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Speciation of Manganese Using a Pneumatic Flow Injection Analysis-Tandem Spectrometer System

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A pneumatic flow injection-tandem spectrometer system, without a delivery pump, was used for the speciation of manganese (Mn). In this system the suction force of the pneumatic nebulizer of a flame atomic absorption spectrometer (FAAS) was used for solution delivery through the manifold. Mn(VII) and total Mn (Mn(VII) and Mn(II)) concentrations were determined using a UV-Vis spectrometer and FAAS, respectively. The Mn(II) concentration was determined by the difference between the two. The calibration curves were linear up to 15.00 mg L⁻¹ for Mn(VII) and total Mn, with a detection limit of 0.08 mg L⁻¹ and 0.05 mg L⁻¹ for Mn(VII) and Mn, respectively. The mid-range precision and accuracy were < 1.89% and ± 2.50% for the 2 species, respectively, at a sampling rate of 80 samplings h⁻¹. This system was used for the determination of Mn(VII) and Mn(II) in spiked and natural water, as well as industrial water.

Key Words: Pneumatic flow injection analysis, tandem spectrometer, manganese, speciation, UV-Vis spectrometer, flame atomic absorption spectrometer.

Introduction

Manganese (Mn) is an essential element for humans and plants. It participates in hemopoietic functions and the transmission of genetic information.^{1,2} Mn deficiency in humans is related to delayed blood coagulation and hypercholesterolemia, and abnormal Mn metabolism can contribute to diabetes mellitus.³ Furthermore, it is useful to the synthetic process of thiamine and ascorbic acid.⁴ However, many problems can occur when the concentration of Mn is beyond a certain limit. In public water supplies, Mn causes such difficulties as the staining of clothes and plumbing fixtures (black water), and encrustation of water mains. However, although Mn is of little direct toxicological significance, with the exception of the purple permanganates (MnO₄⁻), which have bactericidal properties, it may have a protective effect and control the concentrations of other

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elements, including toxic heavy metals in surface waters. Therefore, the determination of Mn in public and industrial water is important for the environment and for human health. The concentration of Mn found in natural water is generally quite low. Although the concentration in certain reservoirs has at times been as high as 10.00 mg L^{-1} , average concentrations are usually $0.10\text{-}1.00 \text{ mg L}^{-1}$.⁵ The current World Health Organization (WHO) guideline for maximum Mn levels is 0.50 mg L^{-1} for human health and 0.10 mg L^{-1} to avoid staining problems.⁶

Few reports have been published on the determination of different oxidation states of Mn, including titration⁷ for Mn(III)/Mn(IV), electron spectroscopy for chemical analysis (ESCA)⁸ of Mn(II)/Mn(III)/Mn(IV), direct current polarography (DCP) and differential pulse polarography (DPP)⁹ for Mn(III)/Mn(II), and polarographic determination of Mn in gasoline triethanolamine complexes of Mn(II) and Mn(III),¹⁰ as well as crosslinked chitosan flame atomic absorption spectrometry,¹¹ chemiluminescence,¹² modified carbon paste electrode,¹³ and flow injection analysis (FIA)-spectrophotometry⁴ for Mn(II)/Mn(VII). Moreover, different instrumental methods for Mn speciation have been summarized by Pearson and Greenway.¹⁵ However, there are several disadvantages of using these methods, such as the use of complicated chemical systems and techniques, using expensive reagents, low selectivity, and low sample frequency. Moreover, some methods require 2 determinations for each sample: first determining one of the species, followed by reduction/oxidation of the corresponding redox form and quantification of the total amounts of Mn or other species.

Flow techniques present several useful analytical features: in particular, the possibility to attain high sample throughput, and minimal sample handling or manipulation, which eliminates many of the stringent clean particles often necessary for standard Mn determination. FIA 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. Four basic sections of an FIA system are as follows: pump, injector valve-loop, reactor, and detector. The pump is the heart of an FIA system. Different kinds of pumps, such as a peristaltic pump, HPLC pump, and syringe pump, have been used in all FIA systems.^{16,17}

