

## Extraction and Formation of Iron(III) Thiocyanate Complexes: Application for Spectrophotometric Determination of Iron

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Extraction of iron(III) from sulphuric and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium (TPP) chloride and cetyltrimethylammonium (CTMA) bromide in chloroform was investigated. Optimum conditions for extraction by both extractants were determined. The extraction behaviour of CTMA was found to be more efficacious than that of TPP because less thiocyanate and extractant was required. Better extraction efficiency of CTMA can be attributed to surface-active properties of this substance. Formation of an extractable iron(III) thiocyanate complex with CTMA or TPP was also determined spectrophotometrically by measuring the absorbance of the organic phase at 473 nm or 506 nm, respectively. The composition of the extracted iron(III) complexes was determined by distribution and spectrophotometric methods. The molar ratio Fe:SCN:TPP of the extracted complex was 1:4:1; accordingly, its composition was [TPP][Fe(SCN)<sub>4</sub>]. The molar ratio Fe:CTMA of the extracted complex was 1:3. The molar ratio Fe:SCN in the complex extracted with CTMA could not be determined because of the turbidity in solutions containing less than 0.01 mol dm<sup>-3</sup> thiocyanate ion, but it was concluded that the composition of the extracted complex was [CTMA]<sub>3</sub>[Fe(SCN)<sub>6</sub>].

*Key words*  
iron  
thiocyanate  
extraction  
spectrophotometry

### INTRODUCTION

The best known reaction of aqueous iron(III) is with thiocyanate ion to form an intense red colour and it is therefore of use in detection and quantitative estimation of trace quantities of iron(III).<sup>1</sup> Owing to the stepwise complex formation in solution, a mixture of various iron(III) thiocyanate complexes with coordination numbers from 1 to 6 is formed. Excess of one complex form and transformation of one into another depends largely on the reacting component concentration, solution acidity and the presence of a nonaqueous solvent. In the presence of excess thiocyanate concentration over Fe<sup>III</sup> it is possible to obtain complex anion species having various numbers of coordinate thiocyanate anions.<sup>2</sup>

The colour of aqueous solutions of Fe<sup>III</sup> thiocyanate is unstable owing to the reduction of Fe<sup>III</sup> by SCN<sup>-</sup>, which makes the quantitative measurements somewhat difficult.<sup>3</sup> The stability of the iron(III) complex can be enhanced by adding a second ligand to form a new mixed complex, which can be extracted into an organic solvent. Extraction increases the sensitivity of the thiocyanate method, but little information is available on the iron(III) species in the organic phase.<sup>4,5</sup>

The present investigation is an attempt to study the stoichiometry of the extracted iron thiocyanate complex in chloroform with cetyltrimethylammonium (CTMA) bromide and tetraphenylphosphonium (TPP) chloride. Also, we will compare the extraction properties of

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cetyltrimethylammonium (CTMA), which is a cationic surfactant and an ion-pair extractant, and of tetraphenylphosphonium (TPP) chloride, which is only an ion-pair extractant.

We found in our experiments that the iron(III) species extracted in chloroform by CTMA and TPP is present as iron hexathiocyanate and tetrathiocyanate complexes, respectively.

## EXPERIMENTAL

### Reagents

Standard iron solution  $c(\text{Fe}^{\text{III}}) = 0.1 \text{ mol dm}^{-3}$  was prepared by dissolving  $\text{FeCl}_3 \times \text{H}_2\text{O}$  (Kemika) in  $0.1 \text{ mol dm}^{-3}$  HCl. The solution was standardized by titration with EDTA.<sup>6</sup> To prevent the formation of iron(III) hydrolysed species in water, working samples of lower concentrations of iron(III) were prepared daily by diluting aliquots of the stock solutions. Tetraphenylphosphonium chloride (analytical grade, Fluka) and cetyltrimethylammonium bromide (cryst. pure, Serva) were dissolved in reagent grade chloroform. All chemicals used were of the p.a. purity grade.

