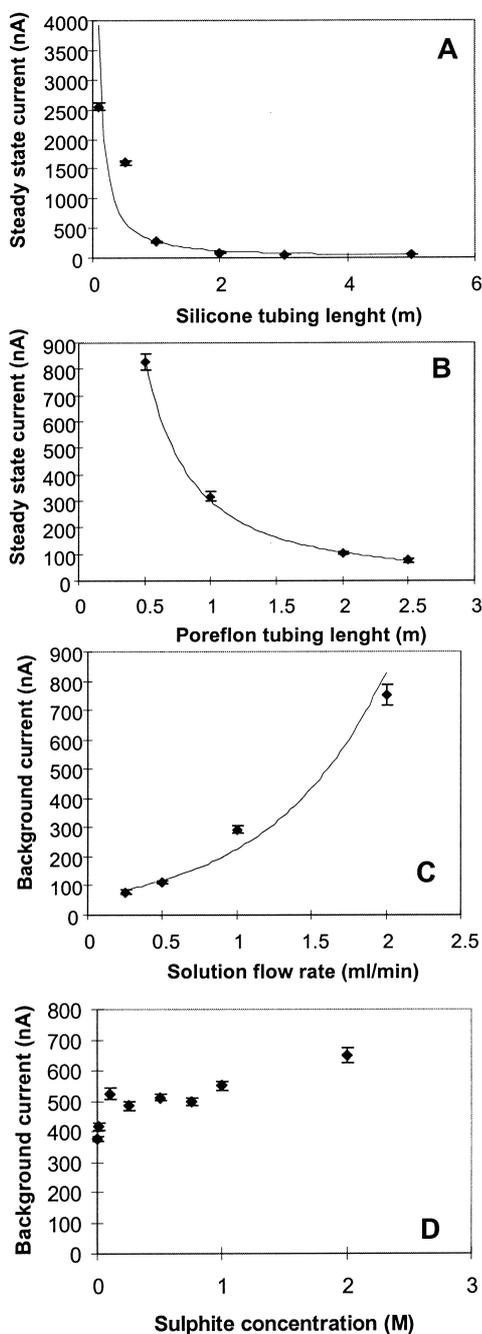SD % is the standard deviation of the final 20 s of the steady state current.

Fig. 4. Effects of varying deoxygenation parameters on the steady state oxygen concentration: (A) Effect of varying the silicone tubing length; (B) effect of varying the Poreflon tubing length; (C) effect of varying the solution flow rate; (D) effect of varying the sulphite concentration.

Table 4
Comparison of the efficiency of different chemical oxygen traps in the deoxygenator

| O_2 scavenger	Steady state current (nA)
None	3773 ± 59
Nitrogen (50 ml min^{-1})	334 ± 11
Sulphite 0.01 M	420 ± 11
Mn(OH)$_2$ 0.015 M	403 ± 9
Ascorbic acid 0.01 M	3256 ± 162
Sodium borohydride 0.01 M	2879 ± 54

3.2. Chemical deoxygenation

For measurements in the field it is useful to minimise or eliminate the use of gas for deoxygenation. For this reason several chemical oxygen scavengers were tested in the deoxygenation unit. The steady state background current (and standard deviations (SD) of at least three separate experiments) for chemical scavengers are compared with that using nitrogen in Table 4. The results show that in optimal conditions the efficiency of some chemical scavengers was almost as good as that of nitrogen. In the presence of oxygen, Na_2SO_3 is oxidised according to the following reaction:
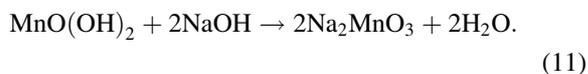
$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \qquad (8)$$

The removal of oxygen by Mn(OH)$_2$ is explained by the following reactions [17,18]:

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2 \qquad (9)$$
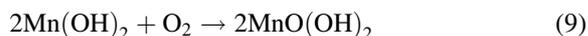
This is slowly dehydrated to MnO_2:

$$MnO(OH)_2 \rightarrow MnO_2 + H_2O \qquad (10)$$
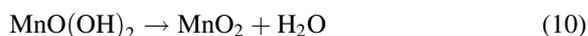
However, in alkaline solutions MnO(OH)$_2$ forms an insoluble salt of Mn(IV)

$$MnO(OH)_2 + 2NaOH \rightarrow 2Na_2MnO_3 + 2H_2O. \qquad (11)$$

The final products of these reactions are therefore MnO_2 and Na_2MnO_3 which were found to accumulate on the external wall of the silicone tubing. Some precipitation of Mn(IV) occurred already during preparation and handling of the solution. Na_2SO_3 was more convenient as it did not form a precipitate and was therefore less likely to block the tubing perimeter.

