Spectrophotometric determination of manganese(II) by picolinaldehyde nicotinoylhydrazone

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Manganese (II) forms a yellow coloured complex with a reagent picolinaldehyde nicotinoylhydrazone (PANH), which can be quantitatively extracted into chloroform in the pH range 8.7-10.5. Beer’s law was obeyed over the concentration range of 0.02-1.5 ppm with absorption maxima at 385 nm. The molar absorptivity and Sandell’s sensitivity of the extracted species was found to be 4.606 x 10^4 L mol^-1 cm^-1 and 1.19 ng cm^-2 respectively. The nature of the complex was determined by different methods and it was found to be 1:2 (Metal: Ligand). Interference due to diverse ions has been studied. The proposed method is simple, rapid, accurate, sensitive and has been applied for separation and determination of Mn(II) in synthetic mixtures and real samples.

Experimental Procedure

**Apparatus and reagents**

The absorbance measurements were made on Shimadzu 160 A UV-Vis spectrophotometer and GBC 932 AA, atomic absorption spectrophotometer. Elico, model EQ-610, pH meter with combined glass electrode for the pH measurements.

The stock solution of manganese(II) was prepared by dissolving 4.503 g of MnCl₂.4H₂O in 250 mL of distilled water with few drops of concd HCl and was standardised gravimetrically¹³. The working solutions were prepared by appropriate dilutions. The reagent was synthesised by the reported method¹⁴.

**Method**

To an aliquot of solution containing 0.2-15 μg of Mn(II), 1 mL of 3.54 x 10^-3 M reagent was added and the pH of solution was adjusted by 2 mL of buffer (HCl+NH₄OH) of pH 9 and the total volume was made 10 mL using distilled water. Prior to pH adjustment, addition of reagent is necessary to prevent manganese precipitation. The solution mixture was transferred into a separatory funnel and was equilibrated for 30 s with 10 mL of chloroform. The absorbance of yellow organic phase containing Mn(II)-PANH complex was measured spectrophotometrically at 385 nm against reagent blank.

**Determination of manganese(II) in synthetic mixtures and real samples**

The present method was applied in determination of manganese (10 μg) in various synthetic mixtures and metallurgical samples containing known amounts of manganese. The results were found to be in good agreement (Table 1).

Aluminium drilling sample (0.12 g, Ita Lab) was dissolved by heating with 15 mL concd HCl and 2 mL HNO₃ and evaporated to nearly dryness. The residue formed was extracted in 20 mL of distilled water and finally dilution was made to known volume.

Manganese as micronutrient has a very important biological significance. Industrially it has also a great significance, especially in steel industry used as a hardening agent and as an additive to counter act the effects of the sulphur in steel and the major percentage is consumed by steel industry. Manufacturing of dry cells and alloys also consume significant amount of manganese. Thus determination of manganese in chemical and biological samples is often required.

Number of reagents had been reported¹⁻¹² for the spectrophotometric determination of manganese, however these methods suffer from the limitations such as longer extraction time³⁻⁷, lower sensitivity and molar absorptivity¹⁻²,⁴,⁶⁻¹⁰,¹⁻², requires standing time³⁻⁵,ᵐ⁻⁸⁻⁹, and interference from large number of ions¹⁻⁻¹¹ usually associated with manganese. In the present investigation, picolinaldehyde nicotinoylhydrazone (PANH) is used for the first time as an analytical reagent for the extractive separation and spectrophotometric determination of manganese(II) at trace levels.
WAR et al.: SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE(II) BY PICOLINALDEHYDE

Each of mild steel samples (0.5 & 0.512 g, Ita Lab) was dissolved in 10 mL of aqua-regia and was evaporated nearly to dryness and extracted with 10 mL of 2M HNO₃ and diluted to known volume with double distilled water.

Fe-Mn powder sample (0.2 g, Ita Lab) was opened in 10 mL of aqua-regia and was evaporated nearly to dryness and extracted with 10 mL of 2M HNO₃ and diluted to known volume with double distilled water.

Fig. — Extraction of manganese(II) as a function of pH

Fig. 2 — Absorption spectra of manganese(II)-PANH and PANH. Spectrum A: Mn(II)-PANH against reagent blank, Spectrum B: PANH against chloroform

Results and Discussion

Extraction as a function of pH

Manganese(II) from the pH range of 1.0-11.5 using HCl to NH₄OH medium was extracted with PANH with chloroform as solvent and the extraction was found to be quantitative from 8.7-10.5 pH. Hence all the extractions were carried out at pH 9.0 (Fig. 1).

Extraction as a function of PANH concentration

Manganese(II) was extracted with varying concentration of PANH (4.42×10⁻⁵ to 6.63×10⁻¹ M). It was observed that the extraction of 10 μg of manganese(II) was quantitative (99.63 %) with 1.77×10⁻⁴ M PANH in 10 % ethanol. Excess of reagent concentration did not show any effect on the extraction and spectrophotometric determination of manganese(II). Hence, a somewhat higher concentration, 3.54×10⁻⁴ M of PANH was used for further studies.

