The solvent extraction of metals

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THE SOLVENT EXTRACTION OF METALS

A Thesis submitted in partial fulfilment of the requirements for the degree of

BACHELOR OF SCIENCE

(Honours)

by

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(Supervisor - Mr. F. M. Hall)

Wollongong University College,
The University of New South Wales,
November, 1968.
SUMMARY

The solvent extraction chemistry of the oxinates of aluminium, iron, chromium, and nickel have been studied, particularly that of aluminium.

Conditions for the quantitative analytical determination of aluminium by extraction of its oxinate have been put forward.

Investigations have been made to incorporate this method in the analysis for aluminium in steels containing iron, chromium and nickel as interfering elements. A number of complexing reagents were studied in order to remove the interference of these elements. A limited success only was achieved.

Spectrophotometric measurement of the absorbance of U.V. light at 390 m\(\mu\) has been found the most suitable method for determining trace quantities of aluminium oxinate.
PART I  INTRODUCTION

(A) Theory
   (i) Extraction of Oxine
   (ii) Extraction of Aluminium Oxinate

(B) Solvent Extraction Techniques

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(A) Preliminary Extractions
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   (ii) Chromium
   (iii) Iron
   (iv) Nickel

(B) Study of Complexing Agents of Iron
   (i) Tartaric and Citric Acids
   (ii) Tiron and Nitrilotriacetic Acid
   (iii) α-Picolinic Acid
   (iv) E.D.T.A.
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   (vi) 1, 10-Phenanthroline
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PART I

INTRODUCTION

(A) THEORY

(i) Extraction of Oxine
(ii) Extraction of Aluminium Oxinate

(B) SOLVENT EXTRACTION TECHNIQUE
There is a need in analytical chemistry, particularly industrially, for quantitatively determining very small amounts of Aluminium in the presence of large amounts of Iron, Chromium and Nickel, as in a stainless steel. In fact, certain grades of steel require a strict concentration range of 0.001% - 0.005% Aluminium. On a one gram sample of steel this amounts to only 10 μg of Aluminium in the lower limit.

Solvent extraction is known as a very suitable method for separating traces of metals and, with the above analytical problem in mind, the aims of this thesis were:-

(i) To investigate the solvent extraction chemistry of Aluminium, Iron, Chromium and Nickel, paying particular attention to that of Aluminium.

(ii) To investigate the analytical methods suitable for determining very low quantities of Aluminium in the organic extract.

(iii) To investigate the removal and/or prevention of interferences from Iron, Chromium and Nickel, to the extraction of Aluminium (particularly with regard to Iron).

Previous work (for example see references 12, 20, 27 and 28) on the extraction of Aluminium has shown 8-hydroxyquinoline to be, as yet, probably the most successful chelating agent for the complete extraction of Aluminium. In consequence, a major part of the experimental work of this project has been based on the extraction of the Aluminium Oxinate complex into Chloroform as the organic solvent.
(A) THEORY

Since the pioneering work of Berg on the analytical applications of 8-hydroxyquinoline (oxine, 8-quinolinol), many monographs have treated this subject. The most fundamental studies were performed by Goto, Fleck and Ward, Moeller, Morrison and Freiser, Lacroix, Irving and others who elucidated the effect of pH on the precipitation of metal oxinates or their extractability by an organic solvent immiscible with water. However, the close similarity between the extractability - pH curve and the familiar dissociation curve and the rational method of analysing the experimental extractability - pH curve was first explained successfully by Kambara and Hashitani.

In their work, a theory of Aluminium oxinate extraction is developed and the theoretical prediction is confirmed by experimental investigation so that the extraction of Aluminium is on a more theoretically concrete basis. The theory put forward by Kambara and Hashitani is as follows:

(i) Extraction of Oxine

According to Irving and Williams, cationic, anionic, and molecular species of oxine in the aqueous phase will be shown by $\text{H}_2\text{Ox}^+$, $\text{Ox}^-$, and $\text{HOx}$ respectively. The amphoteric dissociation can thus be represented by:

$$K_1^i = \frac{[\text{HOx}]_w}{[\text{H}_2\text{Ox}^+]} \left\{\text{H}^+\right\} \quad \ldots (1)$$
\[ K_2 = \frac{[\text{Ox}^-]}{[\text{HOx}]} \left\{ H^+ \right\} \]

