

## Spectrophotometric Determination of Iron(III) after Separation by Adsorption of its Pyrrolidinedithiocarbamate on Naphthalene

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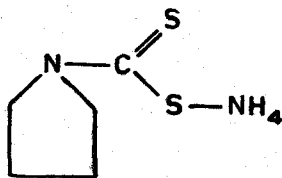
**Abstract.** A method for the spectrophotometric determination of trace amounts of iron(III) after adsorption of its pyrrolidinedithiocarbamate on naphthalene is presented. Iron(III) forms a water-insoluble chelate with ammonium pyrrolidinedithiocarbamate in the *pH* range 2.9-6.6. This chelate is quantitatively adsorbed onto microcrystalline naphthalene at room temperature. The effects of variables, such as *pH*, amount of reagent and naphthalene, digestion and shaking time, and diverse ions, have been examined. The method has been applied to the determination of iron(III) in standard reference materials and environmental samples and the results compared with 1,10-phenanthroline method.

### 1. Introduction

Ammonium pyrrolidinedithiocarbamate (APDC), also known as ammonium salt of 1-pyrrolidine carbodithioic acid, has attracted great interest as a chelating agent. Tellurium, copper and niobium have been determined spectrophotometrically using this complexone<sup>1-3</sup>. Kellner<sup>4</sup> has successfully separated cobalt and copper as their APDC complex using thin layer chromatography whereas Shimizu *et al.*<sup>5</sup> carried out the spectrophotometric estimation of copper, cobalt and arsenic after extracting their APDC complex into molten naphthalene. Atomic adsorption spectroscopic determination of traces of toxic metals like lead and arsenic as their APDC complexes extracted into MIBK or nitrobenzene has been suggested. Polarographic studies of iron(III)-1-pyrrolidine carbodithioate have also been carried out by Kitamura *et al.*<sup>8</sup> in MIBK. Recently, APDC has been recommended for the determination of palladium, nickel and copper<sup>9-11</sup>.

Extraction methods, however, are limited to complexes having large formation and partition coefficient, both of which increase with temperature. This fact has been

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profitably exploited by the author (MS) for extraction of metal complexes into molten naphthalene. A new method has now been developed in these laboratories for the separation and microdetermination of metal ions by adsorption of the metal complex on microcrystalline naphthalene generated *in situ*. Naphthalene containing complex is then dissolved in a suitable solvent for photometric measurements. In this communication we report the microdetermination of iron(III) as its complex with ammonium pyrrolidinedithiocarbamate.

## 2. Chemicals and Equipment

Standard iron(III) solution was prepared from iron(III) chloride solution (1000 ppm) obtained from Wako Pure Chemical Industries Ltd., Japan. A 0.2 per cent aqueous solution of APDC and 20 per cent naphthalene solution in acetone was used for complexation and adsorption studies respectively. Unimolar solution of ammonia, ammonium acetate and acetic acid in recommended proportions, were used as buffers to control the pH of the solution.

Hitachi model 200-20 double beam spectrophotometer and Toa-Dempa HM-5A pH-meter equipped with a combination electrode were employed for absorption and pH-measurements respectively.

## 3. Procedure

To 40 ml of sample solution containing 2-49  $\mu\text{g}$  of iron(III) in a tightly stoppered erlenmeyer flask, add 20 ml of 0.2 per cent APDC solution and adjust pH of the solution to 4.7 using suitable buffer solution. Mix the solution well and allow to stand for 20 min at 25-30°C. Transfer into this solution, as far as possible, 2.0 ml of 20 per cent naphthalene solution in acetone and shake vigorously for 1.5 min. Separate the solid by filtration using a filter paper (Whatman No. 1 or No. 5C, Tokyo Roshi Co., Japan) placed flat on a filter disc or through a sintered glass No. 2 disc. Wash with water and dry at 50-60°C in a oven. Dissolve the product in chloroform and make up to 10 ml and measure absorbance at 357 nm against the reagent (prepared similarly) as blank.

## 4. Results and Discussion

Fig. 1 shows the absorption spectra of the reagent and iron(III) APDC complex in naphthalene-chloroform solution. The iron(III)-chelate shows three peaks at 357,

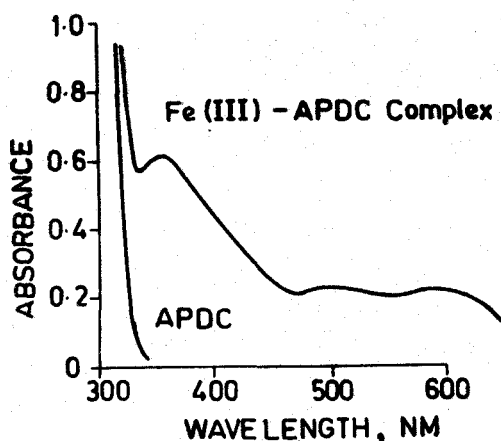


Figure 1. Absorption spectra of APDC and iron(III) complex in naphthalene— $\text{CHCl}_3$ ;  $\text{Fe(III)}$ :  $30\mu\text{g}$ ;  $\text{pH}$ : 4.7; digestion time: 20 min; 0.2% APDC: 2.0 ml; reference: water.

