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Short Communication

Determination of manganese in water at parts per billion levels by atomic absorption spectrophotometry

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Abstract

A method is described for the determination of ppb levels of manganese in the presence of higher amounts of iron in water. The method involves complexing of manganese with APDC and NaDDC under stabilised condition and two step extraction of Mn^{2+} in acidic aqueous medium. Detection limits and sensitivity for original aqueous sample are 2 and 3 ppb respectively.

Key words: Manganese, water, atomic absorption spectrophotometry, sodium diethyl dithiocarbamate, methyl isobutyl ketone, ammonium pyrrolidine dithiocarbamate.

1. Introduction

Manganese and iron are the cause of many consumer complaints regarding the quality of water in public supplies due to aesthetic reasons[1]. Regular monitoring of manganese in mine water in particular, and ground and municipal supply water in general, both due to aesthetic and health reasons, is essential. Effectiveness of such programme depend-on accuracy, precision and sensitivity of analytical methods used for manganese determination. Atomic absorption spectrophotometric methods have now been universally accepted for trace metal analysis in water[1,2]. However, manganese in aqueous solution at or below its permissive limit (50 ppb), prescribed by international regulatory agencies[3,4], cannot be determined without preconcentration. Moreover, excess of iron interferes in Mn determination[5]. A suitable method of preconcentration is complexing metals with organic ligands and subsequently extracting the metal complex in suitable organic solvents[6]. However, complexes of manganese have not been found stable under normal conditions. A method for the determination of manganese by atomic absorption spectrophotometry is reported. Manganese is complexed with a mixture of ammonium pyrrolidine dithiocarbamate (APDC) and sodium diethyl dithiocarbamate

(NaDDC), the mix ligands complex is extracted in methyl isobutyl ketone under stabilised condition and subsequently back extracted in hydrochloric acid. The acid extract is atomised for manganese determination.

2. Materials and methods

An atomic absorption spectrophotometer Perkin–Elmer model-303 equipped with Boling burner, premix chamber and null read-out recorder was used. Resonance line of 279·5 nm wavelength, lamp current 20 mA, slit width of 0·7 nm, burner height 10 mm below flame, air as oxidant at 30 psi pressure and 24 l/min flow rate and acetylene as fuel at 8 psi pressure and 4 l/min flow rate were used. All glassware were acid cleaned and rinsed with deionised water. The reagents including standard manganese sulfate, ammonium pyrrolidine dithiocarbamate, sodium-diethyldithiocarbamate, methylisobutyl ketone and hydroxyl amine hydrochloride were of analytical grade. Stock manganese solution (1000 μg/l) was prepared by dissolving 3·08 g of manganese sulfate ($MnSO_4 \cdot H_2O$) in minimum amount of hydrochloric acid and making it to 1000 ml with deionized distilled water. Standard manganese solutions were prepared by subsequent dilution of stock solution with 1% hydrochloric acid. Hydroxylamine hydrochloride 3%, APDC 1% and NaDDC 1% were prepared in deionized distilled water. The pH of APDC and NaDDC was adjusted to 8·2 with 1N NH_4OH/1N HCl solutions.

2.2 *Preparation of sample*

The sample for extractable manganese was prepared by taking 200 ml well-mixed water sample in a beaker, adjusting its pH between 2·5–3·0 with reagent grade hydrochloric acid, boiling vigorously for 5 minutes, cooling and then filtering through 0·45 μm membrane filter. The sample for dissolved manganese was prepared by directly filtering the water sample through 0·45 μm membrane filter.

2.3 *Procedure*

The water sample (200 ml) was taken in a separatory funnel and 100 ml of concentrated hydrochloric acid was added to it. The mixture was mixed well. A 10 ml portion of MIBK was added in acidified water sample and content was shaken vigorously for 2 minutes and organic phase was drained off. Aqueous phase was transferred to a beaker and boiled for some time to expel adhered organic phase and reduce the volume to approximately 150 ml. This aqueous solution was then cooled and its pH was adjusted to 8·2 $\pm$ 0·2 with ammonium hydroxide using a sensitive pH meter. The volume was made up to 200 ml with deionised distilled water and sample was transferred to a 250 ml separatory funnel. One ml of hydroxylamine hydrochloride followed by 1 ml each of APDC and NaDDC solutions were added to it and content was shaken gently for 30 seconds. A 10 ml portion of MIBK was added and content was shaken vigorously again for 2 minutes, releasing in-built gas pressure after every 30 seconds. The layers were allowed to separate. Aqueous layer was drained off and organic layer was

transferred to a 60 ml separatory funnel. Hydrochloric acid 1 ml was added in organic phase and mixture was shaken for 1 minute. Deionised distilled water (4 ml) was added to it and the content was shaken for a further period of 2 minutes. After phase separation, the aqueous acid layer was collected in 10 ml polypropylene bottle and stored in cold for manganese determination. Blank containing 200 ml deionised distilled water and standards containing 2, 4, 6, 8 and 10 μg of manganese in 200 ml deionised water were run similarly. Aqueous solutions of samples, standards and blank were atomised and respective absorbance readings were recorded from atomic absorption spectrophotometer. Manganese was determined from calibration curve prepared by plotting absorbance against concentration.

