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Determination of manganese in drinking water by anodic stripping voltammetry at a mercury film electrode

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Manganese determination in drinking water by anodic stripping voltammetry (ASV) using a mercury film electrode is described. Manganese concentration can be determined in water samples without any chemical pretreatment. The optimal conditions of determination by the ASV method are the following: deposition potential –1.75 V, accumulation time 5–30 s, square wave voltammetry stripping mode. The detection limit for 30 s of accumulation time is about 0.4 μg l^{-1}; relative standard deviations in the working range of manganese concentrations do not exceed 0.10. Calcium, magnesium and iron ions at real concentrations do not interfere with manganese determination. A comparison of the ASV method with the standard photometric method for drinking water analysis has shown the equivalency of these methods; however, ASV can be used for the determination of low manganese concentrations and is insensitive to iron ions in water samples.

Key words: manganese, anodic stripping voltammetry, mercury film electrode, drinking water

INTRODUCTION

Manganese is a naturally occurring element that is found in rock, soil, and water. It is ubiquitous in the environment and comprises about 0.095% of the Earth's crust [1]. Manganese ions are common in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions, and these are the most important sources of drinking water. Manganese concentrations in natural surface and groundwaters rarely exceed 1 000 μg l^{-1} and are usually below 200 μg l^{-1} [2]. For example, in more than 40% of groundwater for centralized water supply in Lithuania manganese concentrations are above 100 μg l^{-1} [3].

Manganese is an essential element for all living organisms and does not belong to very toxic metals. The estimated no-adverse effect level for adults is 11 mg per day, and this limit was used by the World Health Organization to set a health-based guideline value of 400 μg l^{-1} of manganese for drinking water [4]. However, the re-evaluation of this guideline is under discussion due to the possible higher toxicity of manganese for children [5]. On the other hand, drinking water discoloration, staining of sinks and clothing, unacceptable taste can be caused by manganese concentrations even as low as 50–100 μg l^{-1}. Therefore, the EU Directive on the quality of water intended for human consumption gives the limit value 50 μg l^{-1} for manganese [6]. Later, the same value was accepted in the Lithuanian hygiene standard for drinking water [7].

Various spectroscopic techniques are nowadays widely used for manganese determination; however, the electroanalytical techniques remain to be interesting alternatives due to their high sensitivity, straightforward procedures and low cost. Anodic stripping voltammetry (ASV) using mercury electrodes has been employed for manganese determination in the eighties [8, 9]. Due to the low solubility in mercury and quite a negative deposition potential of manganese, the cathodic stripping techniques using the accumulation of the analyte by oxidation of Mn^{2+} ions to MnO_2 at non-mercury solid electrodes have been developed [10–13]. Also, manganese determination by adsorptive stripping voltammetry based on manganese complex adsorption at the electrode has been reported [14–16]. It should be noted that in recent works, electrodes with mercury for the determination of manganese in various matrices have been employed again. These electrodes contain a negligible amount of mercury, e. g., an *in situ* deposited film on glassy carbon [17], a renewable mercury film on silver [18], or a solid silver amalgam [19].

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The purpose of this work was to develop a reliable and simple technique for the determination of manganese in drinking water in the range of real concentrations, using anodic stripping voltammetry at a mercury film electrode.

EXPERIMENTAL

A PU-1 polarograph in a square wave voltammetry mode (f = 25 Hz, V = 100 mV s^{-1}, E_{SW} = 90 mV) was used for manganese accumulation / stripping and for the deposition of a mercury film. Voltammograms were recorded with an XY-recorder N 307.

Mercury films were deposited electrochemically on a 8 mm^2 glassy carbon electrode F 3500 (Radiometer) from stirred 50 mg l^{-1} Hg^{2+} ion solution in 0.05 mol l^{-1} HCl. The deposition potential and time were –1.1 V and 5 min, respectively. The surface of the glassy carbon electrode was thoroughly polished with 3 μm diamond paste and re-polished with alumina slurry (0.3 μm) before each experiment. After 10–15 measurements, the mercury film was wiped out from the glassy carbon electrode with wet filter paper, and after a short polishing with alumina slurry a new film was deposited. All potentials were measured against a saturated Ag / AgCl reference electrode. The auxiliary electrode was platinum wire.

The electrochemical cell was a glass beaker about 4 cm in diameter. The volume of the solution in the cell was 30 ml. The stirring of the solutions during the deposition was carried out by a magnetic stirrer.