### Extraction Procedures

The iron(III) distribution ratio was determined at room temperature by shaking equal volumes ( $5 \text{ cm}^3$ ) of the organic and aqueous phases of a given composition with a mechanical shaker in a  $50 \text{ cm}^3$  conical flask for 20 min. After the phases were separated by gravity, an aliquot of the organic or aqueous phases was used.

A calibration curve for spectrophotometric determination of iron(III) was prepared by taking known amounts of standard solution of iron(III), forming the complex and measuring the absorbance of the organic phase *vs.* reference solution at 473 nm and 506 nm for CTMA and TPP, respectively, using a Varian Cary 3 spectrometer. Iron distribution was determined by absorbance measurements in the organic phase. Iron concentrations in the aqueous phase were calculated from the difference between the maximum and constant absorbances of the organic phase at 473 nm or 506 nm at optimum conditions for extraction ( $A_0$ ) and the measured absorbance value before reaching complete complex formation in the organic phase ( $A_x$ ).

Iron concentrations in the aqueous phase were also determined after appropriate dilution by flame atomic absorption using a Unicam 919 AA spectrometer with a specialized computer program. Iron concentrations in the organic phase were calculated from the difference in iron concentrations in the aqueous phase before and after extraction.

## RESULTS AND DISCUSSION

### Optimal Conditions for Extraction

Extraction of iron(III) from sulphuric and hydrochloric acid solutions containing an excess of thiocyanate ions

TABLE I. Dependence of the percent of extraction and the absorbance of the organic phase on acid concentration of the aqueous phase<sup>(a)</sup>

$c(\text{H}_2\text{SO}_4)$ $\text{mol dm}^{-3}$	pH <sup>(b)</sup>	E(CTMA) %	$A_{473}(\text{CTMA})$	E(TPP) %	$A_{506}(\text{TPP})$
without addition	3.74	96.48	0.462	95.70	0.371
0.05	1.10	97.67	0.707	94.80	0.413
0.1	0.82	97.54	0.705	93.26	0.409
0.2	0.70	97.80	0.709	89.60	0.425
0.4	0.46	97.48	0.704	83.48	0.383
0.5	0.35	97.61	0.704	81.29	0.389
1.0	0.14	97.25	0.707	69.52	0.302
1.5		96.85	0.709	67.32	0.275
2.0		96.29	0.697	64.01	0.258
3.0		94.97	0.685	61.18	0.238

<sup>(a)</sup>  $c(\text{Fe}^{\text{III}}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ ;  $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$  with  $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$  and  $c(\text{SCN}^-) = 0.2 \text{ mol dm}^{-3}$  with  $c(\text{TPP}) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

<sup>(b)</sup> measured.

with CTMA bromide and TPP chloride in chloroform was investigated. An iron(III) thiocyanate complex formed in the aqueous phase was extracted (about 98 %) with CTMA in the acidity range from  $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol dm}^{-3}$  to  $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$ . In the same acidity range, using TPP, the complex extraction decreased as acid concentration increased from about 95 to 64 % iron(III) (Table I). Extraction from the hydrochloric acid solution was less efficient, which may be ascribed to the formation of mixed ligand ions. Therefore, all investigations were carried out with  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$  sulphuric acid solutions to eliminate the possible influence of chloride ions from hydrochloric acid.

The effect of thiocyanate concentration on the formation and extraction of the iron(III) thiocyanate complex was examined by varying the thiocyanate concentration in the aqueous phase. Extractions started from solutions containing the analytical iron(III) concentration  $2 \times 10^{-5} \text{ mol dm}^{-3}$  and sulphuric acid concentration  $0.2 \text{ mol dm}^{-3}$  using an excess of extractants in chloroform. For maximal extraction of iron(III) (about 98 %) with CTMA ( $3 \times 10^{-3} \text{ mol dm}^{-3}$ ), a thiocyanate concentration  $5 \times 10^{-2} \text{ mol dm}^{-3}$  or higher was required (the molar ratio of thiocyanate to iron was  $\geq 2500:1$ ). However, with  $2 \times 10^{-2} \text{ mol dm}^{-3}$  TPP, only a maximum of 80 % of iron(III) was extracted from a solution containing more than  $0.20 \text{ mol dm}^{-3}$  thiocyanate (the molar ratio of thiocyanate to iron was  $\geq 10^4:1$ ) (Figure 1a). It was obvious that the increase of thiocyanate concentration caused increased iron(III) extraction. Excess of thiocyanate over the iron(III) concentration shifted the complex equilibrium toward formation of iron(III) thiocyanate complex anions. This suggests that the anionic iron(III) thiocyanate was extracted by both extractants.