Where square brackets represent the concentration and the subscript \( w \) refers to the aqueous phase. \( \left\{ H^+ \right\} \) is the hydrogen ion activity and \( K_1' \) and \( K_2' \) are the Bronsted acidity constants. Partition of molecular oxine between aqueous solution and the immiscible organic solvent - chloroform, denoted by the suffix 0 - is given by:-

\[ D' = \frac{[\text{HOx}]}{[\text{HOx}]} \frac{0}{w} \]

Where \( D' \) is the partition coefficient, in which activity is approximately replaced by concentration. When \( V_0 \) litre of organic solvent is shaken with \( V_w \) litre of aqueous solution the total amount of oxine is given by:-

\[ G_{\text{Ox}} = Y \left[ \text{HOx} \right] w \]

where

\[ Y = D' V_0 + \left\{ 1 + \frac{\left\{ H^+ \right\}}{K_1'} + \frac{K_2'}{\left\{ H^+ \right\}} \right\} V_w \]

Next, let \( y \) be the concentration ratio of molecular form in aqueous phase to the total amount of oxine in the same phase. Then it can be found that:-
\[ y = \frac{1}{1 + \frac{\{H^+\}}{K_1} + \frac{K_2}{\{H^+\}}} \]  

(6)

In acidic medium where \(-\log K_2 = pK'_2 \gg \text{pH}\), and neglecting the term \(K_2/\{H^+\}\) in the denominator of equation (6), there is the following approximate expression:

\[ y = \frac{1}{2} \left\{ 1 + \tanh \left( \frac{2.303}{2} (\text{pH} - pK'_1) \right) \right\} \]

(7)

\[ \text{pH} = pK'_1 + \log \frac{y}{1 - y} \]

Such an expression containing a hyperbolic function was first introduced by Irving and Williams.\(^1^9\) In the same manner, in alkaline medium, where \(\text{pH} \gg pK'_1\) it is deduced that:

\[ \text{pH} = pK'_2 + \log \frac{1 - y}{y} \]

(8)

Extractability of oxine by chloroform, denoted by \(z\), can now be obtained in an analogous manner. Defining \(B\) by:

\[ B = \log \left( \frac{D^' V_o}{V_w} + 1 \right) \]

(9)

one obtains the following equation in an acid medium:

\[ z = \frac{\text{[HOx]}_0}{c_{\text{Ox}}} \cdot \frac{V_o}{c_{\text{Ox}}} = \frac{\lambda}{2} \left\{ 1 + \tanh \left( \frac{2.303}{2} (\text{pH} - pK'_1 + B) \right) \right\} \]

(10)
where \( \lambda \) shown by:-

\[
\lambda = \frac{D_{Vo}}{D_{Vo} + V_w}
\]

is approximately equal to unity. The \( pH \) value of half-extraction is shown by:-

\[
(pH_{1/2})_{z\text{-acidic}} = pK_1' - B
\]

whence

\[
\text{pH} = (pH_{1/2})_{z\text{-acidic}} + \log \frac{z}{1 - z}
\]

In the case of alkaline solution one derives:-

\[
z = \frac{\lambda}{2} \left\{ 1 - \tanh \frac{2.303}{2} \left( \text{pH} - pH_{1/2} \right) \right\}
\]

where the \( pH \) value of half-extraction is:-

\[
(pH_{1/2})_{z\text{-alkaline}} = pK_2' + B
\]

Likewise the distribution of oxine as cationic, anionic and molecular species in the aqueous phase can be deduced and, because it has a similar form, is omitted.
As an experimental verification of this theory the work carried out by Moeller and Pundsack\(^3\) can be used. They accurately determined the distribution of oxine in various forms between chloroform and aqueous solutions at 25\(^{\circ}\)C with considerable dependence on the pH value of the latter phase. The numerical values shown by them were recalculated and tabulated in a different manner by Hollingshead.\(^{17}\) In Fig. I are drawn the theoretical $y$ - pH and $z$ - pH curves and the points found experimentally are indicated by open circles. The following curves are shown:

A. $y$ - pH curve showing concentration ratio of molecular species to the total amount of oxine in the aqueous phase (cf. Equations (6), (7), (8)).

B. Concentration ratio of cationic species to total amount in the aqueous phase.

C. Concentration ratio of anionic species to total amount in the aqueous phase.

A' $z$ - pH curve showing the extracted fraction of the total amount of oxine in both phases (cf. Equations (10) and (13)).

B' Fraction of oxine in cationic form.

C' Fraction of oxine in anionic form.

