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Determination of manganese in water samples by flame atomic absorption spectrometry after cloud point extraction

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Cloud point extraction has been used for the preconcentration of manganese, after the formation of a complex with 1-(2-thiazolylazo)-2-naphthol (TAN), and later analysis by flame atomic absorption spectrometry using octylphenoxypolyethoxyethanol (Triton X-114) as surfactant. The chemical variables affecting the separation phase and the viscosity affecting the detection process were optimized. Under the optimum conditions (*i.e.*, pH = 9.2, [TAN] = 2.0×10^{-5} mol l^{-1}, [Triton X-114] = 0.05%, added methanol volume = 0.2 ml), preconcentration of 50 ml of sample solution permitted the detection of 0.28 ppb for manganese. The enhancement factor was 57.6. The proposed method has been applied to the determination of manganese in water samples.

Introduction

Manganese is a necessity for the proper function of several enzymes and is an essential micro-nutrient for the function of the brain, nervous system and normal bone growth. It is present in large quantities in various steel materials as a hardening agent. It also finds application in pharmaceutical preparations. However, excessive intake can cause lesions, headache, psychotic behavior, drowsiness and other related symptoms and/or diseases. Thus manganese is an important element from the environmental perspective.

In general, concentrations of manganese in fresh waters[1] are within the range 0.02 to 130 μg l^{-1}. Therefore the determination of this metal as Mn^{2+} ion often requires a method offering low detection limits. Although atomic spectrometric methods are a powerful analytical tool for the determination of trace elements in environmental samples, preconcentration techniques combined with AAS[2] are still necessary. The iminodiacetate-containing resin Chelex-100 is the most commonly employed chelating resin for the removal and preconcentration of trace heavy metals from waters.[3–5] A chelating poly(dithiocarbamate) resin (PDTC) has been proposed by Yebra-Biurrun *et al.*[6] for the preconcentration of manganese from water samples prior to its determination by flame atomic absorption spectrometry. However, that technique is rather time-consuming and requires a large amount of sample.

Separations and preconcentration based on cloud point extractions are becoming an important and practical application of the use of surfactants in analytical chemistry.[7] Preconcentration steps based on phase separation by cloud point extraction (CPE)[8–10] offer a convenient alternative to more conventional extraction methods. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, speedy and of lower toxicity to the environment than those concentration extractions that use organic solvents. The CPE method also provides results comparable to those obtained with other separation techniques. Accordingly, any species that interacts with the micellar system, either directly (generally hydrophobic organic compounds) or after a prerequisite derivatization reaction (*i.e.*, metal ions after reaction with a suitable hydrophobic ligand) can be extracted from the initial solution and may also be preconcentrated.

The cloud point methodology has been used to separate and preconcentrate organic compounds prior to their determination in a hydrodynamic analytical system such as high performance liquid chromatography (HPLC)[11–18] and CE.[19]

The phase separation phenomenon has also been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes.[20–27] This method was used for the first time to preconcentrate zinc (II),[28] using 1-(2-pyridylazo)-2-naphthol (PAN) as the hydrophobic ligand and the surfactant PONPE 7.5 as the extraction medium. Later, the same ligand and the surfactant Triton X-114 were used for the preconcentration of cadmium,[29] nickel and zinc.[30] Recently, this method was used to determine lead[31] and for the speciation of chromium.[32]

In the present work we report on the results obtained in a study of the cloud point preconcentration of manganese, after the formation of a complex with TAN, and later analysis by flame atomic absorption spectrometry using Triton X-114 as surfactant. The proposed method was also applied to the determination of manganese in water samples.

Experimental

Apparatus

A Shimadzu AA-680 atomic absorption/flame emission spectrometer (Shimadzu, Japan) equipped with deuterium background correction and manganese hollow-cathode lamps (Shimadzu, Japan) as the radiation source were used. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The sample and the acetylene flow rates and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution (1.0 μg ml^{-1}) in methanol containing 0.1 mol l^{-1} nitric acid. An MP4 centrifuge (International Equipment Company, USA) was used to accelerate the phase separation.