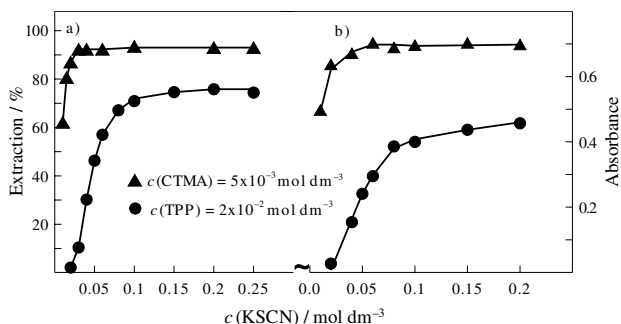


Figure 1. Dependence of the percent of extraction of iron(III) (a) and absorbance on thiocyanate concentration (b).  $c(\text{Fe}^{\text{III}}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ ,  $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $c(\text{TPP}) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

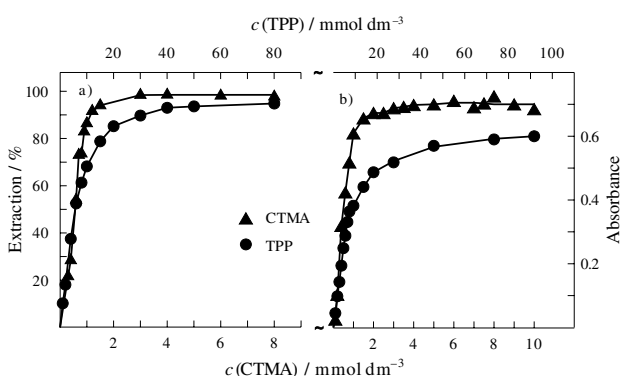


Figure 2. Dependence of the percent of extraction of iron(III) (a) and absorbance (b) on extractant concentration.  $c(\text{Fe}^{\text{III}}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ ,  $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$  with CTMA and  $c(\text{SCN}^-) = 0.2 \text{ mol dm}^{-3}$  with TPP.

When the aqueous phase containing sulphuric acid ( $0.2 \text{ mol dm}^{-3}$ ) was equilibrated with chloroform containing CTMA ( $3 \times 10^{-3} \text{ mol dm}^{-3}$ ), a stable turbid emulsion was formed, perhaps as the result of the solubilisation of chloroform molecules with the micelles of cationic surfactants.<sup>7</sup> The emulsion was so stable that separation of phases was impossible even after 5 hours. No turbidity appeared if the molar excesses of thiocyanate over CTMA higher than 1.5:1 were present in the examined system. Accordingly, only solutions containing  $[\text{SCN}^-]:[\text{CTMA}] \geq 1.5:1$  were suitable for further studies.

The effects of CTMA and TPP concentration on the extraction of iron(III) at optimal acidity and thiocyanate concentration were also studied. For maximal extraction (about 98 %) of iron(III) ( $2 \times 10^{-5} \text{ mol dm}^{-3}$ ), the molar ratio of CTMA to  $\text{Fe}^{\text{III}}$  had to be at least 150:1 ( $3 \times 10^{-3} \text{ mol dm}^{-3}$  CTMA) and the molar ratio TPP to  $\text{Fe}^{\text{III}}$  was found to be 4000:1 ( $8 \times 10^{-2} \text{ mol dm}^{-3}$  TPP) (Figure 2a).

Under optimal conditions for extraction in the whole acidity range, the distribution equilibrium was attained in less than 5 min. The shaking time of the aqueous and organic phases of 20 min was sufficient to achieve reproducible results by measuring the non-extracted iron in the aqueous phase by atomic absorption spectrometry.