Table 5
Oxygen removal efficiency (in % of the oxygen in air-saturated water) of a 0.5 M sodium sulphite solution over an extended period of time

Time (h)	Steady state current (nA)	SD (%)	Efficiency (%)
0	531	3.1	86
1	558	3.1	85
3	652	2.1	83
5	739	2.9	80
26.5	786	3.0	79
51.5	783	3.2	79
69.5	744	3.0	80

SD % is the standard deviation of the final 20 s of the steady state current.

Optimisation of the sulphite concentration (Fig. 4(D)) showed unexpectedly that the lowest concentration (0.01 M) was most effective, while the highest (2 M) was least effective. It is probable that this is due to a "salting out effect", in which the oxygen solubility is much diminished at higher sulphite concentrations, which inhibited the dissolution into the sulphite solution with the concomitant removal from the seawater through the membrane.

Efficiency and reproducibility as a function of time were tested using a solution of 0.5 M sulphite as chemical scavenger (Table 5). The deoxygenation efficiency decreased from 86% to 80% in the first 5 h and remained stable for the remaining tested period. The reproducibility of the nitrogen deoxygenation as a function of time was not affected by a systematic change in time because nitrogen was continuously flushing in the container, allowing for on-going removal of oxygen from the container.

3.3. Effect of in-line deoxygenation on metal measurements in seawater and interferences

To assess the efficiency at which the oxygen interference with CSV analysis was eliminated, the time was determined required to attain reproducible metal peaks. Thereto the deoxygenation unit was used to remove dissolved oxygen prior to the determination of copper and cobalt by FIA with detection by CSV, using either silicone or Poreflon (Fig. 5(A)–(D)). It was found that stable cobalt peakheight was obtained with silicone or Poreflon tubing within 5 scans (equivalent

to 5 min) after the beginning of the deoxygenation (Fig. 5(A) and (B)). The copper peak improved within the same period, but it was found that copper peaks could also be obtained without deoxygenation (Fig. 5(C) and (D)), because a fast square-wave frequency (200 Hz) could be used for its detection, and as its peak potential is further away from the oxygen peak. However, even at this frequency the peak appeared on the shoulder of the oxygen peak and would be subject to measuring errors at low concentrations. The copper peak-shape improved with lowered oxygen concentration causing a flatter baseline.

A drawback of using in-line deoxygenation could be due to possible interaction (chemical or physical) of the samples with the tubing. In particular silicone tubing appeared to be prone to adsorbing copper complexes, whereas the Poreflon tubing did not appear to be subject to this drawback. A change in response due to a changed metal concentration was completed within 5 scans (ca. 5 min) for cobalt using either silicone or Poreflon (Fig. 6(A) and (B)), so carry-over effects were minor with both types of tubing for this metal. However, a greater carry-over effect occurred when copper was determined using silicone tubing than using Poreflon tubing (Fig. 6(C) and (D)) indicating that the metal complexes were adsorbing on the silicone tubing, desorbing again when the concentrations were lowered. A longer flushing time (ca. 20 scans) was therefore required using silicone tubing to obtain a stable response for copper (Fig. 6(C) and (D)). On the other hand the change in response due to a changed copper concentration was completed within 5 scans (ca. 5 min) using Poreflon tubing. This comparison showed that the copper–oxine complex was interacting with the silicone tubing. For this reason chemically inert tubing as Poreflon is preferable.

The effect of adsorption can be overcome by using longer flushing times between sample changes. Thus the same copper concentration was obtained, when the system was calibrated by a copper addition, using Poreflon (6.2±0.7 nM) or silicone tubing (6.5±0.7 nM).