Herein, the authors report the designed of a simple, cheap, and fast pneumatic FIA-tandem spectrometer (PFIA-TS) system to work without the usual pumps, for the speciation of Mn(VII) and Mn(II). The method is suitable for Mn speciation with only one injection and without the need to use an oxidant/reductant in the carrier stream. This technique has been designed with the aim to combine the advantages of an FIA system and 2 kinds of spectrometry. The basic element of PFIA-TS is using the suction force of the pneumatic nebulizer of an FAAS for solution delivery (carrier) through the FIA manifold. Therefore, the usual pumps in FIA systems have been eliminated. The potentials of the automated methodology were evaluated using the spectrophotometric monitoring of Mn as a model of chemistry. In this system, Mn(VII) and total Mn (Mn(VII) and Mn(II)) concentration were determined using a UV-Vis spectrometer and FAAS, respectively. The Mn(II) concentration was determined by the difference between the two.

Experimental

Reagents

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(II) solution containing 100.00 mg L^{-1}

Mn(II) was prepared by dissolving 0.3107 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (May & Baker Ltd, Dagenham, UK) and diluting to 1 L with water. The 100.00 mg L^{-1} Mn(VII) solution was prepared by dissolving 0.0304 g of KMnO_4 (Merck) in 100 mL of water. Working standard solutions of Mn(VII) and Mn(II) used for calibration were prepared by the appropriate dilution of the above solutions. Water of pH 6.1 was used as the carrier solution. Stock solutions of interfering ions (1.00 mg L^{-1}) were prepared by dissolving the appropriate salts in water.

Apparatus

A scheme of the single-line PFIA-TS system is presented in Figure 1. In this system, the suction force of the pneumatic nebulizer of a Philips FAAS (Model PU 9110X) was used for solution delivery (carrier) through the manifold. A 6-way injection valve (Rheodyne, Model 7125) allowed the sample to be loaded directly into a $400\text{-}\mu\text{L}$ loop, and subsequently injected into the carrier stream. Manifold lines consisted of 0.8-mm i.d. polyethylene tubing. The injection valve was kept at the loading position for the first 5 s of every run, to load the sample. Then, it was switched to the injection position to inject the sample to the carrier stream. The valve was kept in the injection position for another 30 s to ensure that the entire sample was flushed out of the sample loop. Next, the valve was again switched to the loading position to fill the sample loop for the next run. The generated products were channeled to the 10-mm long optical flow cell and Knauer UV-Vis detector at 526 nm, and then to a Philips FASS (Model PU 9110X) with an air-acetylene flame and 5-cm long optical path (burner). The carrier flow rate in this manifold was 2.1 mL min^{-1} . The signals from the UV-Vis detector were performed with a computer via Chromstar software (Bruker, Germany). The light source for the FAAS was a Mn hollow cathode lamp. The wavelength was set to 279.5 nm with a spectral slit-width of 0.5 nm and a lamp current of 9 mA.

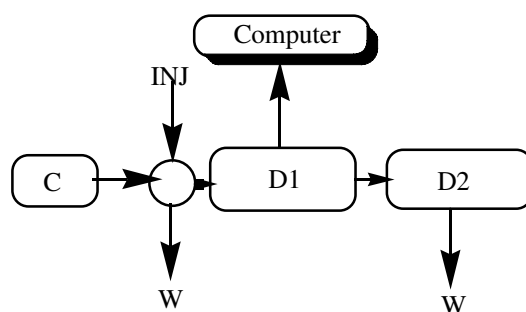


Figure 1. Schematic diagram of the PFIA-TS system used for the speciation of manganese. C: carrier (water with pH 6.1); INJ: injector loop valve; D1: UV-Vis detector; D2: FASS detector; W: waste.

Results and Discussion

Optimization of the experimental condition

The performance of the proposed flow injection system depended only on the loop volume. In this system, the carrier is water and one analyte, MnO_4^- , a color compound; therefore, optimization for reactor length is not necessary. The response of the system was also studied for various sample injection volumes (loop volume) (20, 80, 100, 150, 300, 400, 500, 1000, and 2000 μL). The peak height increased with an increase in

volume. Larger volumes resulted in higher, yet broader peaks. Consequently, the sampling frequency and the peak capacity sharply decreased. A 400- μ L volume was selected as the loop volume.

