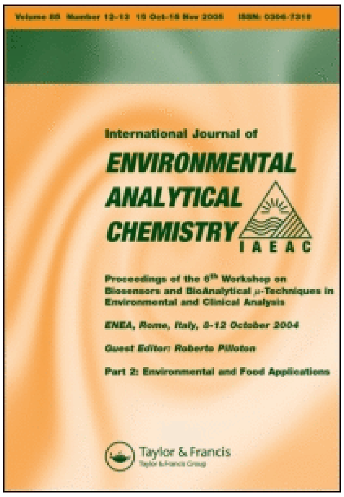

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DETERMINATION OF Mn(II) IN TAP WATER

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Two analytical methods for the determination of Mn (II) in tap water are discussed. One employs differential pulse anodic stripping voltammetry with a sensitivity of (0.4–2.2) nA ng^{-1} cm^3 and a detection limit of 0.3 $\mu g\ dm^{-3}$. The other one is flame atomic absorption spectrometry with preconcentration on the selective chelating sorbent Spheron Oxin. The method is convenient for over 5 $\mu g\ dm^{-3}$ (10^{-7} M) of Mn (II), and for less than 5 $\mu g\ dm^{-3}$ with standard addition before sorption.

KEY WORDS: Mn (II) determination, water, DPASV and flame AAS, preconcentration on 8-hydroxyquinoline-loaded resin

INTRODUCTION

Recent problems with an irregular increase of the manganese concentration in drinking water in Bratislava (Czechoslovakia) have made it necessary to evaluate methods for its determination over a wide concentration range.

In previous studies[1–3], analysis has been based on the deposition of $MnO_2 \cdot nH_2O$ at +0.4 V on a graphite or platinum electrode with inverse cathodic scanning. This method eliminates the problem of the relatively low solubility of manganese in mercury (0.0018%, w/w) and generation of intermatallic alloys. The same principle of cathodic stripping voltammetry with a flow-through coulometric system for 5×10^{-7} M of manganese on a glassy carbon electrode was used by Trojánek and Opekar[4]. Wang and Mahmoud[5], who used cathodic stripping voltammetry with adsorptive preconcentration of the Mn (II)-Eriochrome black T chelate at pH 12 on a static mercury drop electrode, report a very low detection limit for Mn (II) of 0.03 $\mu g\ dm.^{3-}$

The determination of manganese in sea water by differential pulse stripping voltammetry on a mercury film electrode (in situ) was published by O'Halloran *et al.*[6,7]. In buffered samples the plating potential was −1.7 V vs. SCE and the inverse anodic peak $Mn^\circ \rightarrow Mn(II)$ occurred at −1.6 V. The detection limit was 0.01 $\mu g\ dm^{-3}$. Zgadova *et al.*[8] have used a similar procedure in unbuffered water for $10^{-6} - 10^{-8}$ M Mn (II).

Alternative methods for the determination of manganese are spectrophotometry and atomic absorption spectrometry. The Czechoslovak norm CSN 83 05 20, part 21, prescribes photometric determination of Mn as MnO_4^- after oxidation with

$S_2O_8^{2-}$, or flame atomic absorption spectrometry (AAS) for levels of over 0.05 mg dm^{-3}, which is a very high level, higher than normal Mn concentrations in natural surface and drinking waters. The upper limit allowed for drinking water in Czechoslovakia according to norm CSN 75 71 11, valid since January 1st, 1991, is 0.1 mg dm^{-3}.

EXPERIMENTAL

Methods

Electrochemical determination by fast-scan differential pulse anodic stripping voltammetry (FSDPASV) was performed in unbuffered tap water using a Polarographic analyzer PA 3 (Laboratorní přístroje, Prague, Czechoslovakia) with hanging mercury drop electrode vs. Ag/AgCl electrode. The weight of a mercury drop was 1.70 or 0.78 mg, which corresponds with a 40 or 80 msec opening of the needle valve, respectively; scan rate, 20 mV sec^{-1}; amplitude of superposed voltage, 100 mV.

Flame AAS was carried out on a AA spectrometer Type BQ 10 (Varian, Springnvale, Australia) in 1 M HNO_3, at 279.5 nm in an oxidizing acetylene-air flame using a standard programme[9].

Samples

The samples of tap water were taken after 5 min flowing of tap water and were analysed within 2 h.

