

## Testing a Flux Cell for Determination of Manganese in Freshwater

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### Abstract

A flux cell with vitreous carbon tubular electrodes, as auxiliary and working electrodes, was tested. The following procedure was used: (1) study and optimization of the mercury deposition conditions at the working electrode, (2) study the electrodes position and distance in order to minimize dispersion of the sample, (3) study of the linearity and reproducibility using different concentrations of manganese ( $2 \cdot 10^{-7}$  to  $6 \cdot 10^{-7}$  M), with differential pulse anodic stripping voltammetry (DPASV) and square wave stripping voltammetry (SWSV). Good linear correlation was obtained for concentration of manganese used.

**Keywords:** Voltammetric cell, tubular electrodes, manganese, DPASV, SWSV.

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### Introduction

Manganese creates serious problems in public water supplies. The problems are most extensive and critical with underground water, but are also encountered in waters drawn from rivers and impounded surface supplies during certain seasons of the year [1].

It has been shown, on the basis of thermodynamic considerations, that Mn(IV) is the only oxidation state for manganese in oxygen-containing water. Thus, this

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form can be reduced to soluble Mn(II) only under highly anaerobic reducing conditions. This evidence shows that the development of anaerobic conditions is essential for appreciable amounts of manganese to gain entrance to water supplies. Mn(II) is the soluble form of manganese, and is thermodynamically stable under anaerobic conditions [1, 2].

Manganese interferes with laundering operations, imparts objectionable stains to plumbing fixtures, and causes difficulties in distribution systems by supporting the growth of iron bacteria. The U.S. Environmental Protection Agency (U.S.E.P.A) has established that water supplies ought not to contain more than 0.050 mg/L of manganese [1].

Voltammetric techniques, such as anodic stripping voltammetry (ASV), has been widely used recently due to its speed, simplicity, low cost, high sensitivity and capability of multielement determination [3]. Batch voltammetry consumes more time and chemicals, and flow techniques have been developed for voltammetric analysis to solve those drawbacks [4, 5].

A mercury film electrode (MFE) is usually employed for ASV in flow systems since it provides better stability, well defined peaks in the voltammogram, high sensitivity, and also reduces the risk of exposure to mercury vapour. The mercury film (MF) can be plated in-situ together with the analytes during a deposition step, or before the measurements are taken. However, a drawback of the MFE preparation by the in-situ method is the production of mercury-contaminated wastes [4, 6].

The aim of this work was to test a voltammetric flux cell using a pre-plated MFE as a working electrode for the determination of manganese. Vitreous carbon tubular electrodes were used as auxiliary and working electrodes. The tubular configuration is the most recommend for this kind of systems, because they minimize distortion of the sample [7]. Two voltammetric techniques, DPASV and SWSV, were used for comparison. SWSV is known to be a faster technique, which could contribute to reduce the measuring time, and it is also known to be less influenced by the presence of oxygen which is also an important factor in flux analysis [3].

The use of a voltammetric flow cell to determine manganese is interesting due to its applicability to in-situ studies of manganese, especially in its determination in water reservoirs used for potable water. Potentiometric stripping analysis for manganese(II) in natural waters, with batch and flow approaches, have already been done, with good results for the flow determinations [5].

## **Experimental**

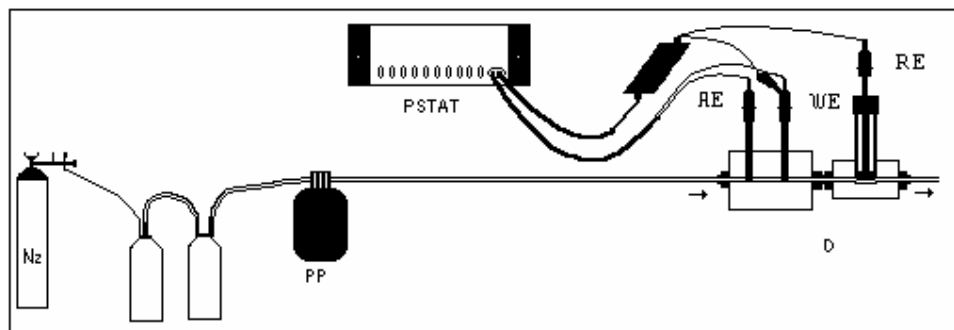
### ***Apparatus***

The flow system consisted of a peristaltic pump (Gilson, Minniplus 3) and an electrochemical flow cell. All connections within the flow-injection system were made with 0.8 mm internal diameter teflon tube. An Ecochemie Autolab PGTAT 12 potentiostat was used, controlled by a PC using General Purpose Electrochemical System- GPES (Fig 1-a).