Reagents and solutions

The non-ionic surfactant Triton X-114 was obtained from Sigma and was used without further purification. Stock standard

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solutions of manganese at a concentration of 1000 μg ml^{-1} were obtained from Spectrosol. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A solution of 2.0 × 10^{-3} M TAN (Lancaster, Morecambe, UK) in Triton X-114 was prepared from the commercially available product. A stock standard buffer solution, 0.05 mol l^{-1}, was prepared by dissolving the appropriate amount of $Na_2B_4O_7 \cdot 10H_2O$ in water. Nitric acid (Merck, GR) and methanol (Merck, HPLC grade) were used. Water was doubly distilled in a purity still and purified with a Milli-Q system (Millipore, Bedford, MA, USA). The materials and vessels used for trace analysis were soaked in 10% nitric acid for at least 24 h and subsequently washed four times with Milli-Q water.

Procedures

For the cloud point extraction, aliquots of the cold solution containing the analyte, Triton X-114 and TAN, buffered at a suitable pH, were kept for 15 min in the thermostatic bath at 40 °C. Since the surfactant density is 1.37 g ml^{-1}, the surfactant-rich phase typically settles through the aqueous phase. The separation of the phase is accelerated by centrifuging at 5000 rpm for 15 min. After cooling in an ice-bath, the surfactant-rich phase became a viscous phase, which could then be separated by inverting the tubes to discard the aqueous phase. In a later step, in order to reduce the viscosity and facilitate sample handing, 200 μl of a solution of methanol containing 0.1 mol l^{-1} HNO_3 were added to the surfactant-rich phase. The samples were introduced into the flame by conventional aspiration.

Tap water, river water, sea water and reservoir water samples were filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter and were stored at 6 °C in the dark. To 50 ml of water sample, 1.0 ml of a solution containing 2.6% Triton X-114 and 1.0 × 10^{-3} mol l^{-1} TAN and 1.0 ml of 0.1 mol l^{-1} $Na_2B_4O_7 \cdot 10H_2O$ buffer solution (pH 9.2) were added. After phase separation, the above steps were followed.

Results and discussion

Effect of pH

Cloud point extraction of manganese was performed in different pH buffer solutions. The separation of metal ions by the cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, thus obtaining the desired preconcentration. Extraction yield depends on the pH at which complex formation is carried out.

Fig. 1 shows the effect of pH on the extraction of manganese complexes. It can be seen that the yield increases with an increase in pH up to 9, thereafter the yield is almost constant and close to 100%. Hence the optimum pH value of 9.2 was chosen for the analytes. In addition, the influence of the buffer amount was assessed, while the other experimental variables, except buffer solution amount, remained constant. The results have shown that if 0.5 ml or larger volume of buffer solution was added in 50 ml solution, no obvious variation took place in the extraction yield. Therefore it was concluded that addition of 1.0 ml of buffer solution throughout the course of experiment would serve the purpose.

Effect of the TAN concentration

The yield of the extraction as a function of the concentration of the complexing agent is shown in Fig. 2. 50 ml of a solution of 7.27 × 10^{-7} mol l^{-1} manganese in 0.05% Triton X-114, buffered at pH 9.2, containing various amounts of TAN were subjected to the cloud point preconcentration process. The yield increases up to a TAN concentration of 8 × 10^{-6} mol l^{-1} and reaches 100% extraction efficiency. A concentration of 2 × 10^{-5} mol l^{-1} was chosen to account for other extractable species that might potentially interfere with the assaying of manganese.

Effect of Triton X-114 concentration

The variation in extraction efficiency within the Triton X-114 range, 0.01–0.5% w/v, was examined. Quantitative extraction was observed when the Triton X-114 concentration was above 0.05% and this concentration was chosen in order to achieve a good preconcentration factor. The results are shown in Fig. 3.

Effect of viscosity on the analytical signal

Since the surfactant-rich phase obtained after cloud point extraction is very viscous, methanol containing 0.1 mol l^{-1} nitric acid was added to the surfactant-rich phase after the separation of phases, in order to facilitate its introduction into the nebulizer of the spectrometer. Fig. 4 shows the variation of the analytical signal normalized as a function of the volume of

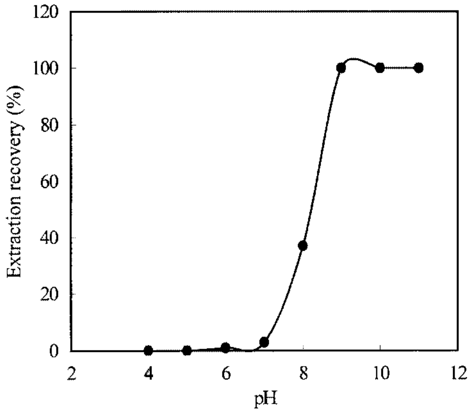

Fig. 1 Effect of pH on the extraction recovery of manganese. Conditions: 7.27 × 10^{-7} mol l^{-1} Mn, 2 × 10^{-5} mol l^{-1} TAN and 0.05% Triton X-114. Other experimental conditions are described under Procedures.