The salts used in the experiments were of analytical grade: $MnSO_4 \cdot 5H_2O$, $Hg(NO_3)_2 \cdot H_2O$, $NaHCO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, $CaCl_2$ (anhydrous), $MgSO_4 \cdot 7H_2O$. Manganese 1 g l^{-1} stock solution was prepared by dissolution of a weighed amount of manganese sulfate in 1 mol l^{-1} HCl. A formaldoxime solution was prepared from hydroxylamine hydrochloride (Fluka) and 35% formaldehyde solution (Sigma-Aldrich). Distilled water (specific conductivity κ = 5–8 μS cm^{-1}) was used throughout the study. All the experiments were carried out in non-deaerated solutions.

Drinking water samples from Antaviliai (AV) and Vingio parkas (VP) wellfields were taken from water-taps. The concentration of calcium and magnesium in drinking water samples was determined by ion chromatography. The alkalinity of drinking water samples was determined by potentiometric titration using hydrochloric acid. The concentration range of iron in drinking water was taken from the Vilnius drinking water quality tables [20].

RESULTS AND DISCUSSION

Since manganese can be deposited on the electrode only at very negative potentials (about –1.7 V), acidic media cannot be used due to a hydrogen wave on the voltammograms. Therefore, sodium hydrocarbonate solution was tested as a working medium. The 0.0036 mol l^{-1}concentration of $NaHCO_3$was chosen because such alkalinity had been determined for drinking water from the tap. The background voltammogram and the voltammogram upon adding 10 μg l^{-1} of manganese are presented in Fig. 1. One can see that the well-defined analytical signal of manganese with the peak potential about –1.5 V can be obtained after 10 s of accumulation.

The main accumulation parameters that influence the determination sensitivity are the deposition potential and accumulation time. Figure 2 illustrates the dependence of manganese analytical signals on the deposition potential. It can be concluded that the potentials for manganese accumulation should be more negative than –1.7 V. The value of –1.75 V was chosen since more negative potentials do not increase the analytical signals substantially but can influence negatively the durability of the mercury film. The effect of accumulation time on manganese analytical signals for two manganese concentrations is shown in Fig. 3. The dependence is clearly linear for the manganese concentration of 2.3 μg l^{-1}; however, it deviates from linearity substantially when the concentration is about ten times higher. The non-linear increase of the analytical signals with accumulation time at higher concentrations may be caused by the low solubility of manganese in mercury. Also, it should be noted that the intercepts on the y-axis after the extrapolation of both curves result from applying a 10-second rest period when the stirring is stopped in order to perform

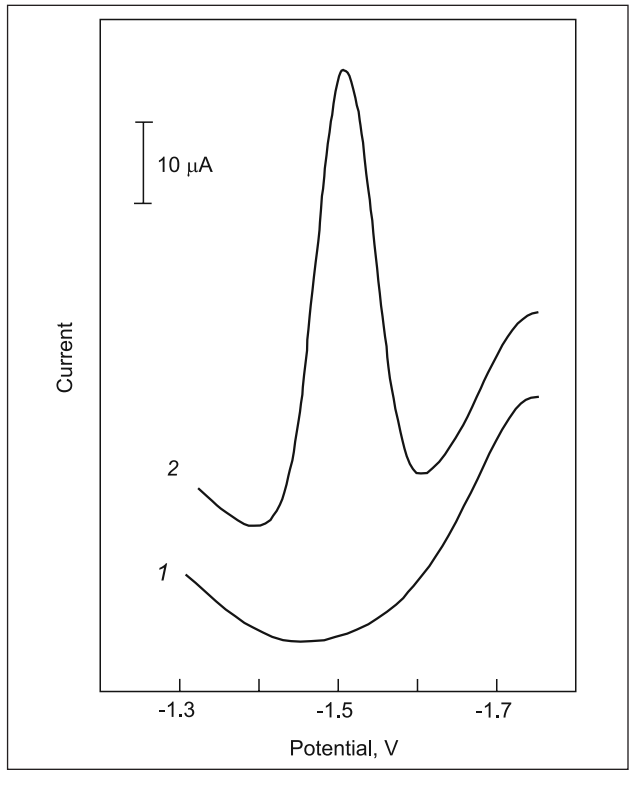

Fig. 1. Voltammograms of manganese in the 0.0036 mol l^{-1} $NaHCO_3$ solution. *1* – background voltammogram, *2* – 10 μg l^{-1} Mn^{2+}. Conditions: deposition potential –1.75 V, accumulation time 10 s

