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Primary-Secondary Wavelengths Spectrophotometric Determination of Manganese in Environmental Water

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At pH 9.5 the conventional reaction of manganese (Mn^{2+}) with formaldehyde and hydroxylamine hydrochloride to form red complex has been applied for the improvement of the determination of trace amounts of manganese in natural water and waste water by the updated method named primary-secondary wavelengths spectrophotometry (PSWS). The results showed that the analytical precision and accuracy were increased and gave the higher determination sensitivity than the ordinary spectrophotometry. The relative standard deviations were less than 7.4% and the recovery rate of Mn between 97 and 109%.

INTRODUCTION

Manganese is one of the necessary elements for body and in other biological system. It exists widely in nature in Mn(II), Mn(III) and Mn(IV) states, for example in natural water, waste water polluted by metal-mine, metallurgical, chemical and other industries. At present Mn is usually determined by colorimetry with formaldehyde[1,2], potassium periodate[3] etc. But the former can give the high sensitivity and selectivity, and accurate determination result, so it remains to be applied widely for the analysis of trace amounts of Mn in environment samples. In this paper the above reaction was first to be used for improvement of determination of trace amounts of Mn by the updated method named primary-secondary wavelength spectrophotometry (PSWS). because PSWS can give the higher precision and sensitivity than the conventional spectrophotometry and give the stable calibration model the result were all satisfactory. The manganese recovery rate was between 97 and 109%, the relative standard deviations (RSDs) less than 7.4% and the detection limit only 0.005 mg/L that was half of the conventional value.

Principle

The principles involved in PSWS method are detailed in my previous reports[4,5], which are different from the other dual wavelength methods[6,7].

EXPERIMENTAL

Visible spectra were recorded with a Model 721 spectrophotometer (Shanghai, China), in a 50 mm glass cell.

Standard Mn(II) solution, 100 mg/L: dissolving 0.1702 g of manganese sulfate ($MnSO_4 \cdot 2H_2O$, A.R., Shanghai Chemical) in 100 mL ion exchange water and adding 5 mL of concentrated sulfuric acid and diluting to 500 mL.

Standard Mn(II) Use solution, 10.0 mg/L: preparing with the above standard Mn solution

Ligand reagent: dissolving 10 g of hydroxylamine hydrochloride in 50 mL of ion exchange water and adding 5 mL of 35% formaldehyde (Beijing Organic Chemical then diluting to 100 mL and store in a plastic bottle.

16% (m/V) NaOH

1mol/L Na_2-EDTA: dissolving 37.2 g of sodium ethylene diaminetetrate (Na_2-EDTA, A.R., Shanghai Chemical) in 50 mL 15% NaOH then diluting to 100 mL to store in plastic bottle.

Ammonia-hydroxylamine hydrochloride mixture: mixing 100 mL of 4.7 mol/L ammonia and 100 mL of 5 mol/L hydroxylamine hydrochloride.

Potassium peroxodisulfate (A.R., Shanghai Chemical)

Concentrated nitric acid and 0.4% (m/V) nitric acid

Recommended Procedures: A known volume of a natural water sample containing less than 40 μg of Mn was taken in a 50 mL volumetric flask and added ion exchange water to about 40 mL. In this solution, add 0.5 mL of 1 mol/L Na_2 EDTA, 0.5 mL of ligand reagent solution and 1.8 mL of 16% NaOH. Mixed and wait for 10 min. After adding 3 mL of ammonia-hydroxylamine hydrochloride mixture, dilute to required volume with ion exchange water and mixed well.

After 20 min. measured transmittancy at 450 and 580 nm, respectively, against a reagent blank.

For a waste water sample, at first it should carry out the pretreatment according to the following method. Add 1 mL of nitric acid, 0.5 g of potassium peroxydisulfate and several glass beads into 100 mL of a waste water sample. Boiling it for 30 min then filtered it. Finally diluted the filtrate to 100 mL. Before the determination of this sample according to the following procedure the above filtrate must be adjusted to pH about 7 using 0.4% nitric acid.

