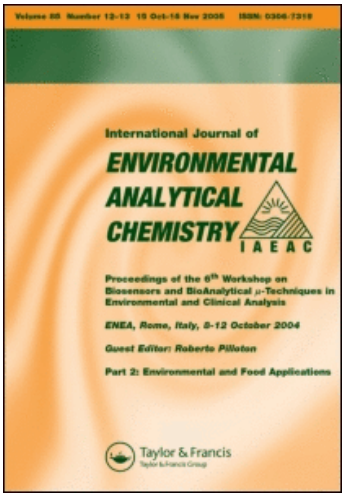

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SOLID PHASE SPECTROPHOTOMETRIC MICRODETERMINATION OF MANGANESE

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A method for the determination of microgram per litre level of manganese has been developed, based on Solid-Phase Spectrophotometry (SPS). Manganese reacts with 3-bromobenzohydroxamic acid to form a 1:3 anionic brown-reddish complex of Mn(III), which is fixed on a dextran-type anion-exchange resin. Resin phase absorbance is measured directly and allows the determination of manganese in the range 5–100 $\mu g\ l^{-1}$, with a RSD of 4%. The method has been applied to the determination of manganese in different samples, namely plant tissue extracts, active charcoals and waters.

KEY WORDS: Solid Phase Spectrophotometry, manganese, water, charcoal, plant tissues.

INTRODUCTION

Solid Phase Spectrophotometry (SPS) is a technique based on the pre-concentration of the species of interest on a solid, aided by complexing (or other reagents) and the subsequent measurement of the absorbance of the species in the solid phase[1].

The reaction between Mn(II) and hydroxamic acids has been studied by several authors both in aqueous solution[2–4] and extraction, as well as in neutral complexes using alcohols as solvents[5], and in charged complexes extracted as ionic-pairs in apolar solvents[6,7,10]. All complexes however share a common characteristic: prior oxidation to Mn(III) before complexation.

The red-wind complex originated by 3-bromobenzyohydroxamic acid with Mn(II) in basic medium is fixed on an anionic resin, providing the basis (in combination with SPS technique) of a method for the determination of microgram per litre levels of manganese.

EXPERIMENTAL SECTION

Reagents

All chemicals used were of analytical grade and the water was doubly-distilled. 3-Bromobenzohydroxamic acid (3BrBHA) was synthesized by the authors[8] and water solutions were prepared by addition of the stoichiometric amount of NaOH.

Ion Exchanger. QAE Sephadex A-25 (chloride form) anion exchange resin was used in original dry state, as obtained from the supplier, in order to avoid contamination.

Manganese stock solution. Work solutions (1000 mgl^{-1}) were obtained by dilution with doubly-distilled water.

Buffer solution ammonia/ammonium chloride (pH = 10.3). It was prepared by dissolving 1.4712 g of analytical grade NH_4Cl in 1000 ml of doubly-distilled water containing 40 ml of concentrated NH_3.

Apparatus

A Spectronic 2000 Bausch & Lomb spectrophotometer with glass cells (1-mm optical path length) was employed for all spectral measurements. All pH measurements were made using a Crison 2002 pH-meter fitted with a glass-saturated calomel electrode assembly and a temperature sounder. An Agitaser 2000 rotating bottle agitator was also used.

Absorbance measurements

The absorbance of the complex species sorbed on the resin was measured in a 1-mm cell at 470 nm and 750 nm against a 1-mm cell well packed with resin equilibrated with blank solution. The net absorbance (A_c) for the complex was obtained by: $A_c = A_{470} - A_{750}$[1].

Procedure

To an appropriate volume of sample containing 0.18–9.10 $\mu mol\,l^{-1}$ of manganese (10–500 $\mu g\,l^{-1}$), 12 ml of 2.0×10^{-3} M 3BrBHA solution and 10 ml of pH 10.3 ammonium chloride/ammonia buffer solution were added, levelling off to 250 ml. The solution was transferred together with 60 mg of Sephadex QAE A-25 resin to a 1–1 polyethylene bottle and the mixture was shaken mechanically for 40 min. The resin beads were subsequently collected by filtration under suction, with the aid of a pipette, and packed into a 1-mm cell together with a small volume of the solution. A blank soltion containing all reagents except manganese was prepared and treated in the same manner.

