

Flow Injection Speciation Analysis of Manganese in Real Samples by Diphenylcarbazide-Spectrophotometric Determination

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The flow injection speciation of manganese in aqueous solution using a spectrophotometry method of detection is presented. Manganese (VII) can be determined spectrophotometrically at 308 nm after the reaction with Sym-diphenylcarbazide in buffered at pH = 3.05 with phosphate. Under the optimized conditions, total manganese concentration can also be determined after oxidation of Mn^{2+} to MnO_4^- and then Mn^{2+} concentration can be calculated from the difference. The linear range of determination is 0.047-4.50 mg/l with a 3σ detection limit of 31 $\mu g/l$. The proposed method is applied to the determination of MnO_4^- and Mn^{2+} in effluent streams and foods with a relative standard deviation better than 1.85%. A sampling frequency of up to 24 h^{-1} can be achieved. Interfering ions can be removed by an ion-exchange column built into the flow injection system.

Key Words: Flow-injection, Speciation, Manganese, Effluent streams, Foods.

Introduction

It is known that excessive intake of Mn^{2+} affects human health¹. In public water supplies, MnO_4^- causes such difficulties as the staining of clothes and encrustation of mains². However, although manganese is of little direct toxicological significance, with the exception of the purple-colored permanganates, which have bactericidal properties, it may have a protective effect and control the concentrations of other elements, including toxic heavy metals in surface waters. The average concentration of manganese usually found in natural waters is in the range 0.1-1.0 mg/l. The current World Health Organization (WHO) guideline for manganese levels is 0.5 mg/l for health and 0.1 mg/l to avoid staining problems³.

To the best of our knowledge only a few reagents, such as dimethyldistearylammonium⁴, neoterazolium⁵ and Sym-diphenylcarbazide⁶, have been used for the determination of total manganese concentration spectrophotometrically, and some methods including electron spectroscopy⁷, DPP⁸, chemical modifier-ETAAS⁹,

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chemiluminescence¹⁰ and crosslinked chitosan-FAAS¹¹ are reported for the speciation of manganese. A simple method of Mn^{2+} oxidation to MnO_4^- by sodium bismuthate and determination of this permanganate spectrophotometrically at 526 nm is reported¹¹. The main disadvantage of this method was its poor detection limit, 0.38 mg/l. In order to improve this limit of detection, the same authors used diphenylcarbazide as spectrophotometric reagent and measured the absorbance of the Mn(VII)-diphenylcarbazide complex at 308 nm. With the use of this new spectrophotometric reagent, the detection limit was improved by a factor of 40⁶.

Furthermore, the use of flow injection (FI) makes this system more attractive. FI requires very little sample handling or manipulation and this eliminates many of the stringent clean particles often necessary for standard manganese determinations. FI constitutes the most advanced form of solution manipulation available to analytical chemists for mixing and transporting the reagents and products of a chemical reaction to the point of measurement.

In this paper a flow injection system for MnO_4^- and Mn^{2+} determination based on the concentration of Mn^{2+} oxidation by sodium bismuthate and complex formation of MnO_4^- with diphenylcarbazide is described. The conditions of the experiments were optimized. The analytical figures of merit are evaluated and the concentrations of manganese in some real samples are measured, and the results are compared with those obtained by GFAAS.

Experimental

Reagents and solutions

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise. All aqueous solutions were prepared with re-distilled water. A stock standard Mn^{2+} solution containing 100 mg/l Mn^{2+} was prepared by dissolving 0.3107 g of $MnSO_4 \cdot H_2O$ (May & Baker Ltd, Dagenham, England) and diluting to 1 l with water. The 0.1 mg/l permanganate solution was prepared by dissolving 0.0304 g of $KMnO_4$ (Merck) in 100 ml of water. Working manganese solutions in the range of 0.030-8.00 mg/l were prepared by appropriate dilution of the stock solution with water. The carrier stream, 1.3×10^{-3} mol/l Sym-diphenylcarbazide (S-DPC), was prepared daily by dissolving 78.6 mg of Sym-diphenylcarbazide (May and Baker Ltd) in 60 ml ethanol (Merck) and diluting to 100 ml with phosphate buffer. A phosphate buffer solution with pH=3.05 was prepared by dissolving 11.9898 g NaH_2PO_4 (May & Baker Ltd) and 0.68 ml H_3PO_4 (85% , Merck) and diluting to 500 ml with water. Mn^{2+} of the real and standard samples was oxidized to MnO_4^- by sodium bismuthate¹¹(Merck) prior to determination with S-DPC.