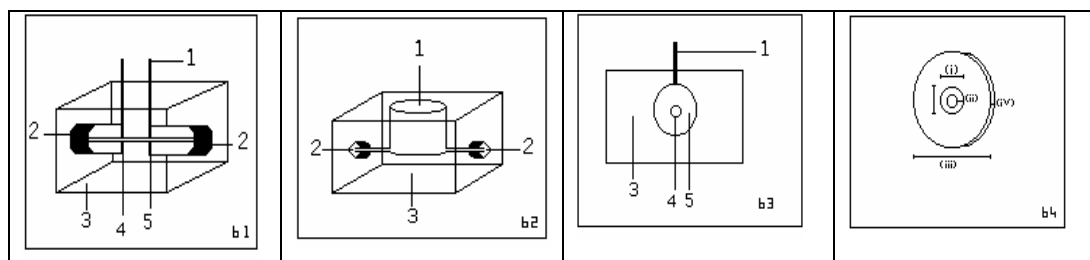
### ***Cell design***

A schematic diagram of the electrochemical flow cell is presented in Fig. 1-b. The flow cell is formed by two compartments made of polymethylmetacrilate (PMMA): (1) the working and auxiliary vitreous carbon tubular electrodes (PMMA compartment dimensions: 27 x 20 x 21 mm), and (2) the Ag/AgCl/2M NaNO<sub>3</sub> reference electrode (TermoOrion-Russell) with 1.5 cm of diameter (PMMA compartment dimensions: 41 x 27 x 20 mm).

The tubular electrodes were prepared by cutting a vitreous carbon rod (VC 007940) with 7 mm of diameter and 100 mm length. The result was two carbon tubular electrodes with 1 mm of thickness and 1 mm of internal diameter. The internal diameter was achieved by doing a hole in the centre. Electrical contact to the inner side of the carbon disk was made with copper wire with 2 cm of diameter. The two compartments were linked by PTFE tube of 0.8 mm (inner diameter; Omnifit).



(a)



(b)

**Figure 1.** (a) Scheme of the all system: PP – Peristaltic Pump, PSTAT- Ecochemie Autolab PGTAT 12 potentiostat, D- Detector, AE- Auxiliary electrode, WE – Working electrode e RE- Reference electrode (b) Scheme electrochemical flow cell: **b.1)** Support for the auxiliary and working vitreous carbon tubular electrodes: **1**-copper wire; **2**-joint spiral; **3**-PMMA support; **4**- electrode surface; **5**-tubular electrode, **b.2)** Support for the reference electrode: **1**-electrode; **2**-joint spiral; **3**-PMMA support, **b.3)** Transversal view of b.1): **1**-copper wire, **3**-acrylic support, **4**-surface sensor and **5**-tubular electrode, and **b.4)** Tubular electrode scheme: (i) internal diameter - 1mm, (ii) and (iv) thickness - 1 mm, (iii) external diameter - 7 mm.

**Procedure** The vitreous carbon tubular electrode (working electrode) was polished with 0.3 and 0.05  $\mu\text{m}$  alumina slurry, before plating the mercury film. The mercury film was deposited applying a potential of  $-1.0\text{ V}$  by chronoamperometry, and using a carrier solution containing  $4 \times 10^{-4}\text{ M Hg(NO}_3)_2$  in  $2.10^{-2}\text{ M NaNO}_3$  (pH 4.5) with a rate of  $0.25\text{ mL min}^{-1}$  for 30 min. The electrode was cleaned for 1 min by applying a potential of  $0\text{ V}$  before each measurement. After each day of measurements, the mercury was removed from the vitreous carbon substrate by reoxidation using a carrier solution containing  $0.5\text{ M NaNO}_3$  (pH 4.5) with a rate of  $0.25\text{ mL min}^{-1}$  for 30 min. Linear potential scans from  $0.3\text{ V}$  to  $0.55\text{ V}$  were performed at a scan rate of  $10\text{ mV s}^{-1}$  until no redissolution signal was left.