RESULT AND DISCUSSION

Absorption Spectra: Fig. 1 gave the absorption spectra of Mn complex solution. This solution absorption reached maximum at 450 nm. According to the

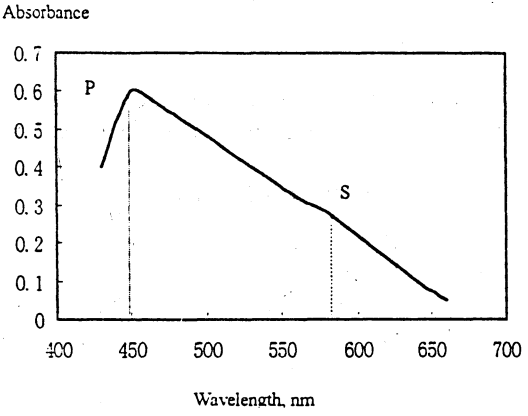

Fig. 1. Absirption spectrum of Mn complex solution with pH 9.5 against reagent blank: **P**, point-620 nm and **S** point-650 nm

relative content in principle the primary wavelength (λ_p) should be selected at 450 nm. The secondary wavelength (λ_s) was arranged at 580 nm here.

Effect of Ligand Addition: Figure 2 showed the effect of the addition of ligand reagent solution on factor y. We found when the addition of ligand reagent solution was more than 0.3 mL, y remained almost constant and reached maximum. In this work, 0.5 mL of ligand reagent solution was selected.

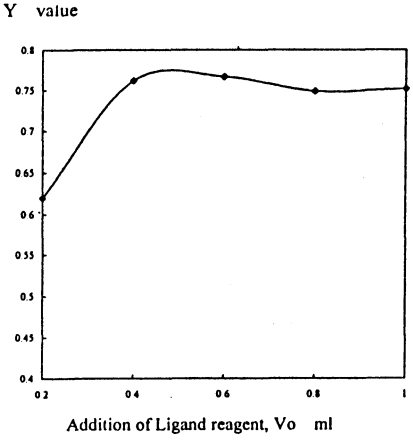

Fig. 2. Effect of ligand reagent solution on factor y

Calibration Graph: A series of standard Mn solutions were prepared and the absorbance of each was measured and plotted. The measurement results and the exponent y's calculation ones were listed in Table-1.

TABLE 1
DETERMINATION OF STANDARD MANGANESE SOLUTIONS

Mn Concern. X, mg/L	Transmittancy*, %		y value
	450 nm	580 nm	
0	100	100	—
0.100	79.5	87.3	0.148
0.200	65.3	81.8	0.340
0.400	42.1	65.7	0.599
0.600	30.6	56.7	0.768
0.800	18.3	43.8	0.961

* absorbance=log (100/transmittancy)

From the above data we established the following expression.

$$y = 1.24\ X^{0.881}$$

Effect of Foreign Ions: The pretreatment of sample was carried out according to the recommended procedure, none of the following ions will affect the direct determination of 20 μg of Mn(<10% error): 100 mg of Cl^-, SO_4^{2-}, PO_4^{3-}, PO_4^{3-}, CO_3^{2-}, NO_3^-; 20 mg of Ca(II), Mg(II), Ti(IV), Br^-, SiO_3^{2-}; 5 mg oa Al(II), Sn(II),

I^-, F^-, NH_4^+; 0.5 mg of Fe(II), Zn(II); 0.1 mg of Cu(II), Co(II), Ni(II), Cr(III) and 20 μg of V(V), Ce(III).

Precision and Detection Limit: Six replicate determinations of standard Mn solutions containing 0.100 and 0.600 μg/mL were carried out, respectively, the relative standard deviations (RSDs) being 2% and 0.9%. However, the RSDs with the single wavelength method was 6.1 and 3.3%. The precision for PSWS was therefore better than that for the ordinary spectrophotometric method.

We used $L_{min} = kS_b/S$ to calculate the detection limit of Mn by PSWS, where k = 4, Sb named as standard deviation and S named as sensitivity. Replicate determination of twenty reagent blanks gave S_b of Y value computed from (Ap + 1)/(As + 1) was equal to 0.002. The analytical sensitivity S was equal to the above α value, 1.24. Therefore the detection limit of Mn was L_{min} = 0.005 mg/L.

Samples Analyzed: As a test of the method Mn was determined in, for example wastewater and surface water. The results were listed in Table 2. We found the results by the recommended method tallied with the conventional method. The RSDs were less than 7.4% and the recovery rate of Mn between 97 and 109%.

TABLE 2
DETERMINATION OF MANGANESE IN WATER SAMPLES

Sample	By conventional method	by PSWS		
		Added	Found	Recovery,%
waste water	5.010	0	4.85, 5.06, 5.03	
		300	7.95, 7.86, 8.01	99
waste water 2#	0.591	0	0.593, 0.571, 0.584, 0.616, 0.610, 0.615	97
		0.800	1.40, 1.36, 1.36	
river water	0.025	0	0.023, 0.024, 0.021, 0.025, 0.026, 0.023	109
		0.020	0.045, 0.046	

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