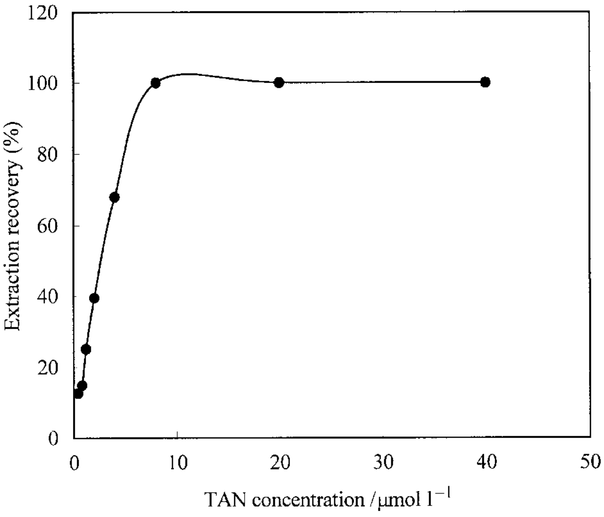

Fig. 2 Effect of TAN concentration on the extraction recovery of manganese. Conditions: 7.27 × 10^{-7} mol l^{-1} Mn, 0.05% Triton X-114 and pH 9.2. Other experimental conditions are described under Procedures.

methanol added to the surfactant-rich phase obtained after phase separation. Obviously, there is an optimum volume of methanol, 100 μl, with respect to absorbance signals. For added volumes of methanol of $\leq$100 μl, the signals are lower because the viscosity is still high and clearly predominates over the dilution. For larger added volumes, the decrease in viscosity of the sample is lower and it is essentially predominated by the effect of dilution. 200 μl of a solution of methanol containing 0.1 mol l^{-1} HNO$_3$ therefore serves as the optimal volume needed to add to the surfactant-rich phase, which will ensure a smooth direct aspiration into the FAAS.

Calibration, precision and detection limits

Calibration curves were obtained by preconcentrating 50 ml of a standard sample solution in the presence of 0.05% Triton X-114 in medium buffered at pH 9.2. The concentrated samples were introduced into the flame by conventional aspiration following the addition of 200 μl of a methanol solution containing 0.1 mol l^{-1} HNO$_3$. In this case, linear relationships between the absorbance measured and the concentration of metal present in solution were obtained. Table 1 gives the parameters of the calibration curves, the relative standard deviation obtained for 5 replicates subjected to the complete procedure at two different concentration levels, and the detection limits. Preconcentration of 50 ml of sample in the presence of 0.05% Triton X-114 permitted the detection of 0.28 ppb for manganese. The enhancement factor, calculated as the ratio of absorbance of preconcentration samples to that obtained without preconcentration, was 57.6.

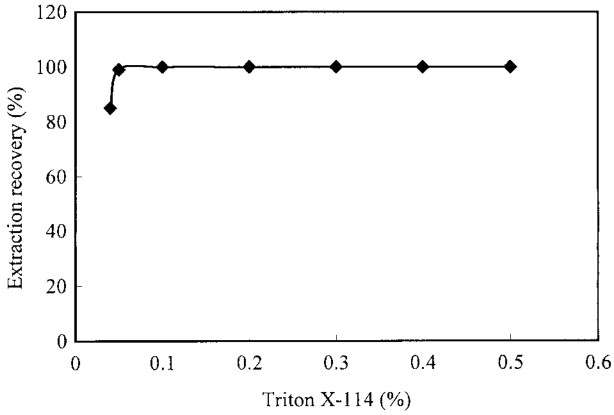

Fig. 3 Effect of Triton X-114 concentration on the extraction recovery of manganese. Conditions: 7.27 × 10^{-7} mol l^{-1} Mn, 2 × 10^{-5} mol l^{-1} TAN and pH 9.2. Other experimental conditions are described under Procedures.