For 500 ml samples (placed in a 1–1 polyethylene bottle) containing 0.09–3.64 $\mu mol\,l^{-1}$ (5–200 $\mu g\,l^{-1}$) of Mn(II), 17 ml of 2.0×10^{-3} M 3BrBHA solution, 20 ml

of pH 10.3 ammonia buffer solution, and 60 mg of Sephadex QAE A-25 resin were added. The mixture was shaken mechanically for 80 min, as indicated in the above procedure.

For 1000 ml samples (placed in a 2-1 container) containing 0.09–1.82 μmol l^{-1} (5-100 μg l^{-1}) of Mn(II), 30 ml of 2.0×10^{-3} M 3BrBHA solution, 40 ml of pH 10.3 ammonia buffer solution, and 60 mg of Sephadex QAE A-25 resin were added. The stirring time was increased to 150 min, following the same procedure as indicated above.

Treatment of samples

Water. Natural water was preserved with conc. HNO_3 (0.25 ml 1,000 ml^{-1}), filtered through a 0.45-μm membrane filter paper (Millipore) and collected in a polyethylene container carefully cleaned with nitric acid). The samples were stored at 4°C until analysis. Analyses were performed with the least possible delay. The usual general precautions were taken to avoid contamination[9].

Activated charcoal. A suitable weight (about 1.5 g) of activated charcoal was treated with 60 ml of 2% trichloroacetic acid solution during two hours. The charcoal is filtered off through Whatman no. 42 paper. The manganese is determined on a 5 ml aliquot, as described in the 250 ml procedure.

Plant tissue extracts. The sample (olive leaves) is collected according to Recalde *et al.*[10] and prepared as described by Lachica[11]. About 2 g of powdered sample (weighed exactly) are treated with 60 ml of 2% trichloracetic acid solution and 1.5 g of activated carbon and shaken for 16 hours[12]. The filtrate is analyzed as described in the general procedure.

Distribution measurements

3-Bromobenzohydroxamic acid, buffer solution and 100 mg of Sephadex QAE C-25 resin were added to a 250 ml water sample containing 3.19 μmole of Mn(II). After 40 min equilibration, the manganese concentration in the resin was determined as described in the procedure. The equilibrated solution was then treated in the same way with a further batch of resin (60 mg) and the remaining manganese was measured as before. The distribution ratio D (mmole of Mn sorbed per kg of resin/mmole of Mn per dm^3 of solution) was calculated from the initial and equilibrium concentrations in the solution. An average value of $(6.7 \pm 0.5) \times 10^4$ was obtained from five replicate experiments.

RESULTS AND DISCUSSIONS

Absorption spectra in resin Phase

3-Bromobenzohydroxamic acid reacts with manganese ion in basic medium originating a brown-reddish complex which is sorbed by an anion exchange resin showing