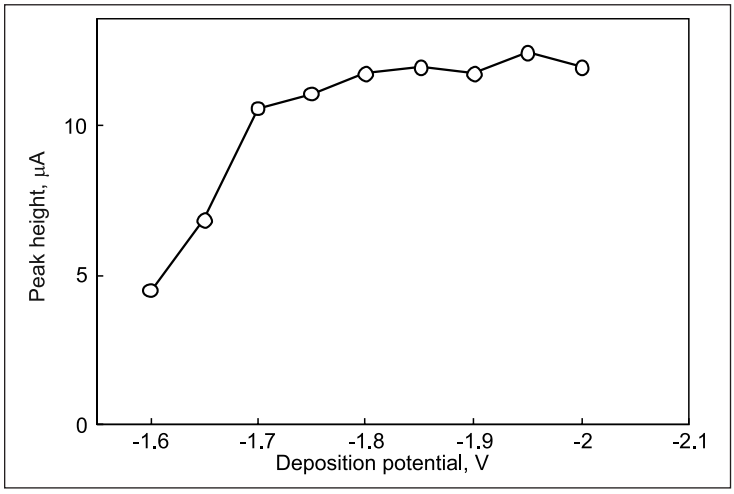

Fig. 2. Dependence of manganese analytical signals on deposition potential. Conditions: drinking water AV with addition of 20 μg l^{-1} Mn^{2+}, accumulation time 5 s

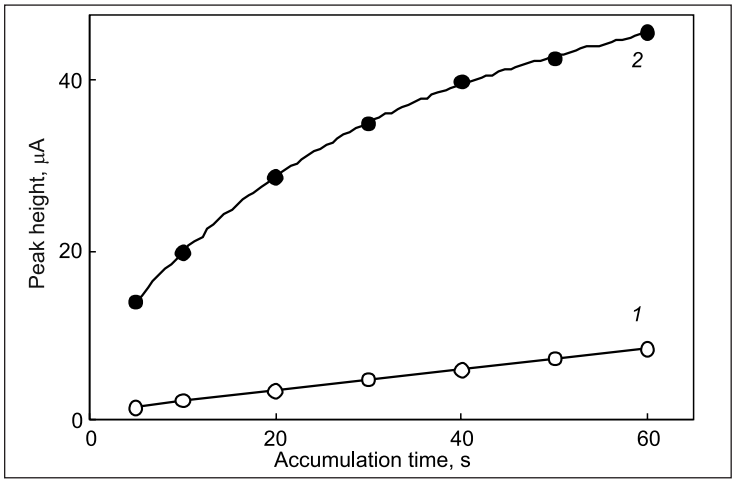

Fig. 3. Dependence of manganese analytical signals on accumulation time in drinking water. *1* – drinking water AV containing 2.3 μg l^{-1} Mn^{2+}, *2* – the same water sample with addition of 20 μg l^{-1} Mn^{2+}. Conditions: deposition potential –1.75 V

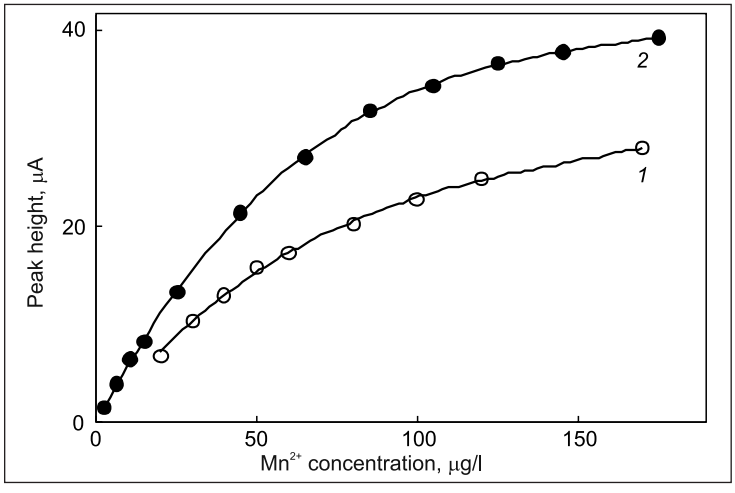

Fig. 4. Dependence of analytical signals on manganese concentration. *1* – 0.0036 mol l^{-1} $NaHCO_3$, *2* – drinking water AV containing 2.5 μg l^{-1} Mn^{2+}. Conditions: deposition potential –1.75 V, accumulation time 5 s

anodic stripping in the quiescent solution. Due to the low accumulation efficiency, the rest period is normally not attributed to the accumulation time, but it has some effect on the analytical signals, especially at short accumulation times.