Measured values of Moeller and Pundsack\(^3\) in whose experiment $V_o = V_w = 25$ ml at a temperature of 25\(^{\circ}\)C.
Fig. 1 - Distribution of Oxine in Various Forms.
Values for $pK_1', \ pK_2', \ \left(pH_1\right)_{\frac{1}{2}}$ z-acidic and \left(pH_1\right)_{\frac{1}{2}} z-alkaline are found, from logarithmic plots of $\log \frac{Y}{1 - Y}$ vs pH and $\log \frac{z}{1 - z}$ vs pH, to be:

\[
pK_1' = 5.05 \quad pK_2' = 9.85
\]

\[
(pH_1)_{\frac{1}{2}} \text{ z-acidic} = 2.45 \quad (pH_1)_{\frac{1}{2}} \text{ z-alkaline} = 12.35
\]

(ii) **Extraction of Aluminium Oxinate**

When concentration of the first-order approximation is replaced by activity, the partition coefficient of aluminium oxinate between organic solvent and aqueous solution is given by:

\[
P' = \frac{\left[Al\ Ox_3\right]_o}{\left[Al\ Ox_3\right]_w} \quad \text{equation (16)}
\]

and the dissociation constant of the chelate compound shown by:

\[
K' = \frac{\left[Al^{3+}\right] \left[Ox^{-}\right]^3}{\left[Al\ Ox_3\right]_w} \quad \text{equation (17)}
\]

Furthermore, the formation of soluble aluminate ion is shown by:

\[
Al^{3+} + 2H_2O \rightleftharpoons Al\ O_2^- + 4H^+
\]
Thus there is:—

\[
K'_H = \frac{[\text{AlO}_2^-]}{[\text{Al}^{3+}]} \left\{ H^+ \right\}^4
\] ..............................(18)

A portion of oxine in the whole system exists now as aluminium oxinate; therefore the total amount of the reagent is shown by:—

\[
G_{Ox} = 3 \alpha \left[ \text{AlO}_3^- \right]_w + \alpha' \left[ \text{Ox}^- \right]_w
\] ..............................(19)

where

\[
\alpha = \gamma V_0 + V_w
\] ..............................(20)

\[
\alpha' = \gamma \frac{\left\{ H^+ \right\}}{K'_2}
\] ..............................(21)

In the same manner, the total amount of aluminium is given by:—

\[
G_{Al} = \left( \alpha + \frac{B}{[\text{Ox}^-]^3} \right) \left[ \text{AlO}_3^- \right]_w
\] ..............................(22)

where

\[
B = K'_V w \left( 1 + \frac{K'_H}{\left\{ H^+ \right\}^4} \right)
\] ..............................(23)
Elimination of $\left[ \text{Al Ox}_2 \right]_w$ from equations (19) and (22) gives:

$$\alpha \alpha' \left[ \text{Ox}^- \right]^4 + \alpha (3 \text{G}_{\text{Al}} - \text{G}_{\text{Ox}}) \left[ \text{Ox}^- \right]^3 + \alpha' B \left[ \text{Ox}^- \right]$$

$$- 3 \text{G}_{\text{Ox}} = 0 \quad \ldots \ldots (24)$$

The solution of this quadruplicate equation is complicated, but it can be rationally solved. From this distribution in varying forms of oxine, it can be reasonably considered that, in acidic medium the concentration of anionic oxine is vanishingly small, so that the first two terms in the left-hand side of equation (24) can be neglected, whereas, in alkaline medium the anionic species becomes predominant, so that the last two terms will now drop out. Thus one obtains, assuming that an excess of oxine is used, the following:

$$\left[ \text{Ox}^- \right] \equiv \frac{\text{G}_{\text{Ox}} - 3 \text{G}_{\text{Al}}}{\alpha'} \equiv \frac{\text{G}_{\text{Ox}}}{\alpha'} \quad \ldots \ldots (25)$$

The extractability of aluminium oxinate is now defined by:

$$x = \frac{\left[ \text{Al Ox}_2 \right]_o \text{V}_o}{\text{G}_{\text{Al}}} = \frac{\text{A} \left[ \text{Ox}^- \right]^3}{\alpha} = \frac{\text{A} \left[ \text{Ox}^- \right]^3 + B}{\alpha} \quad \ldots \ldots (26)$$

$$A = \frac{P' \text{V}_o}{P' \text{V}_o + \text{V}_w}$$
from which the theoretical expression for the extraction wave as a function of acidity could be derived. In acidic solution, in which the concentration of anionic oxine is vanishingly small but practically no hydrolysis of Aluminium ion takes place \( (B \equiv K' Vw) \), equation (25) can be approximately transformed into:

\[
\left[ O_x \right] = \frac{G_{ox} K'_2}{\{H^+\}} \frac{K'}{D V_0} \]