The vitreous carbon surface was observed, before and after polishing, using a magnifying glass (Olympus C011). The vitreous carbon surface was also controlled regularly before and after deposition of the mercury film, and when the mercury film was removed.

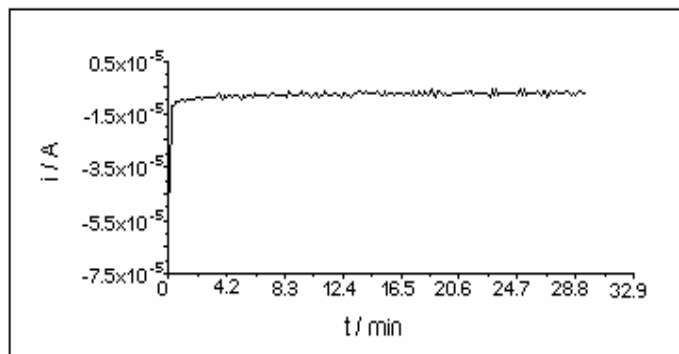
Square Wave Stripping Voltammetry (SWSV) was used under the following conditions: pre-concentration potential =  $-1.7\text{ V}$  for 3 min, scan potential from  $-1.7$  to  $-1.1\text{ V}$ , square-wave amplitude =  $50\text{ mV}$ , step amplitude =  $2\text{ mV}$ , scan rate =  $10\text{ mV s}^{-1}$  and frequency  $50\text{ Hz}$ . Differential Pulse Anodic Stripping Voltammetry (DPASV) measurements were done under the following conditions: pre-concentration potential =  $-1.7\text{ V}$  for 3 min, scan potential from  $-1.7$  to  $-1.1\text{ V}$ , pulse modulation amplitude =  $50\text{ mV}$ , pulse amplitude =  $2\text{ mV}$  and scan rate  $10\text{ mVs}^{-1}$ . These experimental conditions were defined according with a previous work, where HMDE was used as the working electrode and manganese as the metal, for DPASV and SWSV analysis [8]. The peak potential of Mn(II) appeared at  $-1.5\text{ V}$  vs.  $\text{Ag/AgCl}/2\text{ M NaNO}_3$ .

All compounds were reagent grade, and all solutions were freshly prepared with Milli-Q water  $5\text{ }\mu\text{S/m}$  (Millipore) and were deoxygenated before use. Experiments were performed at room temperature ( $\sim 22\text{ }^\circ\text{C}$ ).

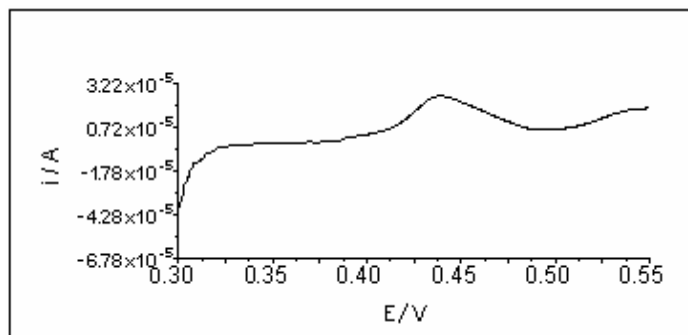
A standard stock solution of Mn(II) of  $1.000 \pm 0.002 \text{ g L}^{-1}$  (Panreac) was used. Dilutions were made from this solution with  $0.5 \text{ M NaNO}_3$  and were acidified with  $\text{HNO}_3$   $0.1 \text{ M}$  (pH 5). A flow rate of  $2.0 \text{ mL min}^{-1}$  was used for the manganese measurements by DPASV and SWSV. A solution containing  $2.0 \text{ }\mu\text{M}$  Mn(II) in  $\text{NaNO}_3$   $0.5 \text{ M}$  was used to study electrodes position. A sequence of three blanks was always performed before each experiment reading.

### Results and Discussion

In order to test the flux cell we had to guarantee a good deposition of the mercury film. Therefore, and because the carbon surface was very rough, it was carefully polished with alumina ( $0.3$  and  $0.05\mu\text{m}$ ) in order to obtain a shining surface, which facilitates the deposition of the mercury film [3].



a)



b)

**Figure 2.** An example of a mercury film deposition (a) and reoxidation (b) on a vitreous carbon tubular electrode ( $Q_{\text{red}} = -11.4 \text{ mC}$  and  $Q_{\text{ox}} = -9.18 \text{ mC}$ ).