3.4. Reproducibility of the FIA-CSV measurements using in-line deoxygenation

The relative standard deviation (RSD %) of the cobalt measurements using silicone and Poreflon
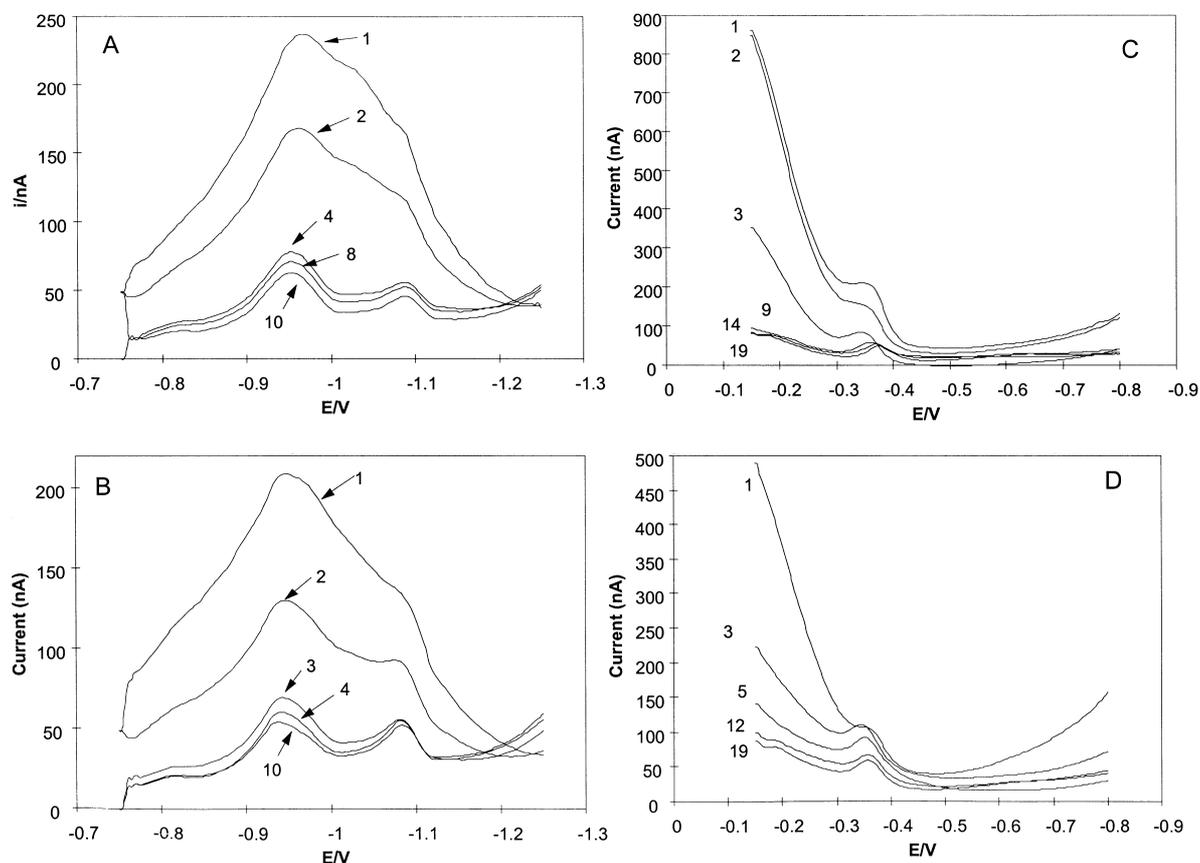
Fig. 5. Effect of deoxygenation on consecutive scans after starting the deoxygenation: (A) CSV scans of cobalt using silicone tubing in the deoxygenation chamber; (B) FIA-CSV scans of cobalt using Poreflon tubing in the deoxygenation chamber; (C) scans of copper using silicone tubing in the deoxygenation chamber; (D) scans of copper using Poreflon tubing in the deoxygenation chamber.

tubing in seawater was 8.3% RSD using silicone and 8.2% RSD using Poreflon at 64 pM cobalt, and respectively 5.5% and 5.9% at 260 pM cobalt (Fig. 6(A) and (B)). Cobalt concentrations obtained were 64±5 pM using silicone and 68±6 pM using the Poreflon tubing.