500 and 490 nm. Since the chelate has highest absorption maximum at 357 nm and the reagent shows no significant absorption at this wave length, subsequent studies have been carried out at 357 nm.

The effect of  $\text{pH}$  of the aqueous phase on the absorbance of iron(III)-chelate was studied in the  $\text{pH}$  range 1.0–8.8. The absorbance of iron(III)-chelate increased sharply at first, and remained constant over the range 2.9–6.6 and then decreased sharply above  $\text{pH}$  6.6. Subsequent studies have been carried out at  $\text{pH}$  4.7 adjusted using suitable buffers. Studies were carried out to determine the maximum amounts of APDC and naphthalene necessary for complexation and adsorption. It was observed that 0.5 ml of 0.2 per cent APDC and 0.5 ml of 20 per cent solution of naphthalene was sufficient for  $30\mu\text{g}$  of iron(III) present. However, during subsequent studies 2.0 ml of 0.2 per cent APDC and 2.0 ml of 20 per cent naphthalene solution was used. Experiments were carried out to study the effect of varying digestion time, shaking time and standing time. Although the reaction of iron(III) with APDC is a fast reaction, a 10 minute digestion time at  $25\text{--}30^\circ\text{C}$  seems desirable. Also, a shaking time of 1–2 minute appears necessary for adsorption after naphthalene solution is added to the chelate. The microcrystalline naphthalene having adsorbed iron(III)-APDC chelate may then be filtered immediately without allowing for any 'standing time'.

Various solvents were tested to dissolve the naphthalene carrying the adsorbed iron(III)-chelate. Although this solute is soluble in dimethylformamide, dioxane, acetonitrile, MIBK, methyl alcohol, dichloroethane and benzene, the resultant solution is unstable and unfit for photometric measurements. It is insoluble in DMSO but gives a stable solution in chloroform.

Interference in the estimation of iron(III) by the above method due to the presence of diverse ion has also been studied. The tolerance limit of various ions (as multiple of iron(III) concentration) is given in parenthesis.  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$  (5000 each),  $\text{Al}^{+3}$ (50),  $\text{Zn}^{+2}$ ,  $\text{Mn}^{+2}$ (10 each),  $\text{Pb}^{+2}$ (5),  $\text{Cd}^{+2}$ (1),  $\text{Cu}^{+2}$ ,  $\text{CO}^{+2}$ ,

$\text{Ni}^{+2}$ ,  $\text{PO}_4^{-3}$  caused serious interference. Under the optimum conditions, discussed above, Beer's law is obeyed over the range 0.23 to 4.9 ppm or iron(III). The molar absorptivity of the complex at 357 nm is  $1.1 \times 10^4$  whereas the sensitivity is  $4.9 \times 10^{-3} \mu\text{g cm}^{-2}$ . Relative standard deviation of ten replicate determinations was found to be 1 per cent.

## 5. Application

This method has been successfully applied to the analysis of iron containing alloys. Results obtained have been compared with those using 1,10-phenanthroline method. Known amount of the sample is dissolved in 1:1 HCl and then treated with 30 per cent  $\text{H}_2\text{O}_2$ . Excess  $\text{H}_2\text{O}_2$  is decomposed by heating and iron extracted into MIBK. It is then back extracted from the organic phase and the above procedure applied for the estimation (Table 1). Iron content of lake water samples has also been determined using APDC as described above.

**Table 1.** Comparative analysis of iron in standard reference materials (alloys) and metals.

Sample	Composition (%)	Iron certified value (%)	Present method (%)	1,10-phenanthro- line method (%)
N. B. S.	Cu : 3.99, Mg : 1.49		0.208	0.218
SRM-85B	Mn : 0.61, Cr : 0.21		0.228	0.216
Al alloy	Si : 0.18, Ni : 0.089	0.24	0.225	0.216
	Zn : 0.03, Ti : 0.022		0.234	0.222
	Pb : 0.021, Ga : 0.019		0.230	0.233
	V : 0.026,			
N. B. S.	Cu : 90.93, Si : 3.03		1.244	1.266
SRM-158A	Zn : 2.08, Mn : 1.11		1.227	1.294
Silicon-	Ti : 0.96, Al : 0.46		1.244	1.275
Bronze	Pb : 0.097, Ni : 0.001	1.23	1.210	1.237
Alloy	P : 0.026,			
Metallic aluminium	—	—	0.150 0.154 0.149 0.152 0.150	0.148 0.145 0.147 0.142 0.142
Metallic magnesium	—	—	0.0021 0.0020 0.0018 0.0017	0.0019 0.0019 0.0019 0.0019

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