### Absorption Spectra of Extracted Complexes

The iron(III) thiocyanate complex, formed in aqueous sulphuric acid solutions, extracted in chloroform as the ion-pair with cetyltrimethylammonium (CTMA) or tetraphenylphosphonium (TPP) cation, gave a red extract that showed maximum absorbance at 473 nm and 506 nm, respectively (Figure 3). The increase in sensitivity and the hypsochromic shift in the wavelength of maximum absorbance may be attributed to surface-active properties of CTMA.

The absorbance at maximum wavelength remained stable for at least 6 hours if CTMA was used as extractant. In the presence of TPP, the extract gradually lost its red colour. All measurements using TPP as extractant were made within a few minutes after phase separation because the variation of the absorbance was not significant in the first 20 minutes (Table II). The fading of the red

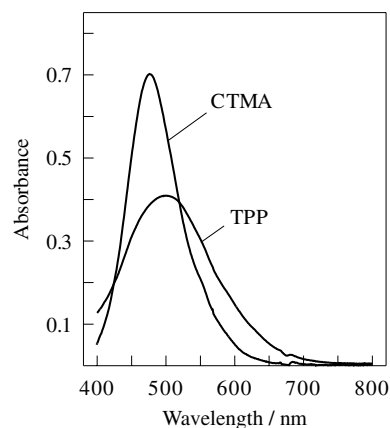


Figure 3. Absorption spectra of iron(III)-SCN complexes in chloroform.  $c(\text{Fe}^{\text{III}}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ ;  $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$  with  $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$  and  $c(\text{SCN}^-) = 0.2 \text{ mol dm}^{-3}$  with  $c(\text{TPP}) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

TABLE II. Time dependence of the absorbance of the organic phase under optimal conditions<sup>(a)</sup>

Time/min	$A_{473}(\text{CTMA})$	$A_{505}(\text{TPP})$
0	0.691	0.432
5	0.703	0.433
10	0.704	0.436
20	0.706	0.432
30	0.707	0.427
40	0.705	0.422
60	0.709	0.410
120	0.709	0.375
180	0.704	0.302
360	0.707	0.252

<sup>(a)</sup>  $c(\text{Fe}^{\text{III}}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ ;  $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$  with  $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$  and  $c(\text{SCN}^-) = 0.2 \text{ mol dm}^{-3}$  with  $c(\text{TPP}) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

colour of Fe<sup>III</sup> thiocyanate was due the reduction of Fe<sup>III</sup> by SCN<sup>-</sup>.<sup>8</sup> It may be suggested that the presence of surfactant CTMA inhibited this reduction.

Acidity dependence showed that the absorbance of the organic phase was constant over 0.05 to 1.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> using CTMA. In the same acidity range, using TPP, the absorbance of the organic phase decreased (Table I). The relatively low absorbance values of the organic phase obtained from aqueous solutions of low acidity may be caused by hydrolysis of iron(III), an effect that appreciably lowers the concentration of iron(III) ions in solution. The noticeable decrease in absorbance for highly acidic solutions may be in connection with the instability of the Fe<sup>III</sup> thiocyanate complex in the aqueous solution. Both effects were lessened when CTMA was used as extractant.

Maximum and constant absorbances of the extracted Fe-SCN-CTMA complex were in the same thiocyanate (Figure 1b) and CTMA (Figure 2b) concentration range as for quantitative extraction. Using TPP, constant absorbances were not achieved in the investigated thiocyanate and TPP concentration range.

The proportionality between the iron concentration in the organic phase and the absorbance at 473 (506) nm was checked. The solutions containing KSCN, H<sub>2</sub>SO<sub>4</sub> and CTMA (TPP) in the optimal conditions and the iron(III) concentration varying from 1 × 10<sup>-6</sup>–4 × 10<sup>-5</sup> mol dm<sup>-3</sup> were prepared. The results show that Beer's law was verified for the range of the iron(III) concentration studied. The value of the molar absorption coefficient was in the order of 3.55 × 10<sup>4</sup> mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup> (CTMA) and 2.10 × 10<sup>4</sup> mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup> (TPP), respectively. Therefore, CTMA was a more suitable extractant for the spectrophotometric determination of iron in the organic phase.