### *Optimization of mercury deposition conditions at the working electrode*

The mercury film is not a perfect film, i.e., it is constituted by small drops. In fact, a good mercury film is obtained when the vitreous carbon surface is completely covered with the smaller drops [9, 10]. Experiments were done trying different deposition potentials and deposition times [9, 11]. We concluded that a homogeneous mercury film was obtained when a potential of -1.0 V was applied during 30 minutes. Fig. 2 shows an example of the deposition chronoamperogram ( $i$  vs.  $t$ ) and the reoxidation voltammogram ( $i$  vs.  $E$ ) curve obtained with the mercury film. The systematic noise observed in the deposition of the mercury film is due to the impulses of the peristaltic pump.

In order to obtain reproducible results the three more important factors were: (1) polishing the electrode vitreous carbon surface which creates a more homogeneous active surface, (2) a deposition potential of -1.0 V which yields a more uniform distribution of mercury on the electrode surface, and (3) a charge deposition of -10 to -11 mC, for a 30 min deposition time, which results in higher peak currents for the manganese. The observation of the vitreous carbon surface, before deposition of mercury film, and the charge of the mercury deposition were also considered.

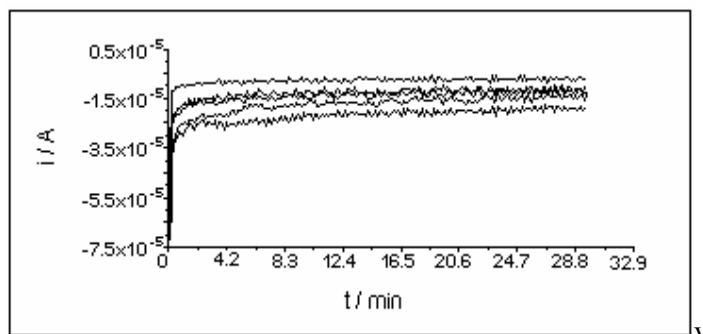
To optimize the mercury film deposition, i.e., to improve the reproducibility of the mercury films obtained, three procedures were tested: (1) a sequence of depositions/reoxidations, (2) a deposition/reoxidation followed by a deposition, and (3) a deposition/reoxidation followed by an ultrasonic cleansing and deposition. The first procedure gave irreproducible films (Fig. 3-a). The second and the third procedures gave reproducible films (Fig. 3-b and 3-c), but surface observation and charge determination indicated that the more reproducible films were obtained with the third option.

Comparing the deposited and removed charges for the third procedure lead us to conclude that approximately 20% of the mercury deposited at the beginning of the experiment was lost during the experiment (Table 1).

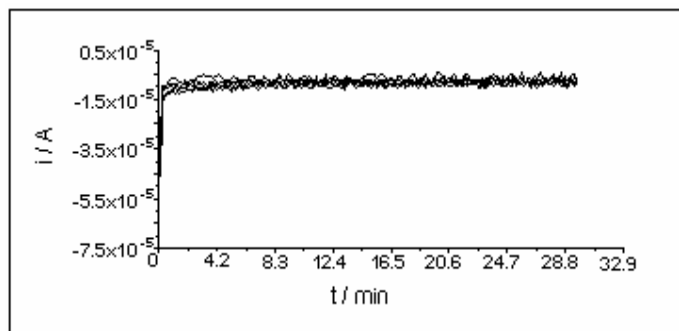
**Table 1.** Comparison between deposited ( $Q_{\text{red}}$ ) and removed ( $Q_{\text{ox}}$ ) mercury from the vitreous carbon tubular electrode, at the beginning and ending of experimental work, respectively, for the third procedure.