FSDPASV determination

A 5 cm^3 sample of fresh tap water without added buffer was put in the electrochemical vessel and bubbled with nitrogren, then manganese was deposited on the mercury cathode at −1.6 to −1.7 V vs. Ag/Ag/Cl with stirring for 40–360 sec. Stirring was terminated and after waiting for 15 sec the inverse anodic scan was recorded. Concentrations of Mn (II) were determined through a linear calibration plot of the anodic wave height vs. Mn content (controlled by means of standard addition).

Flame AAS determination

Samples containing over 0.1 mg dm^{-3} Mn (II) were analysed directly, i.e. without preconcentration, in an air-acetylene flame under conventional conditions[9].

Water samples with lower Mn (II) concentrations were analysed as follows. To 200–500 cm^3 of water were added 20–50 cm^3 0.2 M KH-phthalate buffer or 10–25 cm^3 2 M acetate buffer and the pH was adjusted to 6.4–7.4 with 0.2 M NaOH. Then 0.4 g Spheron Oxin 1,000 (0.025–0.040 mm: Labora, Brno, Czechoslovakia) was added and the vessel shaken for 2 h. The sample was filtered, the sorbent dried at room temperature and desorbed with 5 or 10 cm^3 1 M HNO_3 at ca. 60°C under stirring and reflux. The filtrate was used for flame AAS analysis. Samples containing less than 5 μg dm^{-3} need standard Mn (II) addition before sorption. The concentration of Mn (II) was calculated using a calibration curve.

RESULTS AND DISCUSSION

In our work we used a published DPASV electrochemical method[6,7]. This method uses cathodic deposition at -1.6 to -1.7 V and measurement of the anodic inverse peak, $E_{p,a} = -1.38$ V vs. Ag/AgCl in natural unbuffered water samples. The cyclic voltammogram has peaks at $E_{p,a} = -1.38$ V and $E_{p,c} = -1.41$ V with $w_{1/2} = 60$ mV and $I_{p,a}/I_{p,c} < 2$, which indicates a quasi-reversible behaviour of manganese.

Using DPASV it is possible to determine Mn (II) over a wide range of pH values, i.e. from neutral to weakly alkaline. This does not interfere with the sensitivity, selectivity or precision. For samples containing over 50 μg dm^{-3}, differential pulse polarography can be used without electrochemical preconcentration. A very negative potential of deposition in anodic stripping voltammetry, where many metals are deposited, is somewhat disadvantageous mainly in samples containing under 50 μg dm^{-3}, because of the formation of intermetallic alloys. Interfering metals such as chromium and iron have a low concentration in drinking water which is similar to that of Mn (II); therefore, no interference was observed. Only if Cr (III) contents were 5–10 times higher than the Mn (II) concentration, a decrease of the inverse Mn peak was observed.

Though the solubility of manganese in mercury is relatively low (0.0018%), this is sufficient for the determination in natural water. As a comparison, the solubility of e.g. copper in mercury is only about 30% higher than that of Mn and anodic stripping

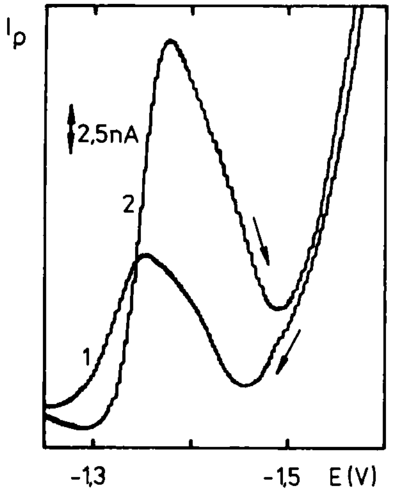

Figure 1 Differential pulse anodic[1] and cathodic[2] scan of tap water containing 3.10^{-6} M Mn (II). Hg drop weight, 1.7 mg; scan rate, 20 mV s^{-1} amplitude 100 mV.