The relative standard deviation of FIA-CSV of copper using silicone tubing was 11% of 6 nM copper, and 10% of 26 nM; using Poreflon tubing it was 12% at 6 nM, and 7% at 26 nM copper.

4. Conclusions

Gas permeation through semi-permeable tubing is shown here to be a successful tool for on-line de-oxygenation prior to FIA-CSV. Many types of tubing can be used including Teflon and PVC, but best results are obtained using silicone and Poreflon tubing. The deoxygenation system is simple to construct by placing the semi-permeable tubing in a 30 ml container from which oxygen is removed by nitrogen flushing, and directing the sample flow through this tubing. The oxygen is removed from on-line using 1 m silicone tubing giving 90% oxygen removal at a residence time of 15–20 s of the water in the deoxygenation reservoir. Background currents similar to batch voltammetric systems (which use 5 min conventional nitrogen purging) were then obtained.

Silicone and Poreflon tubing were shown to have good permeability properties in comparison to other tested tubing, with deoxygenation efficiencies up to 98% using a length of 3 m. The steady state de-oxygenation efficiency was optimal using internal
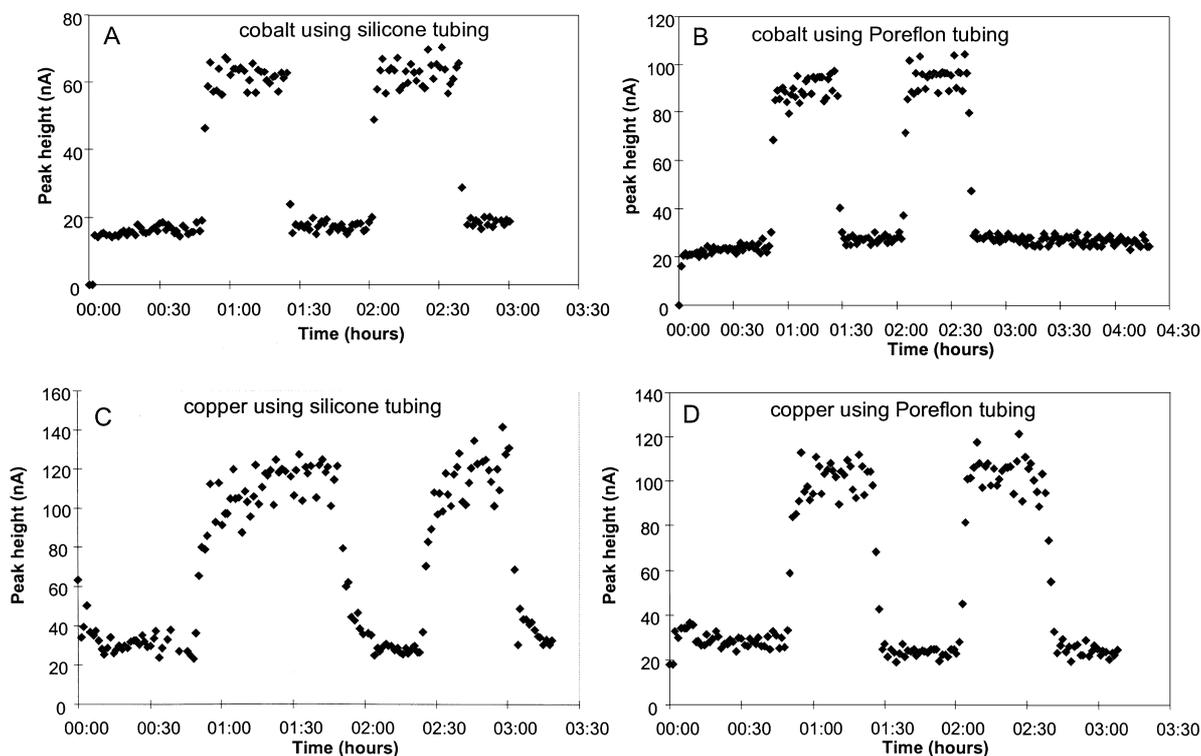
Fig. 6. The CSV-FIA response as a function of time at varying metal concentrations using either silicone or Poreflon tubing in the deoxygenation chamber: (A) for cobalt using silicone tubing; (B) for cobalt peak height using Poreflon tubing; (C) for copper using silicone tubing; (D) for copper using Poreflon tubing.

diameters of 0.5–1.0 mm, with a wall thickness of 0.5 mm. However, a larger internal diameter increased the residence time and this increased the time (from 120 to 250 s) before steady state oxygen removal was achieved after initiating oxygen flushing from the deoxygenation reservoir.