The dependence of the analytical signals on manganese concentration in $NaHCO_3$ solution and drinking water AV sample is shown in Fig. 4. One can see that the shapes of the curves generally do not favour the quantification of manganese determination results. However, for the manganese concentration range up to 30–40 μg l^{-1}, the dependence may be considered as linear enough ($r \approx 0.9950$) for the method of standard additions. Since the reason for the non-linearity is the same as for the dependence on accumulation time, the linearity range, in principle, could be expanded by using a very short accumulation time. However, the accumulation time shorter than 5 s is not convenient in practical analysis. Therefore, the possibility to dilute the samples having high manganese concentrations before the determination was examined. The sample of drinking water was spiked with 40–60 μg l^{-1} of manganese, and the concentration of manganese was determined by the method of standard additions after a fivefold dilution with 0.0036 mol l^{-1} $NaHCO_3$. The positive error in manganese determination could be expected in the case of deviation from the linearity of the dependence of manganese concentration on the analytical signal. The results of the determination presented in Table 1 show that dilution of a sample can expand the working range of determinable manganese concentrations substantially.

The repeatability of manganese analytical signals was tested by performing a series of 9–10 measurements in $NaHCO_3$ solution and drinking water samples for the manganese concentration range 1.3–50 μg l^{-1}. It has been shown that repeatability does not depend on manganese concentration, and the value of relative standard deviation does not exceed 0.05–0.06. The analytical signals obtained in the same solution using different mercury films are more scattered; however, even in this case the relative standard deviation does not exceed 0.10. However, this higher relative standard deviation does not influence the accuracy of manganese determination because the same mercury film is used during the whole determination procedure by the method of standard additions. Normally, a mercury film is suitable for at least 10–15 manganese deposition / stripping cycles. The detection

Table 1. **Determination of manganese in spiked and diluted drinking water samples. Conditions: drinking water AV sample; fivefold dilution with 0.0036 mol l^{-1} $NaHCO_3$; deposition potential –1.75 V; accumulation time 5 s; initial concentration of manganese in water sample was determined by ASV method**

Mn^{2+} concentration in a sample, μg l^{-1}			RSD ($n = 3$)	Recovery, %
Initial	Added	Determined		
3.4	40	43.8	0.013	100.9
3.4	50	54.3	0.038	101.7
3.4	60	63.6	0.031	100.3

limit evaluation based on three standard deviations for the manganese concentration of 1.5 μg l^{-1} gives the value of about 0.4 μg l^{-1} for a 30 s accumulation time.

The determination of manganese in drinking water by the ASV method does not need any pretreatment of a sample, except that a water sample from the tap should be kept for 0.5–1 hour at room temperature so as to achieve an equilibrium with air gases. Ignoring this equilibration time can result in a worse reproducibility of the analytical signals. Manganese concentrations in such untreated drinking water samples have been found to remain stable for up to one week at room temperature.

To elucidate the possible interferences with the determination of manganese in drinking water, the influence of calcium, magnesium and iron ions was investigated. Normally, drinking water samples AV and VP contain about 60 mg l^{-1} of calcium ions, about 16 mg l^{-1} of magnesium ions and less than 95 μg l^{-1} of iron ions (the allowable maximum value for iron according to [7] is 200 μg l^{-1}). Such concentrations of calcium, magnesium and iron ions were found to have no effect on manganese analytical signals; however, the further artificial increase of calcium and magnesium concentrations gradually decreases the manganese analytical signals. For example, manganese analytical signals are roughly two times lower when calcium and magnesium concentrations 3–4 times exceed the natural level. It is possible that these major ions could form insoluble compounds at the surface of the mercury film when the near-electrode layer of the solution becomes more alkaline during the accumulation step. However, in spite of the lower analytical signals, the manganese concentration determined by the method of standard additions in drinking water samples with increased concentrations of calcium and magnesium ions is very close to that without addition of these major ions. One can see from Table 2 that a fourfold increase of calcium concentration and a sixfold increase of magnesium concentration practically do not influence the manganese determination results. Addition of 0.9 mg l^{-1} iron ions, i. e. increasing the iron concentration about ten times in comparison with natural concentrations, has no effect on manganese determination results, either (Table 2). Moreover, increasing iron ions to at least 1.2 mg l^{-1} did not decrease manganese analytical signals.