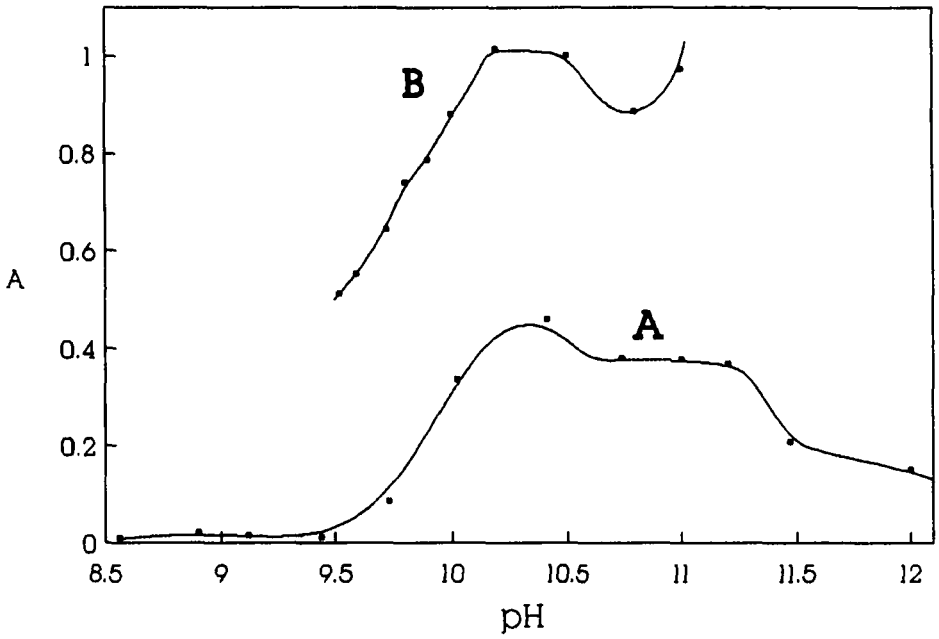

Figure 1 Influence of pH on colour development in resin phase. [Mn] = 8.4 μM; [3BrBHA] = 8.8 × 10^{-5} M; 0.100 g of Sephadex QAE A-25; 250 ml sample. pH adjusted with a) NaOH; b) NH_4^+/NH_3 buffer solution.

a broad absorption peak near 470 nm. The maximum for the complex in solution is about 490 nm and extracted into Adogen-toluene shows two shoulders around 450 and 530 nm[13]. The hydroxamic acid is fixed in the resin but do not absorb in the visible region.

Optimisation of conditions

pH Dependence. Optimum pH for the formation and fixation of the red-brown species falls in the range 10–11 (Figure 1). At pH values below 10 absorbance decreases significantly. At pH values above 11 the resin shows a clear yellow colour; a behavior very similar to that encountered in solution[13].

Different buffer solutions (HCO_3^-/CO_3^{2-}, HBO_2/BO_2^-, NH_4^+/NH_3) was tested. The ammonium chloride/ammonia buffer (pH = 10.3) was found to yield the best results, as the absorbance values showed an 80% increase with respect to other buffers and a 120% with respect to NaOH (Figure 1). It should be pointed out that the optimum pH in the solid phase is slightly higher than in solution (pH = 10.2).

Absorbance does not depend on ionic strength, up to concentrations of 5 × 10^{-3} M regulated with the buffer solution. For higher values, absorbance decreases as usual in SPS studies.

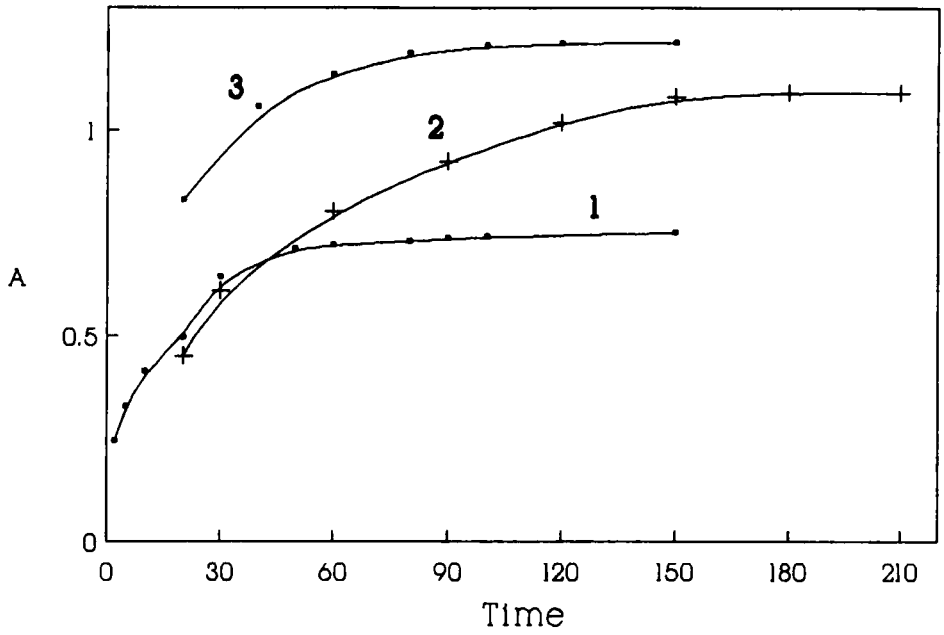

Figure 2 Stirring time dependence of colour development in resin phase. 1.82 μmole of Mn. 0.06 g of Sephadex QAS A-25. 1. 250 ml of sample; [3BrBHA] = 9.6×10^{-5} M. 2. 500 ml of sample; [3BrBHA] = 6.8×10^{-5} M. 3. 1,000 ml of sample; [3BrBHA] = 6.0×10^{-5} M.