The deoxygenation unit was flushed with nitrogen at an optimised flow rate of 50 ml min^{-1}. An increase of the gas flow rate was found to have little effect on the steady state deoxygenation efficiency, but a higher background current was obtained at lower gas flow rates. Furthermore, a lower gas flow increased the time necessary to reach the steady state level of deoxygenation.

CSV trace metal peaks were reproducible (8% SD for 64 pM cobalt and 11% SD for 6.5 nM copper) either using silicone or Poreflon tubing. However, adsorption/desorption processes of the copper–oxine complex on the silicone tubing were found to increase the response time of the system in response to varia-

tions of the copper concentration (Fig. 6(D)). This may be a problem for other metal complexes too, although it did not occur for the cobalt–nioxime species. For this reason Poreflon tubing may be more suitable due to an apparent much greater inertness of this tubing.

Chemical removal (using 0.01 M Na$_2$SO$_3$ in the deoxygenating chamber) after oxygen permeation through 1 m silicone tubing was found to have similar efficiency (89% oxygen removal) as the physical deoxygenation using nitrogen (91% oxygen removal), and had the advantage of reducing the amount of gas necessary to carry out analyses in the field.

Acknowledgements

References

[1] C. Colombo, C.M.G. van den Berg, A. Daniel, Anal. Chim. Acta 346 (1997) 101.

[2] A. Daniel, A.R. Baker, C.M.G. van den Berg, Fresenius' J. Anal. Chem. 358 (1997) 703.

[3] R. Pinet, Invitation to Oceanography, vol. 508, West Publ. Co, St. Paul, 1996, pp. 147–148.

[4] C. Emiliani, Planet Earth, Press Syndicate of the University of Cambridge, Cambridge, vol. 718, 1992, pp. 288–297.

[5] R.C. Weast, M.J. Astle, Handbook of Chemistry and Physics, 61st ed., CRC Press, Boca Raton, 1981, pp. 155–160.

[6] W.J. Blaedel, J.W. Todd, Anal. Chem. 30 (1958) 1821.

[7] B. Persson, L. Rosén, Anal. Chim. Acta 123 (1981) 115.

[8] W.A. Maccrehan, W.E. May, Anal. Chem. 56 (1984) 625.

[9] H.B. Hanekamp, W.H. Voogt, P. Bos, R.W. Frei, Anal. Chim. Acta 118 (1980) 81.

[10] J.N. Barisci, G.G. Wallace, Electroanalysis 4 (1992) 323.

[11] E.P. Achterberg, C.M.G. van den Berg, Anal. Chim. Acta 291 (1994) 213.

[12] A. Trojánek, K. Holub, Anal. Chim. Acta 121 (1980) 23.

[13] L.N. Moskvin, O.V. Rodinkov, A.N. Katruzov, G.L. Grigorev, S.N. Khromovborisov, Talanta 42 (1995) 1707.

[14] J.J. Pedrotti, L. Angnes, G.R. Gutz, Anal. Chim. Acta 298 (1994) 393.

[15] X.S. Chai, L.G. Danielsson, Anal. Chim. Acta 332 (1996) 31.

[16] C.P. Ding, J.H. Wang, Voltammetric methods, in: T.R. Yu, G.L. Ji (Eds.), Electrochemical Methods in Soil and Water Analysis, Pergamon Press, Oxford, 1993, p. 462.

[17] L. Malatesta, Chimica Inorganica, vol. 362, 2nd ed., L' Editrice Scientifica, Milano, 1965, pp. 299–301.

[18] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry: A Comprehensive Text, 4th ed., vol. 1396, Wiley, New York, 1980, pp. 738–739.

[19] Cole-Parmer Instrument Company Catalogue, Hanwell, London, UK.