voltammetry is the common method to determine copper. In order to prevent contamination of the samples, especially of those with extremely low metal concentrations, no buffer was added. Because of the natural ratio of Mn (II) and manganese bound in insoluble compounds, the samples were not acidified. For this reason adsorptive stripping voltammetry was not used either, because all chelating agents interfere and will influence the natural equilibrium: free ⇆ bound Mn. Figure 1 shows peaks of an anodic and cathodic scan (cyclic voltammogram). In Figures 2 and 3 the dependence of the inverse anodic and cathodic peakes on Hg drop size and on the deposition time are shown, respectively. Both figures indicate higher sensitivity for an anodic than a cathodic scan. The dependence of the anodic peak height on Mn (II) concentration is linear over a wide concentration range. From this dependence the sensitivity of our FSDPASV Mn (II) determination was calculated. This holds over the range (1.87–12.5) × 10^7 nA M^{-1} or (0.34–2.27) nA ng^{-1} cm^3. Capodaglio *et al.*[10] have expressed sensitivity for adsorptive DPSCV in the range (0.1 – 1) × 10^9 nA M^{-1} and Colombini *et al.*[11] published the sensitivity for DP polarography without accumulation in the range (0.036–-0.62) nA ng^{-1} cm^3 for the determination of manganese. For this modification we obtained sensitivity in the range (0.04–0.06) nA ng^{-1} cm^3. From these data we must conclude that the values depend on many parameters—on Hg drop size, amplitude of superimposed voltage, stirring intensity, plating potential and time.

Flame AAS with preconcentration was chosen as an alternative method of Mn (II) determination. Because of the insufficient detection sensitivity of flame AAS, which with our apparatus is 0.050 mg dm^{-3}, this method can be used for drinking water only when combined with preconcentration. We have chosen preconcentration on

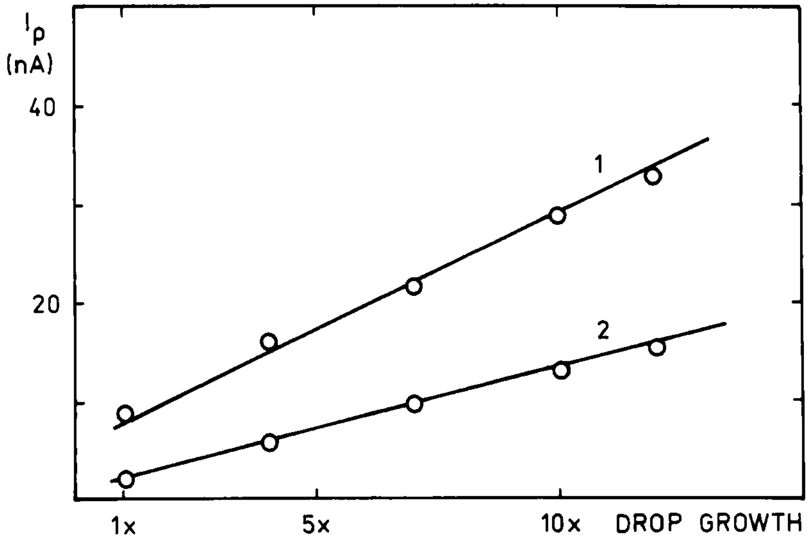

Figure 2 Dependence of *anodic peak height on Hg drop size* of (1) 1.7 mg and (2) 0.78 mg.