Although the speciation of manganese in the water environment depends on a complicated interaction between

Table 2. **The influence of major cations in drinking water on manganese determination. Conditions: drinking water VP sample; deposition potential –1.75 V; accumulation time 5 s**

Concentration of ions added	Mn^{2+} concentration, μg l^{-1} (RSD)		Recovery, %
	before	after	
240 mg l^{-1} Ca^{2+}	34.8 (0.04)	33.3 (0.02)	96
96 mg l^{-1} Mg^{2+}	33.7 (0.08)	32.5 (0.09)	96
0.9 mg l^{-1} Fe^{2+}	36.7 (0.06)	37.1 (0.07)	101

chemical and microbiological factors, the typical manganese species in groundwater are Mn^{2+} ions in weak complexes or ion pairs with major water anions. Therefore, only a few experiments have been performed to test the possible influence of other than Mn^{2+} species on the manganese determination results. It has been found that addition of ascorbic acid as a reducing agent to drinking water samples does not change the manganese determination results. This indicates that there are no electrochemically inert manganese species in drinking water. By the way, manganese analytical signals obtained from the solution of permanganate ions are slightly higher; however, manganese determination results by the method of standard additions are the same as for the solution with Mn^{2+} species.

The results of manganese determination in drinking water samples by the ASV method were compared with those obtained by the standard photometric method employing formaldoxime [21]. For this purpose, water-tap samples were divided to two parts, and manganese content was determined by the ASV and photometric methods. Results of a comparative determination are presented in Table 3. One can see that for drinking water VP samples in which manganese concentration ranges within 70–80 μg l^{-1} the results are really very close, whereas for drinking water AV (concentration range 2–6 μg l^{-1}) relative differences are higher. The statistical paired t-test shows that for a significance level $\alpha = 0.05$ the ASV and standard photometric methods are equivalent for both each type of drinking water samples and the total

Table 3. **Comparison of the results of manganese determination in drinking water by anodic stripping voltammetry and photometric formaldoxime method**

Date	ASV method		Formaldoxime method	
	Mn, μg l^{-1}	RSD	Mn, μg l^{-1}	RSD
Antaviliai wellfield				
12 11 2009	5.8	0.05	6.5	0.27
16 11 2009	6.3	0.10	7.3	0.32
17 11 2009	3.8	0.08	9.7	0.10
18 11 2009	3.8	0.03	2.0	0.35
19 11 2009	2.3	0.16	2.4	0.21
Vingio parkas wellfield				
12 11 2009	81	0.07	74	0.02
16 11 2009	68	0.07	77	0.02
17 11 2009	70	0.11	70	0.02
18 11 2009	79	0.01	79	0.01
19 11 2009	78	0.05	81	0.03

set of the results. On the other hand, it should be noted that for low manganese concentrations the photometric method cannot be considered as very reliable due to its high relative standard deviations of repeated determinations. Another important advantage of the ASV method is its insensibility to iron ions, while their interference is very important for the photometric method.

CONCLUSIONS

Anodic stripping voltammetry using a mercury film electrode can be successfully used for manganese determination in drinking water samples. The working range of determinable manganese concentrations can be expanded up to a few hundred μg l^{-1} by dilution of samples. The detection limit for a 30 s accumulation time is about 0.4 μg l^{-1}, and the relative standard deviations in the working range of manganese concentrations do not exceed 0.10. Calcium and magnesium ions at real concentrations do not interfere directly with manganese determination. A comparison of the ASV method with the standard photometric method for drinking water analysis has shown the equivalence of both methods; however, the ASV method can be used for the determination of low manganese concentrations and is insensitive to iron ions in water samples.

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MANGANO NUSTATYMAS GERIAMAJAME VANDENYJE INVERSINĖS VOLTAMPEROMETRIJOS METODU NAUDOJANT GYVSIDABRIO PLĖVELINĮ ELEKTRODĄ

S a n t r a u k a

Straipsnyje aprašytas mangano nustatymas geriamajame vandenyje inversinės voltamperometrijos metodu naudojant gyvsidabrio plėvelinį elektrodą. Manganui nustatyti vandens mėginio nereikia chemiškai apdoroti. Optimalios nustatymo sąlygos: kaupimo potencialas –1,75 V, kaupimo trukmė 5–30 s, anodinis tirpinimas atliekamas naudojant kvadratinės bangos voltamperometriją. Mangano aptikimo riba kaupiant jį 30 s yra apie 0,4 μg l^{-1}, o santykiniai standartiniai nuokrypiai darbiniame koncentracijų intervale ne didesni kaip 0,10. Realios kalcio, magnio ir geležies jonų koncentracijos geriamojo vandens mėginiuose netrukdo nustatyti manganą. Metodo palyginimas su standartiniu fotometriniu metodu parodė, kad jie yra ekvivalentiški, tačiau elektrocheminis metodas gali būti taikomas labai mažoms mangano koncentracijoms nustatyti, be to, jam netrukdo geriamajame vandenyje esantys geležies jonai.