Now it can be seen that:

\[
x = \frac{A}{2} \left[ 1 + \tanh \frac{2.303 x}{2} \right] \{pH - (pH_1)_{x-acidic} \} \]

\[\ldots(27)\]

where

\[
(pH_1)_{x-acidic} = pK'_2 - \frac{1}{3} \log \frac{p' G_{ox}^3}{K' D'^3 V_w V_0^2} \]

Putting \( A \equiv 1 \) gives:

\[
\text{pH} = (pH_1)_{x-acidic} + \frac{1}{3} \log \frac{x}{1 - x} \]

\[\ldots(29)\]

In alkaline solution, upon simplifying that:

\[
Y \equiv \frac{K'_2 V_w}{\{H^+\}} \quad \text{and} \quad B \equiv \frac{K'_H V_w}{\{H^+\}^4} \]

one deduces:-

\[ x = \frac{1}{2} \left[ 1 + \tanh 2.303 \times 2 \times \left\{ \left( \frac{pH}{2} \right)^{x-\text{alkaline}} - pH \right\} \right] \] .......(30)

or

\[ pH = \left( \frac{pH}{2} \right)^{x-\text{alkaline}} + \frac{1}{4} \log \frac{1 - x}{x} \] ...........................(31)

where

\[ \left( \frac{pH}{2} \right)^{x-\text{alkaline}} = \frac{1}{4} \log \frac{P \cdot V \cdot O \cdot X^3}{K \cdot K_H \cdot V_w^4} \] ...........................(32)

The greater the value of \( K_H \) the more easily the aluminate ion is formed and the lower becomes the pH value of half-extraction. This feature of oxinate extraction has not been explained by Lacroix\(^{23}\) and Irving and Williams.\(^{19}\)

To verify this theory, Kambara and Hashitani\(^{20}\) carried out a series of Aluminium Oxinate extractions into chloroform over a pH range. The results are seen in Fig. II.

From this theory, according to equations (29) and (31), the value for 99.9% extraction in acidic and alkaline media, respectively is shown by:-

\[ pH_{99.9\%} = \left( \frac{pH}{2} \right)^{x-\text{acidic}} + 1 = 5.05 \]

\[ pH_{99.9\%} = \left( \frac{pH}{2} \right)^{x-\text{alkaline}} - \frac{3}{4} = 10.53 \]

That is, complete extraction of aluminium oxinate is expected over a pH range of 5.05 - 10.53.
Fig. 2—Effect of pH on extractability of aluminium oxinate from aqueous solution into chloroform.
Note: The procedure used by Kambara and Hashitani\textsuperscript{20} required addition of the oxine ligand to the solution of aluminium before adjusting the pH. The pH was then adjusted and the extraction made. This was to prevent the precipitation of aluminium hydroxide, in the higher pH range, which would otherwise lead to erroneous results. Sudo,\textsuperscript{39} and Motojima\textsuperscript{32} had previously put forward this idea since Moeller,\textsuperscript{28} Gentry and Sherrington\textsuperscript{12} and Lacroix\textsuperscript{23} used a chloroform solution of oxine to extract aluminium from an aqueous solution and hence did not achieve complete extraction over the pH range possible for this.

The pH range of extraction of 100\% for these workers is indicated below:

<table>
<thead>
<tr>
<th></th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moeller</td>
<td>4.3 - 4.6</td>
</tr>
<tr>
<td>Gentry and Sherrington</td>
<td>4.74 - 6.00</td>
</tr>
<tr>
<td></td>
<td>and</td>
</tr>
<tr>
<td></td>
<td>8.37 - 11.0</td>
</tr>
<tr>
<td>Kambara and Hashitani</td>
<td>4.75 - 10.0</td>
</tr>
<tr>
<td>Theoretically</td>
<td>5.05 - 10.53</td>
</tr>
</tbody>
</table>
(B) SOLVENT EXTRACTION TECHNIQUES

Advice on techniques for the solvent extraction of metals is plentiful. 7, 14, 31, 35, 37, 40

Solvent extraction techniques involve those techniques in which a solution (usually aqueous) is brought into contact with a second solvent (usually organic), essentially immiscible with the first, in order to bring about a transfer of one or more solutes into the second solvent. The technique is equally applicable to trace levels and large amounts of materials.

