

3,3',5,5'-Tetramethylbenzidine for the Colorimetric Determination of Manganese in Water

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Abstract. Manganese can be determined by colorimetry with previous oxidation of Mn(II) in a strong basic medium, using 3,3',5,5'-tetramethylbenzidine as a chromogenic reagent. The molar absorptivity of the reaction product is $3.4 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$, the detection limit 3 ng/ml, the RSD (0.5 mg/l, $n = 8$) 0.9% and the calibration range (1-cm cells) 0.02–0.8 mg/l V(V), Cr(VI) and Co(II) are the most significant interferences. The new method was compared with an AAS procedure (air-acetylene flame) with previous solvent extraction and also with a colorimetric method for the determination of manganese in sea and drinking water.

Key words: manganese determination, colorimetry, 3,3',5,5'-tetramethylbenzidine, drinking water, sea water.

Colorimetric methods play an important role in manganese determination. A review by Chiswell and Pascoe [1] shows that aromatic amines, azo dyes, oximes, porphyrins and other reagents have been used for the colorimetric determination of manganese. Marczenko [2] has commented that the most significant reagents are permanganate, formaldoxime and 1-(2-pyridylazonaphthol) (PAN). PAN is far more sensitive than the other two reagents. Goto et al. [3] proposed Triton X-100 to dissolve and stabilize the Mn-PAN chelate complex. This method has been adapted to test kits for determining manganese in water. However, PAN has difficulties with manganese concentrations below 0.1 mg/l, because of an overlap of the ligand peak with the peak of the complex [4]. Moreover, a final concentration of calcium ion higher than 40 mg/l causes interference. Another reagent

which has been widely studied is *o*-tolidine [5, 6]; however, this has the drawback of being carcinogenic.

The book "Standard Methods" for the Examination of Water and Wastewater [7] only includes, apart from AAS and AES, a single colorimetric method for manganese determination, based on the oxidation of Mn(II) to Mn(VII) with peroxydisulfate, with a detection limit of about 0.2 mg/l (98% of transmittance and 1-cm cells). Although AAS is more sensitive, it fails for the determination of concentrations below 0.05 mg/l, unless a prior liquid-liquid extraction procedure is used.

In this work a new reagent for the determination of manganese, 3,3',5,5'-tetramethylbenzidine (TMB), is described.

Experimental

Apparatus and Reagents

Spectral measurements and absorbance readings were carried out on a Perkin-Elmer Lambda 16 UV double-beam recording spectrophotometer, using glass cells with path lengths of 1 or 5 cm.

Manganese standard solutions of 1 g/l were prepared by dissolving metallic manganese in hydrochloric acid and the working solutions by further dilution with distilled water.

A TMB solution was prepared by dissolving 0.100 g of TMB (Fluka) in 100 ml of hydrochloric acid 0.1 mol/l.

A Mg(II) solution was prepared by dissolving 125 g of magnesium chloride hexahydrate in distilled water up to 1 l.

Sodium hydroxide (1.5 mol/l) and phosphoric acid (7.5 mol/l) were prepared by appropriate dissolution.

Procedure for the Determination of Manganese in Water

50 ml of sample were placed in an Erlenmeyer flask, 1 ml of Mg(II) solution was added and then, dropwise with stirring, 2 ml of

sodium hydroxide (1.5 mol/l). After standing for 15 min, 2 ml of TMB solution were added, followed by 2 ml of phosphoric acid (7.5 mol/l). The absorbance was measured at 450 nm within 2 h (preferably in the first 10 min) against a similarly treated blank and the content of manganese computed from a standard calibration curve containing 0.02–0.8 mg Mn/l. 1-cm glass cells were used, or 4–200 µg/l when 5-cm cells were used.

For samples which are cloudy or contain chlorine, 50 ml of the sample are treated with 5 ml of 10–12 mol/l HCl and heated to near dryness. 50–60 ml of water are then added and the volume is made up to 100 ml, after previous filtration if necessary.

For seawater samples, use 25 ml of sample instead of 50 ml and dilute to 50 ml with distilled water. Likewise replace 1 ml of Mg(II) with 1 ml of distilled water.

Results and Discussion

Absorption Spectrum

Figure 1 shows a spectrum between 350–550 nm with a single maximum at 450 nm. This spectrum is identical to that given by the quinodiimine compound formed in the reaction of chlorine with TMB [7].

Effects of pH and of TMB and Mg(II) Concentrations

Amounts of TMB from 0.2 to 4 mg were assayed against 0.05 mg of Mn(II). It was proved that absorbance did not change for quantities of TMB of 1 mg or more. The absorbance was a little higher in the absence of Mg(II), which can be explained since Mn(II) is partially enclosed in the magnesium hydroxide precipitate and is not oxidised to Mn(IV).

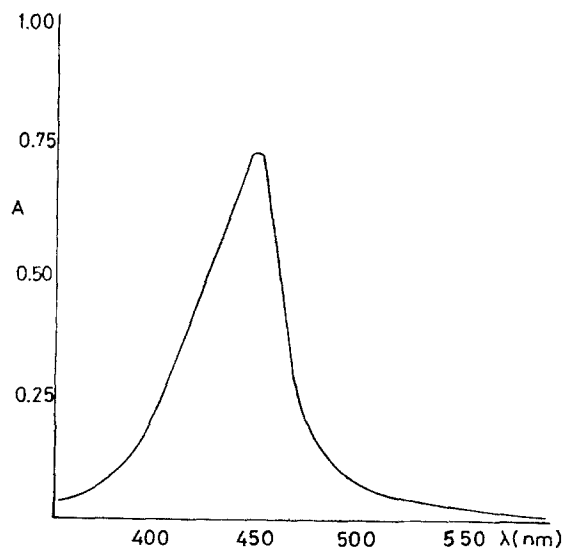


Fig. 1. Absorption spectrum (with 1-cm cell) of TMB-1 mg/l manganese.