Apparatus and procedure

A Shimadzu atomic absorption spectrometer model AA 670, equipped with a graphite furnace atomizer GFA-4A, an autosampler changer 60G, a graphic printer PR4, and a manganese hollow cathode lamp at wavelength 279.5 nm (Hamamatsu photonics K.K., Japan) and operated at a lamp current of 5 mA and pyrolytic graphite coated graphite tubes were used. The sample injection volume was 20 μ l in all experiments. A schematic diagram of the flow-injection system is given in Figure 1. A variable flow-rate liquid chromatography pump (Bruker, Germany, Model LC22) was used to pump carrier streams and the

sample via a de-gasser (Erma, Tokyo, Model ERC-3522) through the manifold at flow rate of 0.25 ml/min. Manifold lines consisted of 0.8 mm i.d. polyethylene tubing.

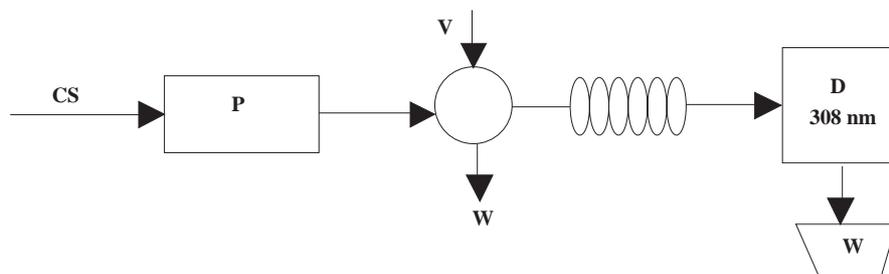


Figure 1. Schematic diagram of the flow-injection system. CS: carrier stream, P: pump, V: injection valve, R: reactor, D: detector, W: waste.

The six-way injection valve (Rheodyne, Model 7125) allowed the sample to be directly loaded into a 20 μ l loop, and subsequently injected into the carrier stream. The injection valve was kept in the load position for the first 10 s of every run to load the sample loop, after which it was switched to the inject position to place the sample plug into the carrier stream. The valve was kept in the inject position for a further 60 s to ensure that the entire sample was flushed out of the sample loop. Switching the valve to the load position to fill the sample loop for the next run followed this. After being placed in the carrier stream, the sample zone was pumped through the reactor. MnO_4^- in the sample zone was reacted with S-DPC in the reactor and the product was channeled to the 10 mm optical path-length flow cell of the variable wavelength UV-VIS spectrophotometric detector (Knauer). The whole procedure, from sample pumping to detection system and data processing and storage, was computer-controlled via ChromStar software for except the injection valve, which had to be done manually.

Results and Discussion

In acidic pH solution (in phosphate buffer with pH of about 3.05), S-DPC reacts with MnO_4^- and produces a soluble orange colored complex with a characteristic strong absorbance at 308 nm⁶. Preliminary tests showed that the DPC-permanganate complex is stable enough to be used for the determination of injected MnO_4^- solution into the S-DPC carrier solution spectrophotometrically in a flow-injection system. Parameters affecting the performance of this FI system were investigated in order to determine the conditions that would produce a linear relationship between signal and concentration over a wide concentration range, with optimum sensitivity, precision and sampling rate.

Optimization of the variables

The performance of the proposed flow-injection system depends on the efficiency of the reaction between MnO_4^- and S-DPC and the stability of this reaction product. The pH, and the concentration of the carrier solution beside the contact time between MnO_4^- and S-DPC are the variables that have the major effects on this efficiency and stability and they must be optimized.

The response of the proposed system was studied in different pH values between 1 and 6. These pH values were established by using phosphate buffer solutions. This experimental test showed a dependence of

the maximum achievable response for MnO_4^- on the pH of the carrier solution. In Figure 2 this dependence is clearly depicted. The peak area of the signal significantly increases from a pH of 1.00 to a pH of 3.05, and decreases afterward. A pH of 3.05 was then selected for further experimental work.

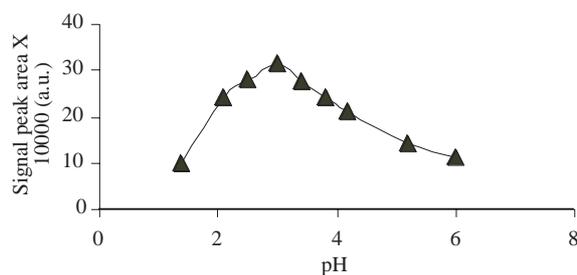


Figure 2. Influence of the carrier solution pH on the analytical signal. $[\text{MnO}_4^-] = 1.75 \mu\text{g/ml}$, Flow rate = 0.25 ml/min, $L = 110 \text{ cm}$ $[\text{S-DPC}] = 0.0013 \text{ mol/l}$.