Mercury Film	$Q_{\text{red}}$ (mC)	$Q_{\text{ox}}$ (mC)	$Q_{\text{ox}}/Q_{\text{red}}$
1	-11.4	-9.18	0.8
2	-10.9	-8.02	0.7
3	-10.7	-8.40	0.8
4	-11.7	-9.03	0.8
5	-10.2	-7.89	0.8

The results obtained are reproducible, i.e., the lost of mercury (about 20%) was similar for the different mercury films produced. These results may be due to the likely disturbance of the electrode surface caused by the manganese solution flux, and the possible formation of  $\text{H}_2$  bubbles formed by the concurrent reduction of  $\text{H}^+$  at the negative deposition potential. The fact that the analysis was performed at a  $\text{pH} = 5$  can only aggravate the bubble formation.

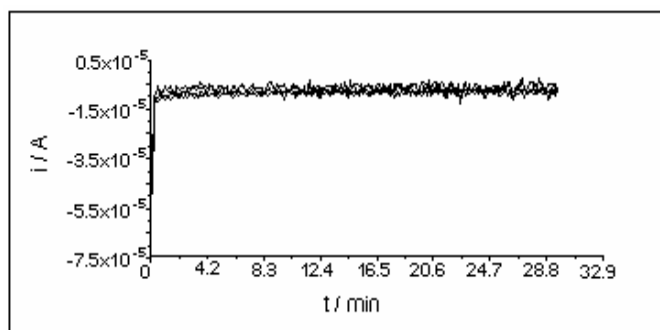


(a)



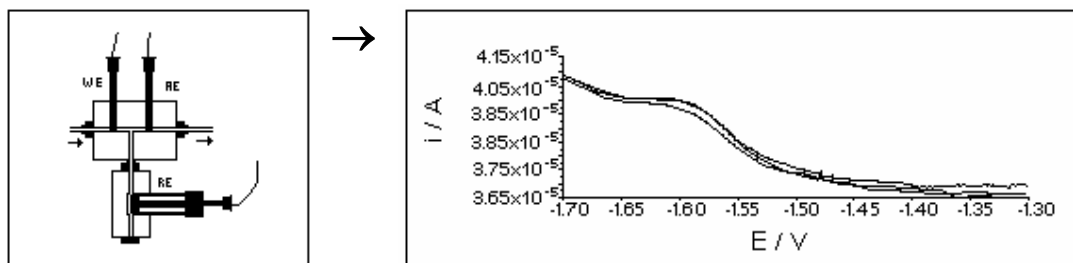
(b)



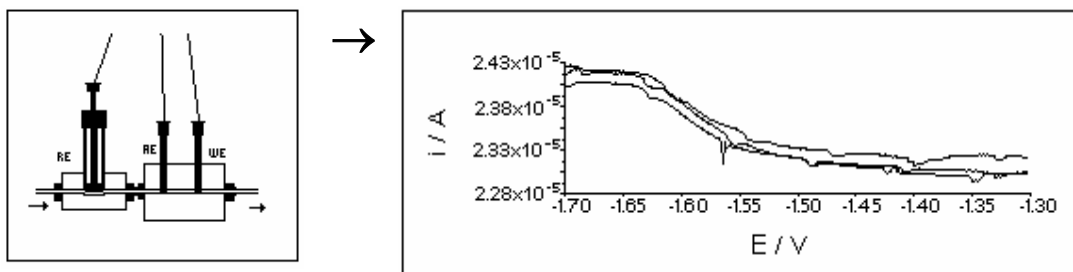


(c)

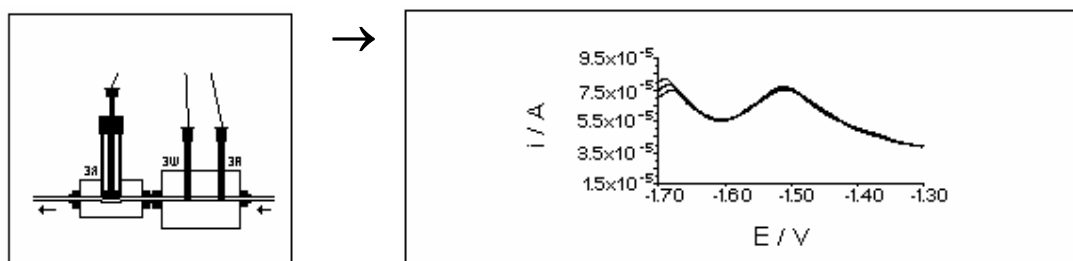
**Figure 3.** Mercury film depositions on a glassy carbon tubular electrode: a) a sequence of depositions/reoxidations, b) a deposition/reoxidation followed by a deposition and c) a deposition/reoxidation followed by an ultrasonic clean and deposition.



