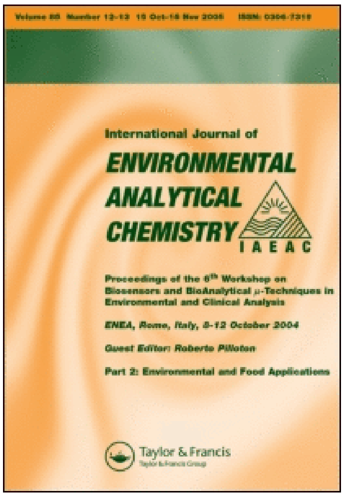

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Atomic Absorption Spectrometric Determination of Traces of Manganese in Natural Waters and Wastewaters after Extractive Separation of its Ternary Complex with Nicotinohydroxamic Acid and Trioctylmethylammonium Cation

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A rapid, sensitive and accurate method is presented for the atomic absorption spectrophotometric determination of manganese after extractive separation from aqueous media as its ternary complex with nicotinohydroxamic acid and trioctylmethylammonium cation into methyl isobutyl ketone. The method permits determination of up to 0.002 ppm (2 ppb) of manganese without any pretreatment and up to 0.1 ppb with pretreatment. The method was applied to the determination of manganese in natural waters and industrial effluents.

KEY WORDS: AAS, manganese, natural waters, nicotinohydroxamic acid.

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INTRODUCTION

Manganese as pollutant

Manganese is an essential micro-nutrient for plants and animals and its deficiency in humans has been implicated with several disease states, including diabetes, nervous instability, convulsions, disorders of cartilaginous growth in infants and children, and rheumatoid arthritis.[1] Exposure to larger than trace concentration of manganese can be toxic; the metal is a respiratory irritant and a systematic poison when inhaled mainly as oxides in excessive amounts.[2] Processing of iron ores, in which manganese is present in significant concentrations, constitutes the major source of manganese pollution. Numerous case studies on the hazards of occupational exposure to manganese have been reported.

Industrial toxicity through inhalation of manganese particulates is of two types; the first results from acute short-term exposure and is known as manganese pneumonitis.[3] Persons working in plants with high concentrations of manganese dust show an incidence of respiratory diseases 30 times greater than normal. Pathological changes include epithelial necrosis followed by mononuclear proliferation. The second and more serious disease results from chronic inhalation exposure to manganese dioxide, generally over a period of more than 2 years. It involves the central nervous system. In some cases the disease symptoms have appeared at much shorter exposure times. Chronic manganese poisoning (manganism) leads to psychiatric disorders characterized by irritability, difficulty in walking, speech disturbances, and compulsive behavior that may include running, fighting, and singing. If the condition persists, a mask-like face, retropulsion or propulsion, and a Parkinson-like syndrome develops.[5] In addition to the injuries to central nervous system, liver cirrhosis is frequently observed. Victims of chronic manganese poisoning tend to recover slowly, even when removed from the exposure.

The permissible concentration[2] of manganese in domestic water supplies is below $0.05\,\mathrm{mg\,l^{-1}}$. The tolerance for manganese in irrigation water on a continuous use basis is $2.0\,\mathrm{mg\,l^{-1}}$ and on a short-term use is $20\,\mathrm{mg\,l^{-1}}$. The maximum allowable concentration of manganese in effluents discharged to a storm sewer or stream is

1.0 ppm. In a recent study on the water quality of seven borewells, monitored fortnightly for one year, Abbasi *et al.*[6] found manganese levels reaching a maximum of 0.17 ppm; the metal levels in all wells were higher in summer than in rest of the year.

It is desirable to have a rapid and accurate method for the determination of manganese in concentrations of 0.05 ppm or lower so that the metal can be frequently monitored in drinking, industrial and irrigation waters for proper environmental management. Recently Salinas *et al.*[7] have proposed a method for the solvent extraction of manganese with isophtalidihydroxamic acid in tolenic Adogen 464 solution and spectrophotometric determination at 470 nm. However the method is not selective; iron (II) and lead (II) interfering even when present in concentrations lower than manganese and a large number of anions and cations interfering when present in concentrations equal to or higher than that of manganese. The sensitivity is also low (>100 ppb) precluding the application of the method in the environmental analysis of manganese.

The present method

In the present method manganese is rapidly and selectively determined by atomic absorption spectrometry at concentrations less than 1 ppb after extractive separation from aqueous solutions as its ternary complex with nicotinohydroxamic acid (NHA) and trioctylmethylammonium cation (TOMAC) into methyl isobutyl ketone (MIBK) at pH $\geqq 9.6$. NHA has been used as an analytical reagent and a drug.[9] It is important in environmental chemistry as a biosynthetic intermediate.[10] We had reported the thermodynamics of protonation and ternary complex formation of NHA with 3d metal ions and heteroaromatic ligands.[11] We now report studies on the rapid solvent extraction of manganese as its ternary complex with NHA and trioctylmethylammonium cation (TOMAC) into methyl isobutyl ketone (MIBK). The MIBK extract was used in the sensitive atomic absorption spectrophotometric determination of manganese in the presence of copper (II), nickel (II), cobalt (II), iron (III) and several other cations and anions commonly found with manganese in environmental matrices. The method was successfully employed in the determination of manganese at sub-microgram levels in natural waters and industrial effluents.