3-BrBHA concentration. The absorbance increases together with the 3-BrBHA concentration, with a plateau occurring from 8.0×10^{-5} M. The minimum molar [3-BrBHA]/[Mn] ratio necessary was 13. Consequently, a 9.6×10^{-5} M reagent concentration was chosen for 250 ml. In the same way, for the 500 and 1000 ml the optimum reagent concentrations were 6.8×10^{-5} M and 6.0×10^{-5} M, respectively ([3BrBHA]/[Mn] ratio 19 and 33).

Other experimental conditions. The effect of stirring time on sorption of the complex on the resin is shown in Figure 2. Optimum stirring times were 40, 80 and 150 min for 250, 500 and 1000 ml, respectively. Absorbance measurements remained stable for at least 20 min after equilibration, and later increased about 15% after 60 min. The best order for adding the reagents was found to be: reagent-manganese-buffer. Particularly, the maximum absorbance was reached when the buffer solution was added after the manganese ion. The use of a large amount of resin (m_r in g) reduces absorbance. The absorbance decreases according to the equation $\log A_c = 0.107 - 1.070 m_r$ ($r = 0.988$). The minimum amount of dry resin yielding the highest absorbance and ease of handling is 60 mg.

Nature of the fixed complex

The stoicheiometry of the fixed complex on Sephadex was established using the molar ratio[14–15] and the Asmus[16] methods at the working pH. The plot A_c vs. [3-BrBHA]/[Mn] molar ratio, obtained by varying the 3-BrBHA concentration, shows an inflexion at 3 molar ratio. Moreover, a straight line appears (for the Asmus method) at 3 *n*-value ($r = 0.988$). Results indicated that a 3:1 anionic complex is fixed on the resin.

The manganese probably acts as a tridentate, as suggested by several authors for manganese complexes of hydroxamic acids[2]. In fact, the complex is not formed and fixed if the reagents are previously deaerated with nitrogen or if hydroxylamine is added, since manganese oxidation is hindered.

The slope of the plot log *D* vs pH in the working pH zone, is a straight line of slope 0.91 in the 9–10 pH range. This suggests the loss of a hydroxamic 3-BrBHA proton per manganese ion complexed. This implies that from the three 3BrBHA molecules in the complex, two act in keto form and the third in enol form, a behaviour already suggested for hydroxamic acids[6,17,18]).

These results agree with those found in the previous study of this complex in solution extracted as an ion-pair with Adogen 464 in toluene[13].

ANALYTICAL DATA

The effect of volume on sensitivity

The sensitivity is improved when increasing the sample volume taken for analysis. This effect may be calculated by measuring the absorbance of resin equilibrated with different volumes (V) of solutions containing the same concentration of Mn(II) and proportional amounts of the other reagents (Figure 3). The experimental data may be adjusted to the equation $A = -0.1655 + 1.6707 \times 10^{-3}\,V - 4.303 \times 10^{-7}\,V^2$ (standard fit deviation was 4.61×10^{-2}). This explains the absorbance tendency to be independent of the volume at higher volume values.

Calibration and precision

The calibration curves, evaluated by the Ringbom's method, are linear in the concentration ranges: 50–400 $\mu g\,l^{-1}$; 25–200 $\mu g\,l^{-1}$ and 10–100 $\mu g\,l^{-1}$ for 250-, 500- and 1000-ml samples, respectively. The analytical parameters are summarized in Table 1. The use of a 2 mm cell (using 100 mg of resin) increases the slope of the calibration curve to 1.158.

Reproducibility

The reproducibility of the proposed method was determined for a manganese concentration of 400, 150 and 100 $\mu g\,l^{-1}$ for 250, 500 and 1000 ml samples, respectively, by performing ten independent determinations. The relative standard deviations (RSDs) were 2.8, 2.1 and 1.9% for 250, 500 and 1000 ml samples, respectively.