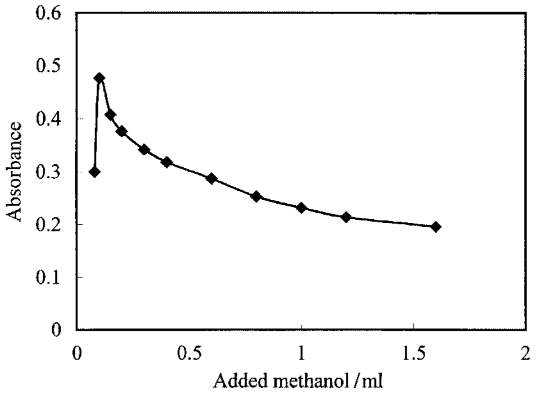

Fig. 4 Effect of added methanol volumes on absorbance of manganese. Conditions: 7.27 × 10^{-7} mol l^{-1} Mn, 2 × 10^{-5} mol l^{-1} TAN, 0.05% Triton X-114 and pH 9.2. Other experimental conditions are described under Procedures.

Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. Other cations that may react with TAN were studied. The results are shown in Table 2 and prove that manganese recoveries are almost quantitative in the presence of interfering cations.

Determination of manganese in water samples

In order to test the reliability of the proposed methodology, it was applied to the determination of manganese in tap water, river water, sea water and reservoir water.

For this purpose, 50 ml of each of the samples were preconcentrated with 0.05% Triton X-114 and a TAN concentration of 2.0 × 10^{-5} mol l^{-1} following the proposed method. The results are shown in Table 3. For calibration, the working

Table 1 Analytical characteristics of the method

Concentration range (ppb)	0–120
Slope	(8.30 ± 0.14) × 10^{-3}
Intercept	0.010 ± 0.003
Correlation coefficient (*r*)	0.9985
RSD (%) (n = 5)[a]	2.17
LOD (ppb)[b]	0.28

[a] Manganese concentration was 10 ppb for which the RSD was obtained.

[b] LOD, limit of detection, calculated as three times the standard deviation (3σ) of the blank signal.

Table 2 Effect of foreign ions on the preconcentration and determination of manganese

Ions	Ion/Mn (w/w)	Recovery (%)
Na$^+$	1000	100.6
K$^+$	1000	101.6
Ca^{2+}	1000	102.2
Mg^{2+}	1000	105.0
Al^{3+}	1000	100.8
Cd^{2+}	20	98.3
Co^{2+}	20	103.1
Cu^{2+}	20	100.0
Ni^{2+}	20	100.6
Fe^{3+}	20	95.6
Pb^{2+}	20	99.5
Zn^{2+}	20	103.3

Table 3 Determination of Mn in water samples (n = 3)

Samples	Concentration[a] (ppb)	Added (ppb)	Measured (ppb)	Recovery (%)
Tap water	2.86 ± 0.15	—	—	—
		10.0	12.5	96.4
		20.0	22.5	98.2
River water	1.86 ± 0.15	—	—	—
		10.0	12.2	103
		20.0	21.7	99.2
Sea water	7.22 ± 0.16	—	—	—
		10.0	17.0	97.8
		20.0	26.6	96.9
Reservoir water	2.16 ± 0.12	—	—	—
		10.0	12.5	103
		20.0	22.6	102

[a] Average of three determinations with 95% confidence level.

standard solutions (0–30 ppb) were submitted to the same preconcentration procedure as used for the sample solutions.

In addition, the recovery experiments of different amounts of manganese were carried out. The results are also shown in Table 3 and confirm the validity of the proposed method.

Conclusions

Cloud point extraction is an easy, safe, environmentally friendly, rapid and inexpensive methodology for the preconcentration and separation of trace metals in aqueous solutions. Triton X-114 is of relatively low-cost and low toxicity. TAN is a very stable, and fairly selective complexing reagent. The surfactant-rich phase can be directly introduced into the nebulizer of a flame atomic absorption spectrometer by dilution with acidified methanol. The proposed method can be applied to the determination of trace metals in various water samples and other environmental samples.

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