(a)



(b)



(c)

**Figure 4.** Electrodes positions in the flux cell and the respective results obtained: (a) the auxiliary and working electrodes perpendicular to the reference electrode, (b) the reference electrode followed by the auxiliary and working electrodes and (c) the auxiliary and working electrodes followed by the reference electrode. WE – Working Electrode, AE – Auxiliary Electrode and RE – Reference Electrode.

***The electrodes position and distance in order to minimize dispersion of the sample***

The shape of the signal is strongly dependent on the geometric and hydrodynamic parameters of the system, which govern the dispersion of the sample along the line between the three electrodes [3].

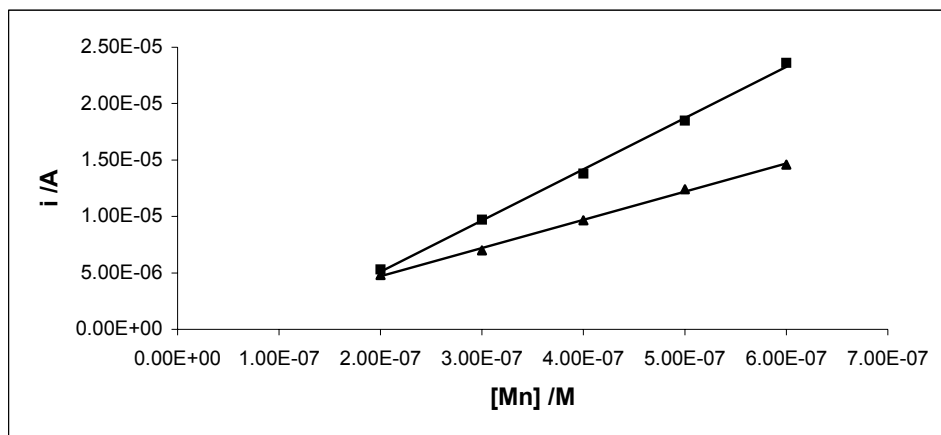
In order to choose the best position for the electrodes, i.e., the smaller distance between each other in order to minimize sample dispersion, measurements were done using square wave stripping voltammetry (SWSV) with the electrodes in different positions: **(1)** the auxiliary and working electrodes perpendicular to the reference electrode (Fig.4-a), **(2)** the reference electrode followed by the auxiliary and working electrodes (Fig.4-b) and **(3)** the auxiliary and working electrodes followed by the reference electrode (Fig. 4-c).

In the first (Fig. 4-a) and the second (Fig. 4-b) cases the values obtained were not reproducible, with a significant amount of noise on the last one. In the third case (Fig. 4-c) the results obtained were very reproducible.

***The linearity and reproducibility study using different concentrations of manganese ( $2 \times 10^{-7}$  to  $6 \times 10^{-7}$  M).***

The reproducibility and linearity of the method were studied using SWSV and DPASV as voltammetric techniques. In these techniques there are two steps: (1) pre-concentration of the metal, i.e., the Mn(II) is reduced at the mercury vitreous carbon electrode by applying a deposition potential of  $-1.7$  V, and (2) the oxidation of Mn(0) to Mn(II) by applying a scan of more positive potentials. Three procedures were tested: (1) pre-concentration and oxidation of manganese with flow, i.e., a solution of manganese passed through the voltammetric cell during the two steps, (2) pre-concentration with flow and oxidation without flow,

i.e., a solution of manganese passed through the voltammetric cell during only the pre-concentration step and (3) pre-concentration and oxidation without flow.

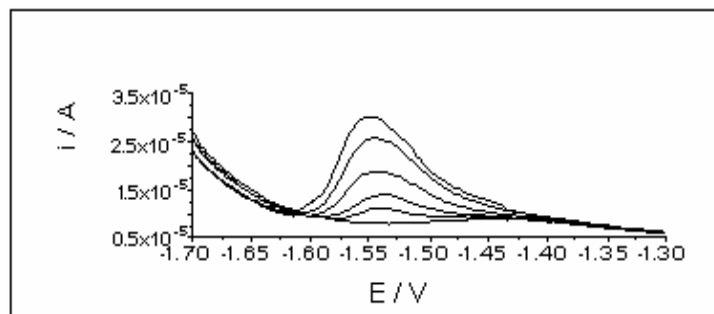


**Figure 5.** An example of manganese calibration curves with the mercury vitreous carbon tubular electrode, using DPASV (▲) and SWSV (■).