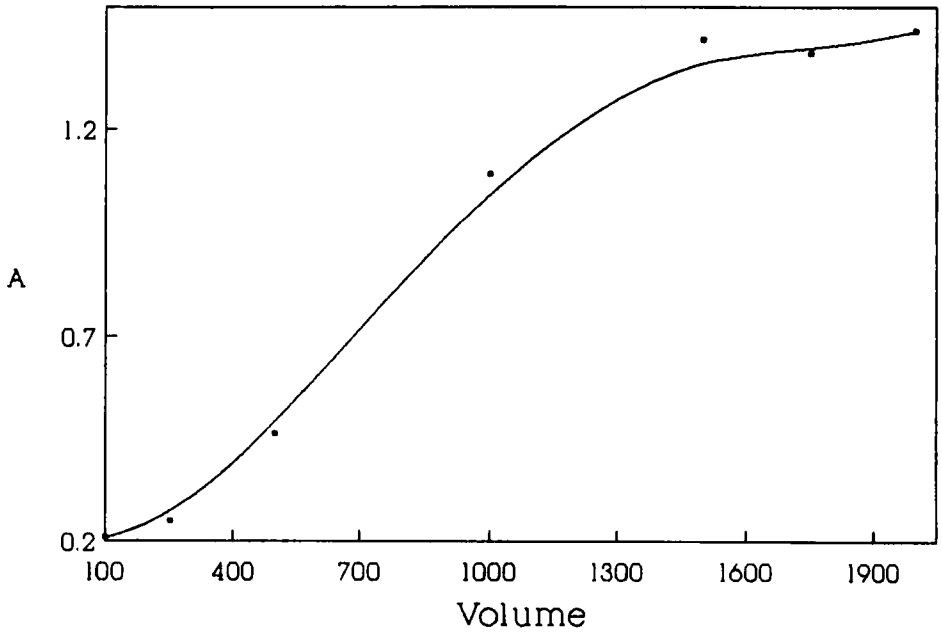

Figure 3 influence of the sample volume on colour development. 1.82 μmole of Mn; [3BrBHA] = 9.6×10^{-5} M; 0.060 g of Sephadex QAE A-25; pH = 10.3 (NH_4^+/NH_3 buffer solution); 100 – 2,000 sample volume; Stirring time = 20 – 310 min.

Table 1 Analytical parameters for SPS manganese determination

	Volume sample system		
	250 *ml*	500 *ml*	1000 *ml*
Intercept	−0.006	0.009	0.037
Slope	2.717	6.140	11.914
Linear dynamic range μg l^{-1}	15–500	10–200	5–100
Correlation coefficient	0.9995	0.9994	0.9952
Detection limit μg l^{-1}	4.4	2.0	1.0
Determination limit μg l^{-1}	14.7	6.5	3.4
RDS (%)	2.8	2.1	1.9

Table 2 Methods for the spectrophotometric determination of manganese

Regent	*Sensitivity*	*Reference*
Periodate	4.1×10^{-5}	22–24
Isoftaldihydroxamic a.	2.7×10^{-5}	4
Diethyldithiocarbamate	2.6×10^{-5}	25–28
Formaldoxime	8.9×10^{-6}	29–30
Nitrobenzeneazocathecol	2.4×10^{-6}	31
1-(2-pyridyl)azo-2-naphthol	1.7×10^{-6}	32–35
3-Bromobenzohydroxamic-SPS	2.0×10^{-7}	present study

The precision of the packing operation was approximately 1.6%[19]. Consequently, the packing of the resin appears to be one of the main factors affecting the reproducibility. Centrifugation of the resin packed in the cell does not improve precision.

Sensitivity and detection limit

The sensitivity, expressed as molar absorptivity, of the proposed method is compared with that of spectrophotometric procedures described in the literature (Table 2). Using the SPS method produces a noticeable increase in sensitivity, especially in relation to the solution methods using the same reagent. In order to compare this increase in sensitivity, the calibration graph for the determination of manganese with 3-BrBHA was elaborated[13], under the experimental conditions described in the present study, but using extraction in toluene- Adogen. The ratio of the slopes SPS method/extraction method was 71.

In SPS methods, sensitivity can be enhanced by increasing the sample volume to be analysed. This increase can be calculated, in practice, from the slope of the calibration curves. The sensitivity ratios for the samples analysed here are: $S_{1000/500} = 1.78$; $S_{500-250} = 1.80$ and $S_{1000/250} = 3.20$, which agree with the expected values obtained using the D value[20], 1.80, 1.89 and 3.40, respectively.