Sample matrix interferences

The investigation of interferences was carried out for the determination of Mn(VII) with a UV-Vis detector by adding the interfering compounds to a Mn(VI) standard solution. The tolerance limit was defined as the concentration of foreign compounds resulting in $\pm 5.0\%$ error in the determination of 5.00 mg L⁻¹ Mn(VII). According to this work, no interference was observed from the compounds, such as Al(NO₃)₃, Ca(NO₃)₂, Mg(NO₃)₂, KNO₃, NaNO₃, Ni(NO₃)₂, KNO₃, K₂SO₄, and K₂CO₃ with weight ratio up to 250, Zn(NO₃)₂, Cd(NO₃)₂, Mn(NO₃)₂, Cu(NO₃)₂, Pb(NO₃)₂, KCl, and KBr with weight ratio up to 95, and CH₃COOK.

Calibration plot and precision

A typical response of the UV-Vis detector in optimum conditions is shown in Figure 2. The results show the stability of the flow rate and repeatability of the proposed system. The linearity of the response was evaluated for analyte concentrations ranging from 1.00 to 100.00 mg L⁻¹ under the above experimental conditions. The calibration graphs were linear up to 15.00 mg L⁻¹ for Mn(VII) and total Mn, which are described by the following equations:

$$\text{P-H} = 56.989 [\text{Mn(VII)}] + 4.683, n = 11, r = 0.9994$$

$$\text{Abs.} = 0.0591 [\text{Mn}] + 0.009, n = 11, r = 0.9990$$

where P-H is peak height in arbitrary units (for UV-Vis detector signals), [Mn(VII)] and [Mn] are the MnO₄⁻ and total Mn concentrations, n is the number of determinations, and r is the correlation coefficient. The detection limits (DLs) were defined as the analyte concentration equal to 3 times the standard deviation of the most diluted standard solution. DLs were 0.08 and 0.05 mg L⁻¹ for Mn(VII) and Mn, respectively. For validation and applications to evaluate the analytical applicability of the method and to check its accuracy and precision, synthetic aqueous mixtures containing Mn(VII) and Mn(II) were analyzed. The precision and accuracy of the method were determined by 7 replicate analyses of standard solutions under optimum conditions. The mid-range precision and accuracy were < 1.89% and $\pm 2.50\%$ for the 2 species, respectively, at a sampling rate of 80 samplings h⁻¹. According to the results presented in Table 1, the concentrations of Mn(VII) and Mn(II) obtained with the proposed method are in good agreement with the expected values.

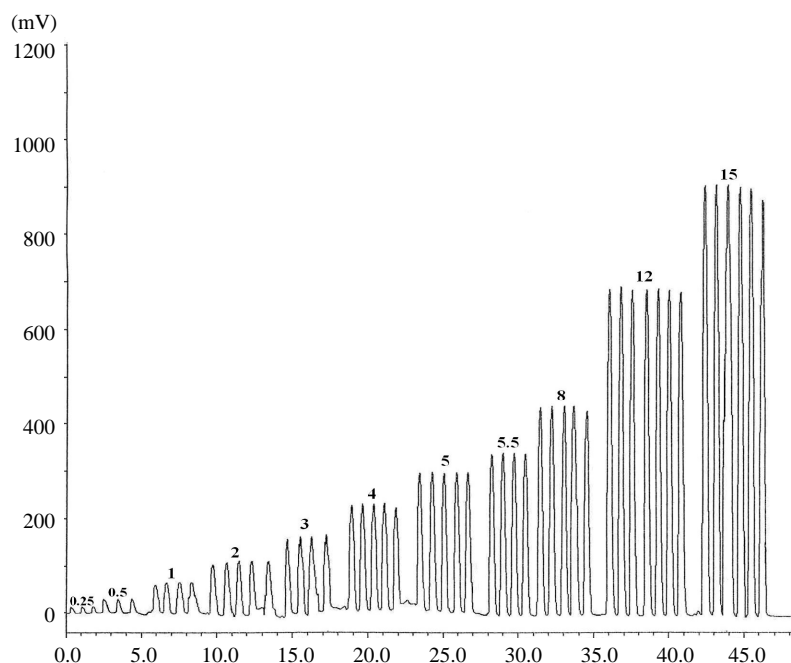


Figure 2. Typical analytical signals of the UV-Vis detector (D1) for determination of MnO_4^- with the PFIA-TS system. Values above peaks are concentration of MnO_4^- in mg L^{-1} .