The current work involved shaking the two layers in pear-shaped separating funnels. The experimental conditions used required agitation of the system for only one minute to effect complete extraction (see Experimental section, A. (i)).

The choice of the solvent used for extraction is governed by the following considerations: 40

(i) A high distribution ratio for the solute and a low distribution ratio for undesirable impurities.

(ii) Low solubility in the aqueous phase.

(iii) Sufficiently low viscosity and sufficient density difference from the aqueous phase to avoid the formation of emulsions.

(iv) Low toxicity and inflammability.
(v) Ease of recovery of solute from the solvent for subsequent analytical processing. Thus the b.p. of the solvent and the ease of stripping by chemical reagents merits attention when a choice is possible.

Chloroform was found suitable in all of these aspects for the current work.

Extractions can be made with one accurately measured volume of organic solvent $^4,^{12},^{27},^{36}$ or with a number of smaller volumes which are subsequently combined and diluted to an exact volume.$^{25,28}$ Both of these methods were used in the current work and both were found to be successful.
PART II
EXPERIMENTAL

(A) Preliminary Extractions
(i) Aluminium
(ii) Chromium
(iii) Iron
(iv) Nickel

(B) Study of Complexing Agents of Iron
(i) Tartaric and Citric Acids
(ii) Tiron and Nitrilotriacetic Acid
(iii) 2-Picolinic Acid
(iv) E.D.T.A.
(v) Thioglycollic Acid
(vi) 1, 10-Phenanthroline
(vii) Potassium Cyanide

(C) Extraction and Spectrophotometric Analysis
(A) PRELIMINARY EXTRACTIONS

(i) The Extraction of Aluminium Oxinate into Chloroform

The purpose of this section of work was to investigate the conditions of pH and ligand:metal concentration ratio needed for the complete extraction of aluminium oxinate from aqueous solution into chloroform.

The method was as follows: - A series of extractions were made at the following pH's - 3, 5, 7, 9 and 11.

In each case the ligand was added to the aqueous aluminium solution which was then adjusted to the correct pH. No account was taken of constant ionic strength. The ligand:metal ratio was varied from 1:1, 2:1 and 3:1.

The extraction was made with one 25 ml aliquot of chloroform and the separation effected.

Analysis of the system was made by precipitating the aqueous layer under conditions for the precipitation of aluminium hydroxide, collecting the precipitate by filtration and burning the sample to Al₂O₃. The extracted Al was then calculated by difference.

On some samples, the organic layer was re-extracted with 10N HCl and a similar analysis carried out as a check to the first method (Appendix 1).
**Results:** The sample taken in each case was 50 mls of 0.02 M Al solution which was prepared by dissolving spectrographically pure aluminium wire in a minimum of hydrochloric acid and making to volume.

Gravimetric analysis of 50 mls of the Al solution gave (i) 0.0276 and (ii) 0.0277 g of Aluminium.

The results are given in tables 1 and 2.

**Discussion:** The extraction results for the samples with 2:1 and 1:1 oxine:aluminium ratios are misleading above pH = 5. This is because there is not enough ligand present to complex the aluminium and hence an interfering precipitate of either aluminium hydroxide or, possibly, hydrated forms of an oxinate complex precipitate out. When shaken to effect an extraction these samples formed emulsions with the organic layer or, in some cases, the precipitate was preferentially suspended in the organic layer. Consequently this amount was separated with the organic layer and analysed as such.

However, at pH = 11, the organic layers were all clear but a gelatinous precipitate rested on the interface of the two liquids. This was greater in the 1:1 sample than in the 2:1 sample and was probably hydrated Aluminium Oxide.