#### Identification of Extractable Iron(III) Complexes

The composition of the thiocyanate iron(III) complex extracted with CTMA or TPP at c(H<sub>2</sub>SO<sub>4</sub>) = 0.2 mol dm<sup>-3</sup> was determined spectrophotometrically in the organic phase.

The results obtained by Job's method of continuous variation<sup>9</sup> (Figure 4) indicated that the molar ratio of Fe<sup>III</sup> to CTMA and to TPP was 1:3 and 1:1, respectively. The molar ratio of iron(III) to CTMA or TPP was also studied by distribution methods (slope analysis).<sup>10</sup> The same method was used for determining the molar ratio of iron(III) to thiocyanate. The concentration of the nonextracted iron(III) in the aqueous phase was determined by atomic absorption spectroscopy.

The dependence of the distribution ratio on analytical extractant concentration was determined by maintaining the optimum sulphuric acid concentration and the excess of thiocyanate concentration in the aqueous phase constant. A one-power extractant dependency was found over the entire investigated range of TPP. These results showed that one TPP cation was bonded to one atom of

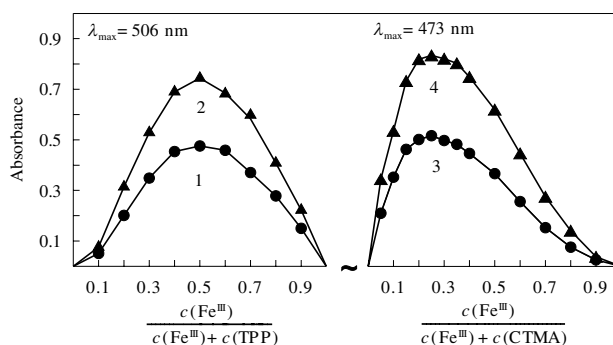


Figure 4. Determination of complex composition by Job's method of continuous variation. c(H<sub>2</sub>SO<sub>4</sub>) = 0.2 mol dm<sup>-3</sup>, c(SCN<sup>-</sup>) = 1 mol dm<sup>-3</sup>. c(Fe<sup>III</sup>) + c(CTMA) = 4 × 10<sup>-4</sup> mol dm<sup>-3</sup> (1); c(Fe<sup>III</sup>) + c(CTMA) = 5 × 10<sup>-4</sup> mol dm<sup>-3</sup> (2); c(Fe<sup>III</sup>) + c(TPP) = 1 × 10<sup>-3</sup> mol dm<sup>-3</sup> (3) and c(Fe<sup>III</sup>) + c(TPP) = 1.2 × 10<sup>-3</sup> mol dm<sup>-3</sup> (4).

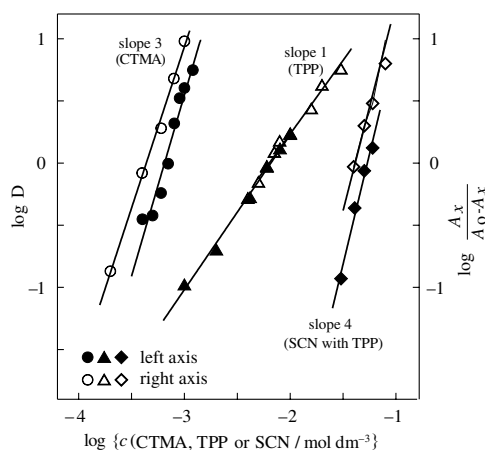


Figure 5. Figure Dependence of the distribution ratio of iron(III) on extractant or thiocyanate concentration. c(Fe<sup>III</sup>) = 2 × 10<sup>-5</sup> mol dm<sup>-3</sup>, c(H<sub>2</sub>SO<sub>4</sub>) = 0.2 mol dm<sup>-3</sup>. log D or log A<sub>x</sub>/A<sub>0</sub>-A<sub>x</sub> versus log CTMA, c(SCN<sup>-</sup>) = 0.1 mol dm<sup>-3</sup> (1); log D or log A<sub>x</sub>/A<sub>0</sub>-A<sub>x</sub> versus log TPP, c(SCN<sup>-</sup>) = 0.2 mol dm<sup>-3</sup> (2); log D or log A<sub>x</sub>/A<sub>0</sub>-A<sub>x</sub> versus log [SCN<sup>-</sup>], c(TPP) = 2 × 10<sup>-2</sup> mol dm<sup>-3</sup>.