MATERIALS AND METHODS

Reagents

NHA was synthesized and purified by the method of Blatt.[12] A standard manganese (II) solution (10^3 ppm) was prepared by dissolving 3.0764 g of $MnSO_4 . H_2O$ in water containing 10 ml of hydrochloric acid and diluting to 1000 ml. This solution was standardized volumetrically.[13] All other reagents were analytical grade. Deionised double-distilled water was used throughout.

Apparatus

The atomic absorption spectrophotometric analysis was done on an IL 951 instrument, employing air-acetylene flame. The instrumental settings used are summarized in Table 1. Radiometer PHM 29 and Elico PE.132 pH meters were used for pH adjustments.

The procedure for the extraction and determination of manganese (II)

An aliquot (50 ml) of sample containing 0.002–0.015 ppm (2–15 ppb) of manganese was taken in a separatory funnel and the pH was adjusted to 9.8 with ammonium hydroxide (8 M). To it 5 ml each of 0.05 M NHA solution and 0.006 M TOMAC solution, both in MIBK, were added and the contents were shaken vigorously for 2 minutes. The phases were allowed to separate and the organic layer

Table 1 Optimum instrumental conditions for the atomic absorption spectrometric determination of manganese

Characteristic	*Setting recommended*
Wavelength	279.3 nm
Lamp current	20 mA
Slit width	0.2 nm
Air flow rate	21.5 litres min^{-1}
Acetylene flow rate	2.6 litres min^{-1}
Height of lightpath above burner	2 cm
Rate of aspiration	5 ml min^{-1}

was transferred into a glass-stoppered tube filtering by a paper moistened in ethyl acetate. The organic layer was aspirated directly into the air-acetylene flame. The atomic absorption was measured with the 279.3 nm resonance line using MIBK as a blank.

RESULTS AND DISCUSSION

Optimization studies on the ion-pair extraction of manganese-NHA-TOMAC ternary system

Effect of pH: The effect of pH on the extraction was investigated for a series of aqueous solutions buffered with NH_4 CI-NH_3 to various pH values. As shown in Figure 1, Mn (II) is quantitatively extracted at pH values higher than 9.6. Extraction does not take place at pH values lower than 7.9. The extraction efficiency was calculated by application of the proposed method for manganese determination in the organic and aqueous phases after extraction.

A maximal and constant absorbance was obtained in the ammonium hydroxide concentration range from 0.06 to 0.4 M.

Effect of NHA and TOMAC concentrations: A molar excess of 40 in NHA and 10 in TOMAC were adequate for the complete extraction of manganese. However, in the proposed method a higher molar excess is recommended because the reagents are also consumed by the interfering metal ions, and the presence of an excess of the reagents is recommended to ensure complete chelation and extraction of manganese.

Shaking time and stability: The extraction is complete after shaking for 2 minutes; however, when the extraction is carried out in the presence of high amounts of foreign ions, longer shaking times (5 minutes) for the complete extraction of manganese are needed.

The atomic absorption of the extracted ternary manganese-NHA-TOMAC system remains constant for at least 24 hrs if it is kept stoppered in a closed glass tube.

Calibration curve: Aliquots (50 ml) of standard solutions containing increasing amounts of manganese (II) from 0–20 ppb were extracted