Table 1. Determination results for Mn(VII) and Mn(II) in synthetic aqueous mixtures.

added/ mg L^{-1}		Total found / mg L^{-1}	Mn(VII)/ mg L^{-1} , (n = 7)			Mn(II)/ mg L^{-1} , (n = 7)		
Mn(VII)	Mn(II)		found	RSD (%)	RE (%)	found	RSD (%)	RE (%)
2.00	4.00	6.06	1.99	1.61	-0.50	4.07	0.88	1.75
2.00	8.00	9.98	2.02	1.85	1.00	7.96	0.50	-0.50
3.00	2.00	5.04	3.01	0.97	0.33	2.03	1.27	1.50
3.00	3.00	5.99	2.96	1.37	-1.33	3.03	1.04	1.00
4.00	2.00	6.03	3.98	1.89	-0.50	2.05	0.98	2.50
4.00	6.00	10.07	3.95	1.63	-1.25	6.12	0.57	2.00
5.00	5.00	10.03	4.94	0.82	-1.20	5.09	0.80	1.80

The proposed method was applied to the analysis of various water samples collected from different locations in Iran. The samples were filtered (Whatman filter No. 1) and determined by the proposed method. Initial concentration of Mn in these samples was determined before spiking. After spiking the samples with known amounts of Mn(VII) and Mn(II), excellent recoveries were obtained and no matrix interference was observed (Table 2). Recoveries for Mn(VII) and Mn(II) were $100.0 \pm 3.0\%$.

Table 2. Determination results and recoveries for Mn(VII) and Mn(II) speciation in water samples collected at different locations in Iran (n = 5).

Sample	added / $\mu\text{g mL}^{-1}$		Mn(VII) found	Recovery	Mn(II) found	Recovery
	Mn(VII)	Mn(II)	/ $\mu\text{g mL}^{-1}$ (n=5)	%	/ $\mu\text{g mL}^{-1}$ (n=5)	%
Sample 1 ^a	0.00	0.00	0.00	-	0.00	-
	2.00	3.00	2.05	102.5	2.98	99.3
	2.00	8.00	1.98	99.0	8.18	102.3
	4.00	6.00	4.05	101.3	6.12	102.0
Sample 2 ^b	0.00	0.00	0.00	-	0.00	-
	2.00	4.00	1.99	99.5	4.04	101.0
	3.00	3.00	2.99	99.7	3.06	102.0
	4.00	4.00	3.97	99.3	4.07	101.8
Drinking water	0.00	0.00	0.00	-	0.00	-
Zahedan city	4.00	2.00	4.09	102.3	1.99	99.5
	2.00	3.00	1.96	98.0	3.02	100.7
	3.00	5.00	2.97	99.0	5.10	102.0
Undrinking water	0.00	0.00	0.00	-	0.00	-
Zahedan city	3.00	2.00	3.05	101.7	3.05	101.7
	1.00	4.00	1.02	102.0	1.03	103.0
	0.5	3.00	0.49	98.0	0.49	98.0
Caspian sea water	0.00	0.00	0.00	-	0.00	-
	3.00	2.00	3.04	101.3	2.02	101.0
	5.00	5.00	4.97	99.4	5.13	102.6
	2.00	4.00	1.95	97.5	4.12	103.0
Groundwater	0.00	0.00	0.00	-	0.00	-
	1.00	5.00	0.97	97.0	5.05	101.0
	3.00	2.00	2.98	99.3	2.06	103.0

^a input water of Neka thermal power station in Iranian Mazandaran province.^b output water of Neka thermal power station in Iranian Mazandaran province.

Conclusions

The results of this work demonstrated the application of a FIA-tandem spectrometer for the speciation analysis of trace Mn(VII) and Mn(II) in water samples. In the proposed system, the pump usually used in a FIA manifold was eliminated and the suction force of the pneumatic nebulizer of an FAAS was used for solution delivery through the manifold. In this system, Mn(VII) and total Mn concentration are determined using a UV-Vis spectrometer and an FAAS, respectively. The method is very simple, rapid, accurate, and

has good sensitivity and selectivity. It provides good reproducibility of results (RSD < 1.89%), which is superior to other speciation methods already described in the literature. The proposed system is inexpensive, stable, and available in every laboratory.

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