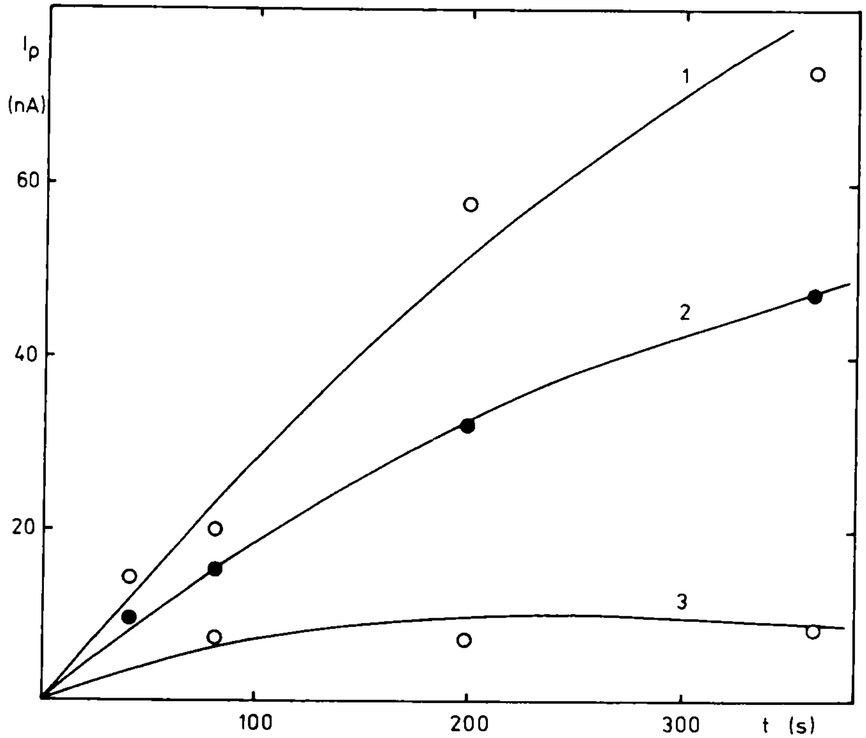

Figure 3 Dependence of peak height for anodic[1,2] and cathodic[3] stripping voltammetry on deposition time. (1) Hg drop weight 1.7 mg; dep. potential, −1.6 V. (2) Hg drop weight 0.78 mg; dep. potential, −1.6 V. (3) Hg drop weight 0.78 mg; dep. potential, +0.3 V.

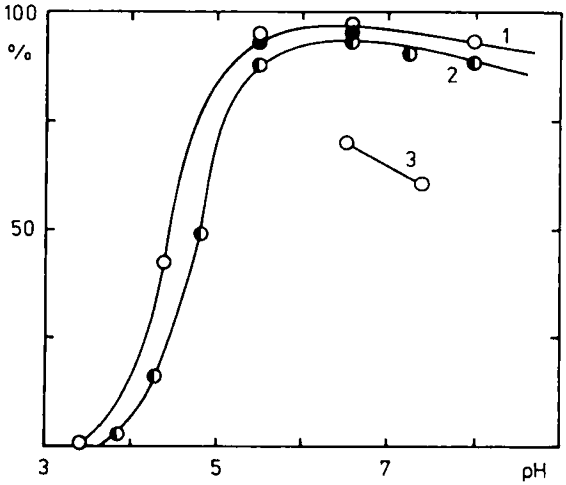

Figure 4 Dependence of sorption efficiency on pH for 1 × 10^{-6} M Mn (II). (1) KH-phthalate buffer with final concentration of 0.05 M and acetate buffer with final concentration of 0.1 M. (2) Britton–Robinson buffer with final concentration of 0.1 M. (3) unbuffered tap water.

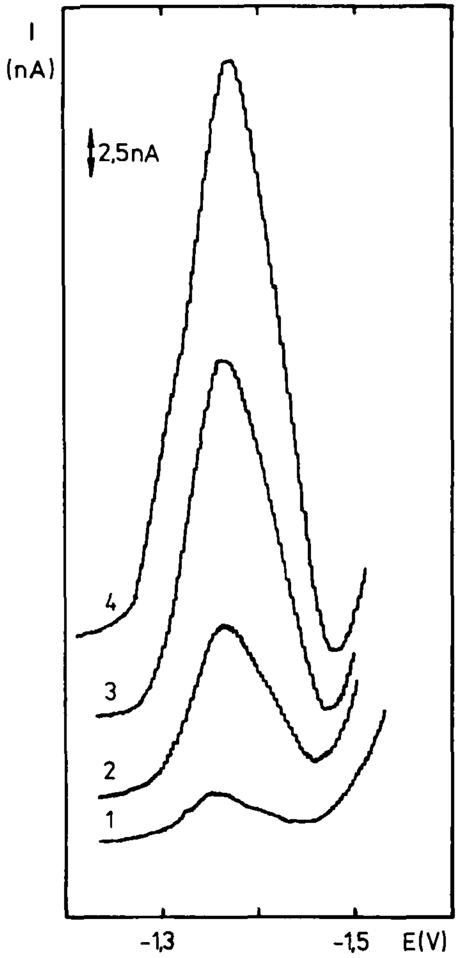

Figure 5 FSDPASV Mn (II) determination in tap water (5.3 $\mu g\ dm^{-3}$ Mn (II)). $E_{ep} = -1.7$ V; $t_{dep} = 80$ s. (1) Tap water, (2) Sample 1 +25 μl 8 × 10^{-5}M Mn (II). (3) Sample 2 +25 μl 8.10^{-5} M Mn (II). (4) Sample 3 +25 μl 8.10^{-5} M Mn (II).

Table 1 Recovery of Mn(II) determination by flame AAS with sorption preconcentration.