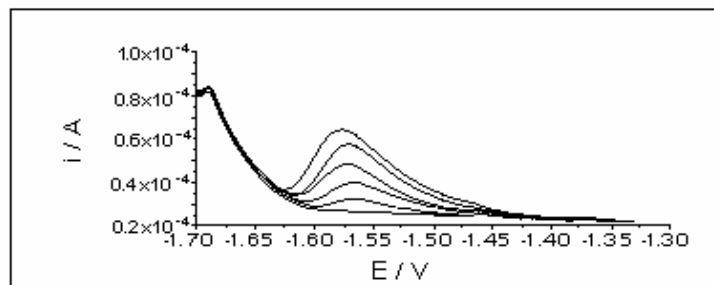
In the first procedure a linear response was obtained for manganese additions of  $1.0 \times 10^{-6}$  to  $2.0 \times 10^{-6}$  M (DPASV) and  $7.5 \times 10^{-7}$  M to  $1.5 \times 10^{-6}$  M (SWSV). However, it was necessary to use higher concentrations to obtain a signal, and in that situation reproducibility was difficult to achieve. For values higher than  $2.0 \times 10^{-6}$  M the mercury film became saturated when using DPASV.

For the third procedure the detection limit was too high, i.e., a peak for manganese appeared only at concentration higher than  $10^{-5}$  M.

For the second procedure good reproducibility and linearity were obtained, in a range of concentrations of  $2 \times 10^{-7}$  to  $6 \times 10^{-7}$  M (Fig. 5). A linear response was obtained for manganese additions of  $2 \times 10^{-7}$  to  $6 \times 10^{-7}$  M, with relative standard deviations on 3 measurements ranging from 10% to 7%, for both voltammetric techniques, DPASV and SWSV. Within the experimental error an estimated detection limit of  $6 \times 10^{-8}$  M (DPASV) and  $8 \times 10^{-8}$  M (SWSV) was obtained considering all the curves, on the basis of 3.3 multiplied by the standard deviation of the curve ( $S_y/x$ ) and divided by its slope.



(a)



(b)

**Figure 6.** An example of the voltammograms obtained for manganese calibration curves, using DPASV (a) and SWSV (b) (calibration curve for DPASV: 0;  $2.0 \times 10^{-7}$ ;  $3.0 \times 10^{-7}$ ;  $4.0 \times 10^{-7}$ ;  $5.0 \times 10^{-7}$ ;  $6.0 \times 10^{-7}$  M Mn(II); and calibration curve for SWSV: 0;  $2.0 \times 10^{-7}$ ;  $3.0 \times 10^{-7}$ ;  $4.0 \times 10^{-7}$ ;  $5.0 \times 10^{-7}$ ;  $6.0 \times 10^{-7}$  M Mn(II)).

As can be observed in Fig. 5, the slope of the calibration curves is higher for SWSV than for DPASV, and the same happened to the height of the voltammograms (Fig. 6). These results, together with the fact that SWSV is a much faster technique, lead us to recommend it for these measurements.

### Final Comments

- (1) The conditions for making a mercury film on a vitreous carbon tubular electrode, used as working electrode, were optimised.
- (2) The flow through cell configurations was optimised in order to achieve the desired balance between high sensitivity and minimum carry-over effects.
- (3) Good linear correlation was obtained for the manganese range of concentration used ( $2.10^{-7}$  to  $6.10^{-7}$  M). As was mentioned before, the U.S.E.P.A. has established that water supplies ought not to contain more than 0.050 mg/L of manganese, i.e.,  $2 \times 10^{-6}$  M of manganese. Therefore, both techniques tested can be applied to analyse sources of potable water, although

for the reasons previously explained we recommend the SWSV. The analysis can be done by passing the water samples through the voltammetric cell during only in the pre-concentration step.

(4) There are good possibilities that further development of this voltammetric cell can yield a system for in-situ analysis of manganese. Among with it, the development of an automatic system, with all the advantages, is also foreseen.

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