iron. Contrary to TPP extraction, the slope of the graph, obtained by plotting log D versus log CTMA, showed that a stoichiometric ratio of CTMA to iron in the extracted complex was 3:1 (Figure 5, left axis). In connection with these investigations, it can be concluded that the anionic iron(III) thiocyanate complexes transferred into the organic phase using TPP or CTMA bear one or three negative charges, respectively.

The dependence of the distribution ratio on the analytical thiocyanate concentration in the aqueous phase was determined by keeping both concentrations of sulphuric acid in the aqueous phase and the CTMA or TPP in the organic phase within the range of maximal extraction. Using TPP as extractant, a fourth-power thiocyanate dependency was found. This indicated that four thiocyanate ions were bonded to one atom of iron, forming

$[\text{Fe}(\text{SCN})_4]^-$ , which was then transferred into the organic phase after the addition of onium salt.

The number of moles of thiocyanate per mole of iron(III) in the complex extracted with CTMA could not be determined because of the turbidity in solutions containing less than  $0.01 \text{ mol dm}^{-3}$  thiocyanate ion. But, it can be concluded that the  $[\text{Fe}(\text{SCN})_6]^{3-}$  complex was transferred into the organic phase. This is consistent with the findings that the anionic iron(III) thiocyanate complexes transferred into the organic phase bear three negative charges. According to literature data, the presence of cationic surfactants permits a higher metal to ligand molar ratio in ternary complexes as a result of hydrophobic interactions.<sup>11</sup> In a previous study, the existence of the anionic iron(III) hexathiocyanate complex was found in a water insoluble ionic association compound with tetramethyl<sup>12</sup> or tetrabutylammonium ion.<sup>13</sup>

The results obtained by the equilibrium shift method,<sup>14</sup> plotting  $\log A_x/A_0 - A_x$  versus  $\log \text{CTMA}$ ,  $\log \text{TPP}$  or  $\log \text{SCN}$  (Figure 4 right axis), were compatible with the results obtained by distribution (slope analysis) and Job's method. This confirmed that the compositions of the extracted complexes were  $[\text{CTMA}]_3[\text{Fe}(\text{SCN})_6]$  and  $[\text{TPP}][\text{Fe}(\text{SCN})_4]$ .

#### Effect of Diverse Ions and Method Application

The effect of diverse ions on determination of iron(III) with CTMA was studied under optimal conditions for spectrophotometric measurements. The amounts of ions tolerated are shown in Table III. Cobalt<sup>15</sup> gives an analogous blue compound, but absorption maximum is so far from that of iron that the concentration of cobalt can be 10 times that of iron without an increase in the absorbance reading for iron. Copper(II)<sup>16</sup> and molybdenum(VI)<sup>17</sup> form analogous compounds of similar colour but using the method of simultaneous equations<sup>18</sup> iron can be determined if a 10-fold excess of copper or molybdenum(VI) is present. Because of complex formation with iron acetate decrease absorbance and must be removed before iron determination as well as chromium(III).

The proposed method was found to be applicable for the determination of iron in various soil samples. The solid sample was decomposed by heating with a mixture of sodium and potassium carbonate. After cooling the

TABLE III. The effect of foreign ions on the determination of iron(III) by the recommended procedure<sup>(a)</sup>

Foreign ions	Concentration tolerated (Molar ratio)
sulphate, nitrate, chloride, ammonium, Na, K, Ca, Mg, Ba, Sr, Ni, Mn <sup>II</sup>	1000-fold
perchlorate, phosphate, Sn <sup>II</sup> , W <sup>VI</sup> , Al <sup>III</sup> , Cd <sup>II</sup>	100-fold
Zn <sup>II</sup> , Co <sup>II</sup> , Hg <sup>II</sup>	10-fold
Cr <sup>III</sup> , acetate	not allowed

<sup>(a)</sup>  $c(\text{Fe}^{\text{III}}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ ;  $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$ ;  $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$ .