However, the possibility of making a calibration curve without Mg(II) was rejected because this element occurs normally in natural waters, usually at concentration levels of 5–50 mg/l. For amounts from 200 to 500 mg/l of magnesium the absorbance remains constant.

The pH has a considerable influence on the manganese oxidation. The optimum range of pH is 12–13, which cannot be reached until all the magnesium has precipitated. This requires 1.3 mmol of sodium hydroxide. The absorbance does not change if the quantity of sodium hydroxide added is between 1.5 and 4 mmol.

Effects of Time and Sequence of Addition of Reagents

A waiting time of 5–20 min after adding the sodium hydroxide solution did not affect the results. This time is sufficient to oxidize Mn(II) to Mn(IV) and to carry out the determination of total manganese contained in the sample.

The reaction product is quite stable. It was demonstrated that absorbance did not change for at least 2 h if the concentration of analyte was equal to or lower than 0.5 mg/l. For higher concentrations a slight decrease in absorbance can be observed, thus, for example, 1 mg/l of Mn(II) decreases in absorbance by 2–3% after 2 h.

The sequence of reagent addition may have a significant influence. Mg(II) addition after sodium hydroxide affords similar absorbance, but precision and linearity are poorer than if Mg(II) is added before sodium hydroxide. On the other hand, the addition of phosphoric acid before TMB prevents the possibility of formation of the reaction product.

Sensitivity, Precision and Range

The detection limit ($y = y_B + 3s_B$) is 3 ng/ml. The RSD (0.5 mg/l, $n = 8$) is 0.9%. The equation for the calibration graph is $A = 0.69C + 0.008$, where C is in mg/l, and the calibration range (1-cm cells) is 0.02–0.8 mg/l.

Effect of Foreign Ions

The influence of other ions on manganese determination can be observed in Table 1 Cr(VI), V(V) and cobalt can seriously interfere, but Cr(VI) and V(V) interact very slowly with TMB. They require 1–2 h for

Table 1. Effect of different ions on the determination of 0.2 mg/l manganese

Ion added	Tolerable ratio ^a (m/m)	Ion added	Tolerable ratio ^a (m/m)
SO ₄ ²⁻ , Cl ⁻	8 × 10 ⁴	Fe(III), Fe(II)	10 ²
NO ₃ ⁻ , HCO ₃ ⁻	5 × 10 ³	Al(III)	10
citrate	5 × 10 ²	Be(II), Zn(II) Cd(II)	5 × 10 ²
F ⁻	3 × 10 ²	Cu(II), Pb(II)	50
Se(IV), As(III), As(V)	10 ²	Ti(IV), Zr(IV)	50
Cr(VI), V(V)	0.2 ^b	Mo(VI), W(VI)	50
Cr(III)	8	Ag(I), Hg(II)	5
Ni(II)	50	Co(II)	0.1

^a 2% error.^b Measurements performed 10 min after adding the last reagent.**Table 2.** Comparison of the proposed method (TMB), AAS and colorimetry with PAN for manganese determination in water

Sample	Mn added (µg/l)	Mn found ^a (µg/l)			RSD ^a (%)		
		AAS ^b	TMB	PAN	AAS	TMB	PAN
Tap water from Burjassot	–	5.2	3.3	3.5	–	–	–
	20	23.0	22.2	25.1	8.8	6.3	6.8
	50	56.5	54.7	52.4	5.0	3.3	3.0
	200	203.9	204.5	202.7	2.2	1.8	1.8
Bottled water	–	4.8	3.9	4.0	–	–	–
	20	26.7	25.2	25.2	8.3	7.0	6.6
	50	52.1	54.0	52.7	4.2	3.5	3.8
	200	203.3	205.2	203.6	1.5	1.6	1.5
Sea water	–	8.6	9.4	C	–	–	–
	20	26.5	27.5	L	10.2	7.4	–
	50	57.3	58.0	O	3.4	3.8	–
	200	206.7	207.2	U D Y	2.4	2.0	–

^a n = 6.^b The determinations by AAS were performed with previous extraction with APDC and MIBK. A Perkin-Elmer 5000 Atomic Absorption Spectrometer was used.

equilibrium to be reached, therefore, in order to decrease the error due to the presence of V(V) and Cr(VI), the spectrophotometric measurement of the sample must be performed as soon as possible.

Applications

The colorimetric determination of manganese with TMB gave results which agreed with those obtained using the AAS procedure (air-acetylene flame) with previous solvent extraction (see Table 2). Recovery using the TMB method was between 90.5 and 102.8%, while by AAS recovery was 89.0–109.5%.

The results with TMB also agreed with those obtained using colorimetry with PAN, except for samples of sea water, in which the PAN method is not applicable unless the samples are drastically diluted.

Conclusions

A simple colorimetric method is proposed, which does not require the use of an organic solvent. Its sensitivity is superior to that of direct AAS and similar to that of AAS after previous solvent extraction with APDC. It has the advantage that the reaction product of manganese-TMB is considerably

more stable than the manganese-APDC chelate and the reaction product of manganese with PAN. The TMB reagent is colourless and, therefore, does not present the drawbacks of PAN and other coloured reagents.

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