The standard deviations of the background absorbance for the blanks, necessary for calculating the IUPAC detection limit ($K = 3$)[21], measured as the average of ten determinations and expressed as SD units, were 0.010, 0.004 and 0.004, for the 250, 500 and 1,000 ml samples, respectively.

Effect of foreign ions

A study of the effect of several potentially interferent species on the determination of manganese, at 250 $\mu g l^{-1}$ was undertaken following the general procedure for the 250 ml sample system. Tolerance is defined as the interferent concentration that produces an error smaller than 5% in the determination of the analyte.

The tolerance values for the ions studied are shown in Table 3. Fe(III), Mo(VI), V(V) and Co(II) interfere in the determination of manganese in this method. However, the interference level can be reduced by diluting the samples, taking into account the

Table 3 Effect of foreign ions on the determination of 250 $\mu g\ l^{-1}$ of manganese

Foreign ion	*Tolerance level mg l^{-1}*
Ca(II), NO_3^-, F^-	>100
Ba(II), SO_4^{2-}, I^-, Sr(II), CO_3^{2-}	40
Mg(II) Cl^-	30
PO_4^{3-}, Br^-, CN^-, $C_2O_4^{2-}$, BO_2^-	20
Zn(II)	10
SCN^-	5
Al(III), Pb(II)	2.5
Cu(II)	1.2
Co(II), Fe(III)	0.4
EDTA, Mo(VI), Fe(II), V(V)	<0.4

sensitivity of the method proposed and the dependence of the sensitivity on the sample volume.

Analytical applications

The SPS method proposed for manganese has been applied for the manganese determination in: a) plant tissue extracts, b) activated charcoal and c) natural water samples.

The determination of manganese in plant tissue extracts (olive leaves) was performed using the direct calibration method, since no matrix effect was observed. Samples were collected from olive plantations near the city of Jaen (Spain). The leaves selected were adults taken from totally developed trees. The average value (three determinations) of the manganese content was found to be 23.5 mg $100\ g^{-1}$ (RSD 0.072). The AAS result obtained (six determinations) was 23.6 mg $100\ g^{-1}$ (RDS 0.013).

On the other hand, the method was applied to the determination of manganese in commercial active charcoals by the direct calibration method for the 250 ml sample method. The average values (five determinations) of the manganese found were 64.8 ± 1.7 mg $100\ g^{-1}$ at active charcoal 1 and 43.4 ± 0.7 g $100\ g^{-1}$ at active charcoal 2. The AAS results were 65.6 ± 1.6 mg $100\ g^{-1}$ and 42.8 ± 0.6 mg $100\ g^{-1}$, respectively.

Finally, the manganese contents in three different water samples (tap water from the city of Jaen, and mineral water from Ortigosa del Monte (Segovia) and San Hilario Sacalm (Gerona)), were lower than the detection limit of the method. To check the accuracy of the proposed method in manganese analysis in water, a recovery study on the above water samples was conducted. In doing so, a different amount of Mn(II) was added to a 250-ml sample system (50, 100, 200 and 400 $\mu g l^{-1}$), 500 ml sample system (20, 50, 100 and 200 $\mu g l^{-1}$) and 1,000-ml sample system (10, 20, 50 and 100 $\mu g l^{-1}$) of the three water samples analysed. The average percentages of recovery, mean of three determinations, were acceptable within the standard conditions established: 99.4, 100.1 and 96.0% for Ortigosa del Monte mineral water (250,

500 and 1,000 ml, respectively); 92.0, 95.5 and 96.4% for San Hilario Sacalm mineral water and 88.8, 95.3 and 96.8% for tap water from Jaen.

The analysis of the Mn(II) added to the water samples analysed was conducted using the calibration curve and the standard addition method. The loss of sensitivity by matrix effect can be evaluated by the slope's ratio between the standard and the standard addition calibration curves. The ratio found was 0.97 for Ortigosa del Monte water, 0.84 for San Hilario Sacalm water and 2.28 for tap water. Precision (expressed as RSD) for the SPS method varies between 1 and 6%. The average precision for the three water samples analysed was 3.3%.

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