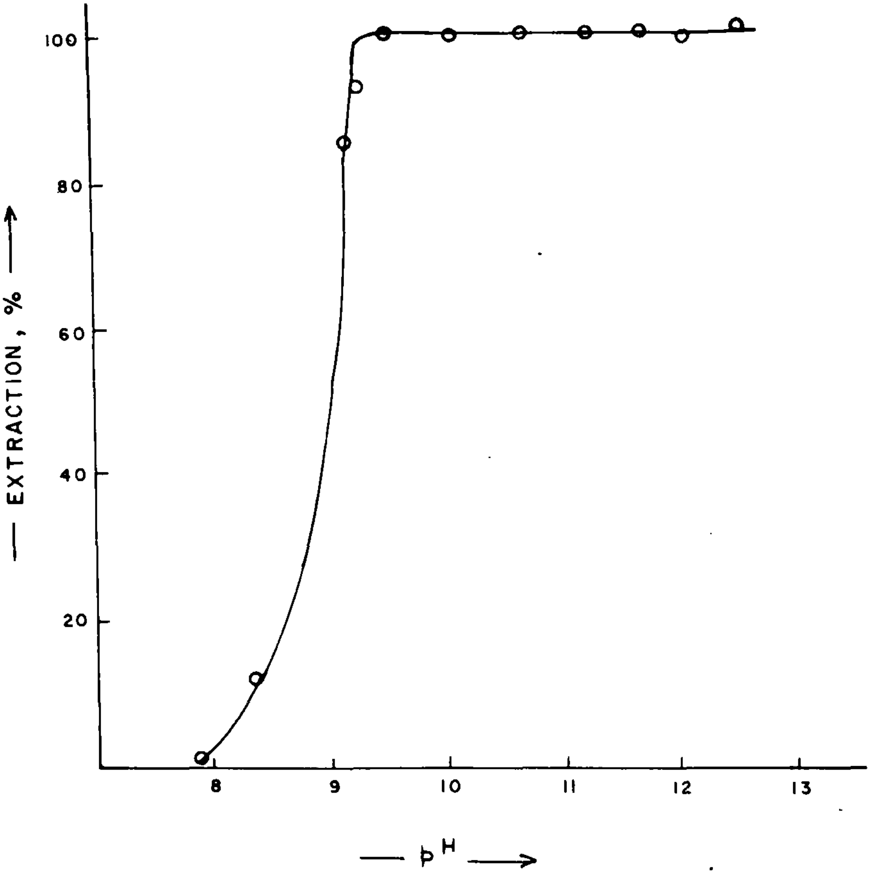

Figure 1 Effect of pH on the extraction of manganese with NHA-TOMAC-MIBK system.

with 10 ml of TOMAC-MIBK mixture as previously described. It was found that the calibration curve was linear in the range 2–15 ppb of Mn (II). The sensitivity was 1.5 ppb for 1% absorption. The coefficient of variation was 1.6% calculated from 10 replicate analyses with 5 ppb of Mn(II). The sensitivity is further enhanced by preconcentration of manganese from lean solutions through evaporation of water and manganese levels down to 0.1 ppb can be determined.

Effect of diverse ions: The tolerance limits of various anions and cations for the determination of 5 μg of manganese (II) within a relative error of ±1.5% are given in Table 2. The limits for iron (III), which is most frequently encountered with manganese in environment, can be further increased 1000-fold by a preliminary extraction of the ion at pH 2 by NHA (0.1 M) into MIBK.

DETERMINATION OF TRACE AMOUNTS OF MANGANESE IN INDUSTRIAL EFFLUENTS AND NATURAL WATERS

The present method was applied to the determination of manganese in industrial effluents and freshwaters. The samples were filtered on-site through 0.45 μm membrane filters and were brought to pH $\sim$2 with nitric acid as per recommended sampling procedures.[14] Manganese was determined with and without standard addition to test the reliability of the method against matrix interferences. The results (Table 3) indicate the accuracy and precision of the present method.

Table 2 Tolerance limits in the determination of 5 μg of manganese (II)

Diverse ions	*Tolerance level, μg*
Lithium, sodium, potassium, rubedium, chloride, nitrate, sulphate, iron (III)[a]	>10000
Beryllium, magnesium, calcium, barium, strontium, aluminium, acetate, fluoride	1000
Copper (II)[b], nickel (II)[b], iron (II)[b], cobalt (II), zinc (II), cadmium (II), mercury (II), vanadium (V)[b], molybdenum (V)[b], tungsten (VI[b], niobium (V)[b], zirconium (VI)[b], titanium (IV)[b]	500

[a] To be removed by preliminary extraction with NHA in MIBK.

[b] Tolerance can be increased substantially by preliminary extraction at pH 2.5 and below.

Table 3 Analysis of manganese in natural waters and industrial effluents

Sample	*Other major constituents (ppb)*	*Manganese added (ppb)*	*Manganese found (ppb)*	*Standard deviation*
Well water	TDS (170×10^3), total hardness (65×10^3), iron (500), copper (7), zinc (4)	Nil	3.01	0.03
Well water	TDS (170×10^3), total hardness (65×10^3), iron (500) copper (7), zinc (4)	2.00	4.98	0.04
Well water	TDS (170×10^3), total hardness (65×10^3), iron (500), copper (7), zinc (4)	5.00	8.05	0.07
Lake water	TDS (65×10^3), total hardness (30×10^3), iron (350), copper (2), zinc (2)	Nil	2.98	0.03
Lake water	TDS (65×10^3), total hardness (30×10^3), iron (350), copper (2), zinc (2)	5.00	8.02	0.06
Lake water	TDS (65×10^3), total hardness (30×10^3), iron (350), copper (2), zinc (2)	8.00	11.01	0.08
Industrial effluent sample I[a]	Sodium (30×10^3), chloride (35×10^3), iron (1200), copper (900), zinc (900), cadmium (700)	Nil	153	2.3
Industrial effluent sample I[a]	Sodium (30×10^3), chloride (35×10^3), iron (1200), copper (900), zinc (900), cadmium (700)	25	179	3.3
Industrial effluent sample II[a]	Sodium (16×10^3), sulphate (9×10^3) chloride (5×10^3), iron (2500), nickel (2300), titanium (2300), vanadium (2900)	Nil	214	3.8
Industrial effluent sample II[a]	Sodium (16×10^3), sulphate (9×10^3) chloride (5×10^3), iron (2500), nickel (2300), titanium (2300), vanadium (2900)	20	232	4.7

[a] Effluents from post-coagulation settling basins.

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