TABLE IV. Soil sample analysis

Sample	Calculated iron content <sup>(a)</sup> / %	
	complexometric titration with EDTA <sup>6</sup>	spectrophotometric with CTMA
clay mineral	$8.16 \pm 0.03$	$8.15 \pm 0.02$
marine sediment 1	$2.43 \pm 0.02$	$2.41 \pm 0.02$
marine sediment 2	$1.71 \pm 0.02$	$1.72 \pm 0.03$

<sup>(a)</sup> Average of three determinations.

melt was dissolved in 1:1 HCl and the solution was then diluted to an appropriate volume. An aliquot of the aqueous solution of the analyte was taken and iron(III) was determined with CTMA by the recommended procedure. The results (Table IV) were compared with those obtained by the complexometric titration with EDTA.<sup>6</sup>

## CONCLUSION

It has been shown that the colour system of iron(III) and cationic surfactant CTMA possesses good stability, high sensitivity and a wide tolerance in the experimental conditions over the Fe<sup>III</sup>-TPP system. Extraction of the Fe<sup>III</sup>-SCN complex with CTMA requires less excess thiocyanate and extractant than with TPP. Iron(III) could be extracted from a wide range of sulphuric acid concentrations, resulting in the formation of an anionic complex containing a larger number of thiocyanate ions in its structure.

The sensitivity of the reaction of thiocyanate with iron(III) is considerably increased when CTMA is used for extraction and sufficient stability is also obtained for spectrophotometric determination. Optimum conditions for spectrophotometric determination of iron(III) with CTMA are the acidic range from 0.05 to 1.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, concentration of thiocyanate  $\geq 0.08 \text{ mol dm}^{-3}$  and concentration of CTMA  $\geq 3 \times 10^{-3} \text{ mol dm}^{-3}$ . The extracted complexes in chloroform have maximum absorbance at 473 nm, obey Beer's law in the range  $1 \times 10^{-6}$ – $4 \times 10^{-5} \text{ mol dm}^{-3}$  and are stable for at least 6 hours. The molar absorptivity of the method is in the order of  $3.55 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ .

Comparison of the extraction and spectrophotometric behaviour of CTMA and TPP shows considerable differences, which can be attributed to the surface-active properties of CTMA.<sup>19</sup> In the presence of CTMA, the coordination behaviour of iron(III) ion and the stability of the anionic thiocyanate iron(III) complex can be changed through the formation of micelles,<sup>20</sup> since the optimal CTMA concentration for quantitative extraction of Fe<sup>III</sup> is higher than the critical micellar concentration (cmc).<sup>21</sup>

It has been established previously, that iron(III) ion is coordinated with six water molecules in aqueous solution.<sup>22</sup> Dehydration occurs during complexation with thiocyanate ions, and all the thiocyanate ions are bonded

to iron *via* their N atoms.<sup>8</sup> The complex thus interacts with the bulk substance mainly through the ligand sulphur atoms which have a poor hydrogen-bonding ability. Therefore, formation of the iron(III) thiocyanate complex prefers the hydrophobic environment present in the micellar solution of CTMA, which enables coordination of iron with six thiocyanate ions.