Mn(II) concentration			*Efficiency (%)*
($\mu g.dm^{-3}$)	*($mol.dm^{-3}$)*		
5.5	1×10^{-4}	5.5 ppm	98-102
0.55	1×10^{-5}	550.0 ppb	93-100
0.055	1×10^{-6}	55.0 ppb	85-95
0.0055	1×10^{-7}	5.5 ppb	75-85
0.0010	1.8×10^{-8}	1.0 ppb	< 60

Table 2 Results of Mn(II) determination in standard solutions.

Mn(II) added ($\mu g\ dm^{-3}$) ξ	*Mn(II) determined* ($\mu g\ dm^{-3}$; $\alpha = 0.05$)								
	FSDPASV ($n = 3$)				*c + flame AAS* ($n = 2$)				
	$\bar{x}_1 \pm s(\bar{x}).t_\alpha$	$e_{\%}$	$s(\bar{x})_{\%}$	R_1	$\bar{x}_2 \pm s(\bar{x}).t_\alpha$	$e_{\%}$	$s(\bar{x})\%$	R_2	$U_{0.05}$
0.55	0.4 ± 0.3	−27.3	17.7	0.23					
1.65	1.8 ± 0.6	9.1	7.8	0.46					
5.5	6.0 ± 1.9	9.1	7.4	1.50	4.6 ± 2.1	−16.4	3.6	0.17	0.838
22.0	20.0 ± 4.4	−9.1	5.1	3.40	19.6 ± 6.2	−10.7	2.5	0.97	0.377
55.0	52.2 ± 6.7	−5.1	1.6	5.20	57.2 ± 8.0	4.0	1.1	1.25	0.715

$\bar{x}_1, \bar{x}_2$—arithmetical average both methods

$$R_1, R_2 = x_{max} - x_{min}$$

$$U_{0.05} = \frac{|\bar{x}_1 - \bar{x}_2|}{R_1 + R_2} \text{ (Moore's criterion)}$$

$e_{\%}$—relative error of average

$$e_{\%} = \frac{100(\xi - \bar{x})}{\xi}$$

$s(\bar{x})$—standard deviation of average

$$s(\bar{x}) = \left(\frac{\Sigma(\bar{x} - x_i)^2}{n(n-1)}\right)^{1/2}$$

$$s(x)_{\%} = \frac{100 \cdot s(\bar{x})}{\bar{x}}$$

the ion-selective chelating sorbent Spheron Oxin, which is an acrylic-type polymer loaded with 8-hydroxy-quinoline. Columns containing this sorbent have been used for the sorption of several metals at rather high concentration levels[12–15]. It is evident from Figure 4 that the sorption is optimal for pH = 6.5–7.5, where sorption is almost quantitative for concentrations of over 1×10^{-7} M Mn (II). The recovery of flame AAS with preconcentration (c + flame AAS) in dependence of the Mn (II) content is given in Table 1. The results confirm the suitability of the method for Mn (II) concentration of over 1.8×10^{-8} M (1 ppb) when using standard addition.

Figure 5 shows an example of DPASV Mn (II) determination in a real drinking water sample containing 5.3 μg dm^{-3} Mn (II).

The precision and accuracy of both methods have been tested with standard solutions (Table 2). Precision is expressed as the relative standard deviation of the average, $s(\bar{x})_{\%}$, and the accuracy by the relative error of the average, $e_{\%}$,[16]. Under common conditions and for normal concentrations both methods give reliable results and the statistical parameters do not overstep the level of 10%. When testing the recovery and fitness of both methods using Moore's criterion, $U_{\alpha = 0.05}$, it is evident that the methods are suitable at the statistical level of $\alpha = 0.05$ (95%), because the tabulated value[16] is $E_{\alpha = 0.05} = 0.915$, which is higher than our calculated values.

Table 3 shows results for tap waters which were taken in the years 1988–1990 and which document the normal Mn (II) level in tap water in our region. Only after breakdown of the piping system, as was manifest from grey-brown colour of the water, a Mn (II) concentration 2–5 times higher than the allowed upper limit, was recorded.

Table 3 results of Mn(II) determination in tap water.

Tap water	*Mn(II) content (μg dm⁻³)*	
	FSDPASV	*c + flame AAS*
1	0.4	<DL*
2	0.9	<DL
3	1.2	1.0**
4	5.3	6.2**
4	5.3	4.6
5	6.5	5.4
6	16.6	18.4**
6	16.4	17.2
7	31.2	29.0
8	not determined	3000–600**

* Below detection limit.

** Spiked with 5.5 μg dm^{-3} Mn(II); addition subtracted.

*** Dark sample after breakdown, determined without preconcentration.

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