The contact time between the sample zone containing MnO_4^- and the carrier solution (S-DPC) inside the reactor is very important for the reaction to proceed sufficiently close to completeness. As this contact time depends on the flow rate of the sample zone through the reactor and also the length of the reactor, the carrier stream flow rate and the reactor length. Flow rates between 0.1 and 2.0 ml/min were evaluated. This optimization is shown in Figure 3. The peak area of the signal increases from a flow rate of 0.10 to one of 0.25 ml/min, and then decreases slowly. The optimum flow rate was found to be 0.25 ml/min, which is rather slow, but this also ensures low reagent consumption.

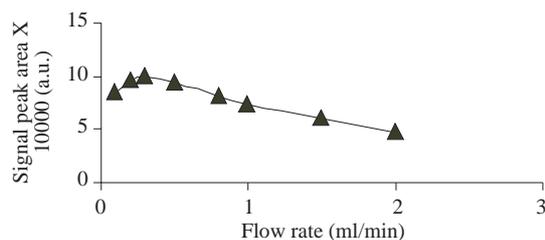


Figure 3. Influence of the carrier flow rate on the analytical signal. $[\text{MnO}_4^-] = 0.513 \mu\text{g/ml}$, $\text{pH} = 3.05$, $[\text{S-DPC}] = 0.0013 \text{ mol/l}$ $L = 110 \text{ cm}$.

The peak area of the analytical signal at a fixed MnO_4^- concentration and optimum pH and flow rate is dependent upon the length of the reactor. The response of the system was studied by varying the reactor length between 30 and 200 cm with the i.d. fixed at 0.8 mm. The results are shown in Figure 4. The peak area significantly increases in length from length 30 cm to 110 cm, remaining nearly constant afterwards. It seems that the reactor length of 110 cm gave sufficient time to the amount of injected MnO_4^- to react a completely reaction with S-DPC. However, 110 cm was chosen as optimum.

Finally the effect of the carrier solution concentration on the performance of the method was evaluated between 0.0001 and 0.003 mol/l. In a series of measurements, a solution with $0.513 \mu\text{g/ml}$ MnO_4^- was analyzed as a function of $[\text{S-DPC}]$ carried through the reactor. The results of these measurements are shown in Figure 5, where the yield is represented by the peak areas. Owing to its S-DPC efficiency the 0.0013 mol/l concentration was chosen as optimal.

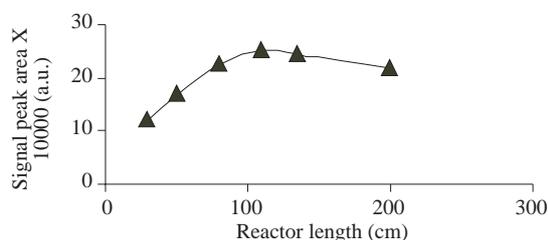


Figure 4. Influence of the reactor length on the analytical signal. $[\text{MnO}_4^-] = 1.28 \mu\text{g/ml}$, $\text{pH} = 3.05$, Flow rate = 0.25 ml/min $[\text{S-DPC}] = 0.0013 \text{ mol/l}$.

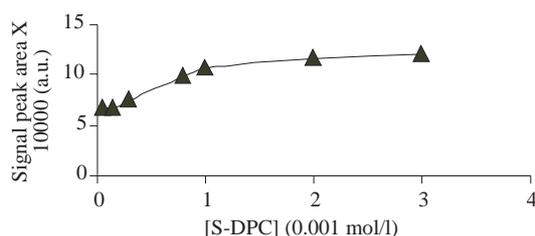


Figure 5. Influence of the Sym-diphenylcarbazide concentration on the analytical signal. $[\text{MnO}_4^-] = 0.513 \mu\text{g/ml}$, $\text{pH} = 3.05$, Flow rate = 0.25 ml/min $L = 110 \text{ cm}$.

Evaluation of the method

Typical analytical signals for the proposed FIA system are shown in Figure 6, which shows the good reproducibility of the FI signals. The linearity of this system was evaluated for MnO_4^- concentrations ranging from 0.03 to $8 \mu\text{g/ml}$ under the optimum experimental conditions mentioned above. The calibration graph was found to be linear in the range 0.047 to 4.5 mg/l and is described by the following equation:

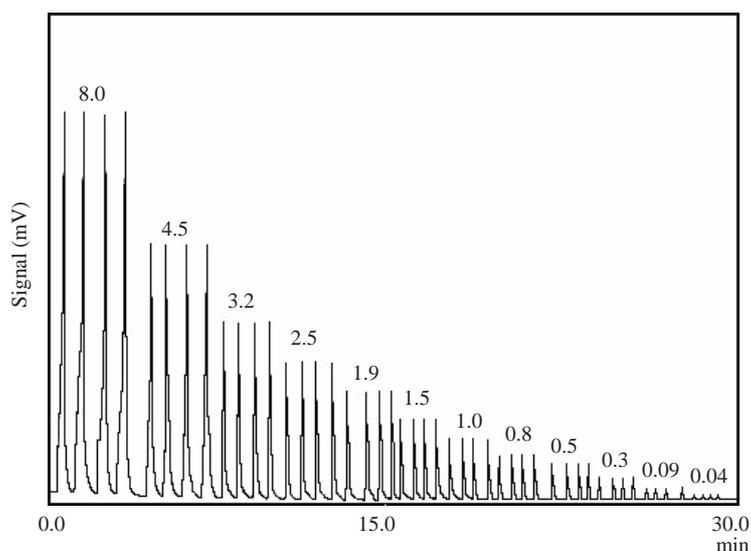


Figure 6. Recorded signals for standard solution of manganese. Values above peaks are concentrations of Mn^{2+} in mg/l . Other experimental conditions are as in Figure 5.

$$Y = 11900 + 169000 X, \quad r = 0.997, \quad n = 11$$

where Y is peak area in arbitrary units, X is the analyte concentration (mg/l), r is the correlation coefficient and n is the number of determinations.

The detection limit was calculated using the equation $D.L. = 3S_{bk}/m$, where S_{bk} is the standard deviation of the blank signal and m is slope of the calibration graph. The calculated detection limit was found to be 0.031 mg/l. The precision of the method was determined by 11 repetitive analyses of standard solutions under optimum conditions. The relative standard deviation (RSD) was 1.85%.

The interference effects of different ions that might be present with manganese in real samples have been reported⁶. Tolerance is defined as the maximum weight ratio of ion to manganese ion concentration producing an error of $\pm 5\%$ peak area in the determination of 1.5 mg/l manganese. According to this work the only interferences for the determination of manganese at 308 nm are cations and anions (Na^+ , Ca^{2+} , Mg^{2+} , Co^{3+} , NO_3^- , SO_4^{2-} , CO_3^{2-} , CH_3COO^- , SCN^- , $C_2O_4^{2-}$, SO_3^{2-} and halides) with a weight ratio up to 110. The only interferences are colored metal ions, Fe^{3+} , Ni^{2+} , V(V) and Cu^{2+} , with a weight ratio of 15 and Hg^{2+} , Cd^{2+} and $Cr_2O_7^{2-}$ with a weight ratio of 1. Interferences caused by the interfering anions can be avoided by passing the samples through an anion exchange column (Dowex-100- NO_3^- , Merck) prior to the oxidation of Mn^{2+} by $NaBiO_3$. To eliminate the interference effect of cations we can pass the samples through a cation exchanger IV- Na^+ (Merck) after oxidizing the Mn^{2+} by $NaBiO_3$ and before injecting the sample into the S-DPC carrier solution.

To test the applicability of the proposed method further, some natural food samples containing manganese were analyzed. Flow injection determinations were carried out in a measuring system equipped with ion-exchange columns. These samples were also analyzed by the standard method of graphite furnace atomic absorption spectrometry¹². The results for the determination of manganese in the samples of beans, lentils, apples and hazelnuts are presented in Table 1. The relative error was between -2.41 and 2.04%.

Table 1. Comparison of the results obtained for natural foods samples using the proposed FIA method and AA standard methods.

Sample	Mn concentration ($\mu g/g$)				% Difference with respect to GFAAS Results
	GF-AAS method	RSD % N = 4	proposed method	RSD % N = 6	
Haricot bean	61.8	2.01	62.3	1.49	0.81
Lentil	52.1	1.99	51.2	1.68	-1.73
Apple	39.3	2.27	40.1	1.57	2.04
Hazelnut	37.4	2.21	36.5	1.85	-2.41

Analyzing several synthetic mixtures containing standard MnO_4^- and Mn^{2+} in the real samples (Zahedan City and Hyrmand river waters, see Table 2) also tested the method. The precision and accuracy of the method are satisfactory. The recovery for the proposed FIA system was also determined. Samples from effluent streams were spiked with standard Mn^{2+} solutions and analyzed and the recovery calculated. The recovery ranged between 97.1 and 99.16%, which was reasonable.

Table 2. Simultaneous determination of MnO_4^- and Mn^{2+} in synthetic mixtures of spiked and standard MnO_4^- and Mn^{2+} in Zahedan city and Hyrmand river water^a samples.

Samples	Manganese added (mg/l)		Manganese found (mg/l)			
	MnO_4^-	Mn^{2+}	MnO_4^-	RSD % N = 6	Mn^{2+} N = 6	RSD %
City water1	1.099	0.275	1.100	1.45	0.272	1.80
City water2	0.824	0.549	0.790	1.70	0.545	1.78
Hyrmand river1	0.549	0.824	0.546	1.64	0.807	1.47
Hyrmand river2	0.275	1.099	0.280	1.71	1.011	1.44

^aIn the South of Iran

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