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## REFERENCES

1. Z. Marczenko, *Spectrophotometric Determination of Elements*, Ellis Harwood LTD., John Wiley&Sons, 1976, pp. 305–319.
2. V. P. Vasilev and P. S. Muhina, *Zh. Neorgan. Himii* **9** (1964) 1134–1140.
3. C. Rozycki, *Chem. Anal.* **11** (1966) 447–460.
4. E. Upor, *Acta Chim. Hung.* **73** (1972) 133–141.
5. K. Jurkiewicz, *Sep. Sci. Tehnol.* **22** (1987) 2381–2402.
6. *Complexometric Assay Methods with Titriplex*, E. Merck, Darmstadt, 1982, p. 42.
7. E. Pelizzetti and E. Pramauro, *Anal. Chim. Acta.* **169** (1985) 1–29.
8. E. Itabashi, *Inorg. Chem.* **24** (1985) 4024–4027.
9. P. Job, *Ann. Chim. Phys.* **9** (1928) 113–203.
10. G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, Inc. New York, 1965 pp. 50–75.
11. S. B. Savvin, I. N. Marov, R. K. Chernova, S. N. Shtykov, and A. B. Sokolov, *Zh. Anal. Khim.* **36** (1981) 850–859.
12. U. Müller, *Acta Cryst.* **B33** (1977) 2197–2201.
13. J. Hernández Méndez, A. Alonso Mateos, and E. J. Martín Mateos, *Analyst* **111** (1986) 217–219.
14. H. Puzanowska-Tarasiewicz, A. Grudniewska, and M. Tarasiewicz, *Anal. Chim. Acta* **94** (1977) 435–441.
15. I. Crnogaj and A. Gojmerac Ivšić, *Abstracts, XVII Hrvatski skup kemičara i kemijskih inženjera, Osijek, 2001*, p. 156.
16. A. Gojmerac Ivšić and B. Tamhina, *Croat. Chem. Acta* **73** (2000) 605–614.
17. A. Gojmerac Ivšić and I. Crnogaj, unpublished data.
18. G. D. Christian and J. E. O'Reilly (Eds.), *Instrumental Analysis*, Allyn and Bacon, Inc. Boston, 1986, pp. 184–185.
19. D. Attwood and A. T. Florence, *Surfactant Systems*, Chapman and Hall, London, 1985, p. 365.
20. M. Jarosz and Z. Marczenko, *Chem. Anal.* **37** (1992) 63–68.
21. K. L. Cheng, K. Ueno, and T. Imamura, *Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, Florida, 1982, p. 480.
22. K. Ozutsumi, M. Kurihara, T. Miyazawa, and T. Kawashima, *Anal. Sci.* **8** (1992) 521–526.

## SAŽETAK

### Ekstrakcija i nastajanje željezova(III) tiocijanatna kompleksa: Primjena za spektrofotometrijsko određivanje željeza

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Ispitana je ekstrakcija željeza(III) iz sumporno i klorovodično kiselih otopina koje sadrže suvišak tiocijanatnih iona s tetrafenilfosfonijevim (TPP) kloridom i cetiltrimetilamonijevim (CTMA) bromidom u kloroformu. Određeni su optimalni uvjeti za ekstrakciju s oba ekstraktanta. Ekstrakcijsko ponašanje CTMA povoljnije je nego TPP, jer je potreban manji suvišak tiocijanata i ekstraktanta. Povoljnije ekstrakcijsko ponašanje CTMA može se pripisati površinski aktivnim svojstvima ove tvari. Nastajanje željezova(III) tiocijanatna kompleksa koji se ekstrahira s CTMA ili TPP također je utvrđeno spektrofotometrijski, mjerenjem apsorbancije organske faze pri 473 nm odnosno pri 506 nm. Sastav ekstrahiranih željezovih(III) kompleksa određen je distribucijskim i spektrofotometrijskim metodama. Molarni odnos Fe:SCN:TPP u ekstrahiranome kompleksu je 1:4:1, pa je prema tome sastav ekstrahiranoga kompleksa [TPP][Fe(SCN)<sub>4</sub>]. Molarni odnos Fe:CTMA u ekstrahiranome kompleksu je 1:3. Molarni odnos Fe:SCN u kompleksu ekstrahiranome s CTMA nije moguće odrediti zbog mutnoće u otopinama koje sadrže manje od 0.01 mol dm<sup>-3</sup> tiocijanatnih iona, ali se može zaključiti da je sastav ekstrahiranoga kompleksa [CTMA]<sub>3</sub>[Fe(SCN)<sub>6</sub>].