Absorption spectra

The absorption spectra of manganese(II)-PANH complex in chloroform showed an absorption maxima at 385 nm against reagent blank. At this wavelength the reagent did not show any significant absorbance.

Fig. 3 — Log-log plot manganese(II) for the determination of composition of the complex

The extraction of manganese from all above sample solution was carried out using 3.54×10⁻¹ M PANH with chloroform. Replicate analyses were carried out and results obtained were compared with those obtained by AAS. They were found in good agreement.
Table 1 – Determination of manganese(II) in synthetic mixtures and real samples

<table>
<thead>
<tr>
<th>Synthetic mixtures</th>
<th>Certified value (%)</th>
<th>Amount found* (%)</th>
<th>S. D. (%)</th>
<th>C. V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(10), Ag(100), Fe(100)</td>
<td>—</td>
<td>99.84</td>
<td>0.151</td>
<td>0.151</td>
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<td>Mn(10), Cr(50), Pd(50)</td>
<td>—</td>
<td>99.86</td>
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<td>Mn(10), Mg(100), Au(100)</td>
<td>—</td>
<td>99.94</td>
<td>0.194</td>
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<tr>
<td>Mn(10), Hg#(100), Cr(50)</td>
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<td>99.90</td>
<td>0.2</td>
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<tr>
<td>Mn(10), V(100), Pt(100)</td>
<td>—</td>
<td>99.80</td>
<td>0.122</td>
<td>0.122</td>
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</tbody>
</table>

Real samples

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>aluminium drilling</td>
<td>0.87</td>
</tr>
<tr>
<td>(Ita Lab)</td>
<td></td>
</tr>
<tr>
<td>Mild steel-1</td>
<td>1.15</td>
</tr>
<tr>
<td>(Ita Lab)</td>
<td></td>
</tr>
<tr>
<td>Mild steel-2</td>
<td>0.74</td>
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<tr>
<td>(Ita Lab)</td>
<td></td>
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<tr>
<td>Fe-Mn powder</td>
<td>53.84</td>
</tr>
<tr>
<td>(Ita Lab)</td>
<td></td>
</tr>
</tbody>
</table>

All values in parenthesis are in µg
* Average of five determinations
# Masked with I

Therefore all the spectral measurements were carried out at this wavelength (Fig. 2).

Effect of equilibration period

The colour development was instant, however shaking time was varied from 5 to 120 s after reagent addition. The shaking time was fixed as 25 s for extraction. There was no adverse effect on composition of complex or colour due to longer equilibration time tried up to 120 s.

Extraction with various solvents

Manganese(II) was extracted with PANH in different solvents. The extraction was found to be quantitative with chloroform (99.63 %), while with amyl acetate, ethyl acetate, n-butyl acetate, xylene, toluene, benzene, carbon tetrachloride and isobutyl methyl ketone the extraction was found to be incomplete (between 47.07-4.75 %). Therefore chloroform was used as the solvent for further studies.

Validity of Beer’s law

The present studies indicate that the system obeys Beer’s law in the concentration range 0.02-1.5 µg mL⁻¹ of manganese(II). The molar absorptivity and Sandell’s sensitivity of the system was found to be 4.606×10⁴ L mol⁻¹ cm⁻¹ and 1.19 ng cm⁻² respectively. The Ringbom’s optimum working range was 0.15-1.28 µg mL⁻¹.

Composition of the extracted species

The composition of the extracted species was determined by Job’s continuous variation method and mole ratio method and was further confirmed by slope-ratio method, a plot of log D against log [PANH] at fixed pH (9.0), where D is distribution ratio of manganese(II) between organic and aqueous phase, and [PANH] is the concentration of reagent in organic phase. A straight-line graph with a slope equal to 2, indicates 1:2 (metal to ligand) complex (Fig. 3).

Effect of diverse ions

Effects of various cations and anions on the extractive separation of manganese(II) were studied and the tolerance limit was set as an amount required to cause an error of ±2 % in the manganese(II) recovery. The tolerance limits for the diverse ions investigated are: F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, ClO₄⁻, BrO₃⁻, IO₃⁻, CO₃⁻, HCO₃⁻, S₂O₃⁻, SCN⁻, acetate, citrate, tartrate, oxalate, urea (20 mg each); S₂O₅²⁻ (12 mg); S₂O₃²⁻, Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Ag⁺, Se⁴⁺, Al³⁺, Sh⁵⁺, Ba²⁺ (10 mg each); W⁶⁺ (7.5 mg); S₂O₅²⁻ (6 mg); Mo⁶⁺ (5 mg); Pt⁴⁺ (2 mg); Cu²⁺, V⁵⁺ (1.5 mg each); Au³⁺ (0.2 mg); Pd²⁺ (0.15 mg); Cr³⁺, CN⁻ (0.07 mg each); U⁶⁺ (0.025 mg); EDTA (0.015 mg); Bi³⁺ (0.005 mg) and interfering ions like Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ are masked with CN⁻ and Hg²⁺ masked by I⁻.

References


2 Chikuma M, Nakaya Y, Yokoyama A, Maitani T & Tanaka