3. Results and discussion

3.1. *Stability of mixed ligand complex*

Sodium diethyl dithiocarbamate (NaDDC) is comparatively more soluble than APDC in MIBK. A significant portion of unused NaDDC is partitioned into organic phase during extraction stage. Presence of this significant amount of NaDDC in MIBK extract seems to have stabilising effect on manganese complexes of APDC and NaDDC. Moreover, manganese complexes break due to its oxidation to higher valence stage. However, the presence of hydroxyl amine hydrochloride prevents this oxidation and provides stable complex.

Stability of mixed ligand complex of manganese with APDC + NaDDC was studied by preparing synthetic samples of water containing 10 μgl^{-1} of manganese. Extracts in MIBK of mixed ligand complexes were atomised in AAS at 0·5, 1, 2, 3, 4, 5, 6, 12 and 24 hours. Percentage recoveries were determined. Results (Table I)

Table I

Comparison of results obtained by present method with Mn-ADPC method

Mn taken (ppb)	Time in hours after extraction	Manganese obtained (ppb)	
		Extraction of Mn-ADPC in MIBK	Extraction of Mn-ADPC-DDC complex in MIBK
10	0·5	91·8 ± 6·7	100·8 ± 1·2
	1·0	91·4 ± 7·3	100·3 ± 1·1
	2·0	87·9 ± 8·4	99·7 ± 1·0
	4·0	81·6 ± 8·2	99·8 ± 1·2
	8·0	69·5 ± 9·2	99·2 ± 1·1
	16·0	54·6 ± 11·2	99·4 ± 1·2
	24·0	30·8 ± 20·6	95·4 ± 1·1

showed that mixed ligand complexes were almost stable for at least 24 hours and relative scattering was less. However, the results obtained by ADPC–MIBK method showed that complex was unstable and results were widely scattered.

Complexes of manganese with APDC[7] and NaDDC[8] have been reported in the literature. Addition of excess of complexing agents and alkaline condition have been advocated[7,9]. However, others observed that manganese complex was stable only for shorter duration in MIBK[10]. Since manganese remains soluble in the aqueous solution up to pH of 8·5[11], stability of Mn complex was studied at pH 8·2. It was found that both the complexing agents and manganese complex remained stable at this pH in the presence of hydroxylamine hydrochloride. Under these conditions, the complex formation was complete and the complex was stable.

3.2. *Iron interference*

The possible interference of As^{3+}, As^{5+}, Ag^{+1}, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+} Fe^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Si^{4+}, Zn^{2+}, Cl^-, NO^-_3, SO^{2-}_4, PO^{3-}_4 was studied by adding varying amounts of anions and cations in synthetic water containing 10 μgl^{-1} of manganese. Diverse ions except iron were found to exhibit negligible interference. Actually precipitate of hydrous iron arises in aqueous phase at concentration of 50 μgl^{-1}, iron and above. This precipitate of iron removes some of manganese from the aqueous phase and hinders in the complete complexation of manganese. Iron was extracted in MIBK as chloro-complex from acidified water. Thus, if a precipitate is obtained on adjusting the pH 8·2, the modified procedure of extraction by MIBK to remove iron as chloro-complex should be followed. Removal of iron by MIBK extraction did not give low recovery which showed that manganese is not extracted in this procedure.

3.3. *Accuracy and precision*

The relative standard deviations of the method at 20 ppb Mn for dissolved and extractable manganese were 5·1 and 4·8 per cent respectively. Dissolved manganese was determined in water from well, deep well and lake with and without the addition of Mn^{2+} at 10 ppb level. Results (Table II) showed that recovery of manganese by the modified method was more than 96 per cent in all the cases and independent of origin of sample.

3.4. *Detection limit and sensitivity*

Analysis of synthetic water samples containing various amounts of manganese showed that the extinction at 279·5 nm was linearly related to the concentration of manganese between 2 and 50 ppb. The limit of detection, *i.e.*, twice of standard deviation of blank replicate was found to be 2 ppb. The sensitivity of manganese, *i.e.*, concentration of manganese giving 0·0044 absorbance or 1% absorption was 3 ppb.

Table II

Determination of manganese in water from different sources

Source of water	Manganese (ppb)			Percentage recovery
	Endogenous	Added	Total recovered	
Well	40	5	45	100
	40	10	50	100
	40	50	88	96
Deep Well	23	5	28	100
	23	10	33	100
	23	50	72	98·6
Lake	35	5	40	100
	35	10	45	100
	35	50	85	100

3.5. *Back acid extraction*

Extraction of trace metals back into acidic aqueous medium has not been studied extensively probably due to the possibility of non-quantitative recovery of metal from organic phase. However, in the case of manganese whose complexes in MIBK are not very stable, back extraction provided highly accurate and precise results. The back extraction also provided the ease of storing process sample for several weeks without any significant change in manganese concentration.

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