The extractions with a 3:1 ligand:metal ratio were all successful and are plotted in Fig. III. Of interest is that this curve is almost identical with the theoretical curve previously mentioned. 20

From these results it can be concluded that:-
<table>
<thead>
<tr>
<th>pH</th>
<th>Oxide-Aluminium Ratio</th>
<th>Grams of Al₂O₃ in Aqueous Layer</th>
<th>Grams of Aluminium in Aqueous</th>
<th>Grams of Aluminium Extracted</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1:1</td>
<td>0.0528</td>
<td>0.220</td>
<td>Nil</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>0.0505</td>
<td>0.257</td>
<td>0.010</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0.0478</td>
<td>0.253</td>
<td>0.0024</td>
<td>0.87</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>0.0376</td>
<td>0.200</td>
<td>0.0077</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>0.0226</td>
<td>0.120</td>
<td>0.0157</td>
<td>56.7</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0.0080</td>
<td>0.042</td>
<td>0.0235</td>
<td>84.8</td>
</tr>
<tr>
<td>7</td>
<td>1:1</td>
<td>0.0106</td>
<td>0.056</td>
<td>0.0221</td>
<td>79.8</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>0.0092</td>
<td>0.049</td>
<td>0.0228</td>
<td>82.3</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0.0020</td>
<td>0.011</td>
<td>0.0266</td>
<td>96.6</td>
</tr>
<tr>
<td>9</td>
<td>1:1</td>
<td>0.0169</td>
<td>0.090</td>
<td>0.0187</td>
<td>67.5</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>0.0087</td>
<td>0.046</td>
<td>0.0231</td>
<td>83.4</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0.0085</td>
<td>0.003</td>
<td>0.0274</td>
<td>99.0</td>
</tr>
<tr>
<td>11</td>
<td>1:1</td>
<td>0.0362</td>
<td>0.142</td>
<td>0.0085</td>
<td>30.7</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>0.0177</td>
<td>0.094</td>
<td>0.0183</td>
<td>66.1</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0.0029</td>
<td>0.015</td>
<td>0.0262</td>
<td>94.6</td>
</tr>
</tbody>
</table>

**Table 1. Analysis on Aqueous Layer.**
Table 2. Analysis of the extracted layer of the samples with a 3:1 oxine: aluminium ratio.

<table>
<thead>
<tr>
<th>pH</th>
<th>Grams of $\text{Al}_2\text{O}_3$</th>
<th>Grams of Aluminium</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0445</td>
<td>0.0236</td>
<td>85.2</td>
</tr>
<tr>
<td>7</td>
<td>0.0520</td>
<td>0.0275</td>
<td>99.2</td>
</tr>
<tr>
<td>9</td>
<td>0.0536</td>
<td>0.0284</td>
<td>102.5</td>
</tr>
<tr>
<td>11</td>
<td>0.0522</td>
<td>0.0276</td>
<td>99.7</td>
</tr>
</tbody>
</table>

Fig. 3. % Extraction of 3:1 oxine: Al vs pH.
(i) The aluminium appears to complex in a 3:1 ratio of ligand; metal. This is consistent with previous work by other researchers.\textsuperscript{9,16,41}

(ii) The aluminium oxinate complex extracts in appreciable quantities into chloroform over the pH range 5-11 under the conditions used.

(iii) In the higher pH range (pH = 11), where aluminium precipitates, as the hydrated oxide, a complete extraction would be effected by adding an excess of the 3:1 ligand:metal concentration ratio.

(iv) Extractions made at pH = 9 with a 3:1 ratio would be most suitable for future extractions.

(ii) The Solvent Extraction of Chromium (III)

50 mls of 0.02 M \textit{Cr}^{3+} prepared from \textit{Cr}_2(\textit{SO}_4)_3 \cdot 8 \text{H}_2\text{O} were extracted under the same conditions as for the previous aluminium series.

Analysis for chrome was carried out by fuming the aqueous layer with HNO\textsubscript{3} and HClO\textsubscript{4} to destroy any remaining ligand and to put the chromium in the hexavalent state. The samples were then treated for titration with ferrous ammonium sulphate (Appendix 2). Those samples extracted at pH = 11 had the organic layer analysed for chromium as a check.

The results may be seen in table 3.

Discussion: These results are misleading above pH = 5 since all samples contained a precipitate which did not entirely extract and hence
<table>
<thead>
<tr>
<th>pH</th>
<th>Ox : Co Ratio</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1 : 1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2 : 1</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>3 : 1</td>
<td>4.6</td>
</tr>
<tr>
<td>5</td>
<td>1 : 1</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>2 : 1</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>3 : 1</td>
<td>5.6</td>
</tr>
<tr>
<td>7</td>
<td>1 : 1</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>2 : 1</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>3 : 1</td>
<td>7.1</td>
</tr>
<tr>
<td>9</td>
<td>1 : 1</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>2 : 1</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td>3 : 1</td>
<td>11.3</td>
</tr>
<tr>
<td>11</td>
<td>1 : 1</td>
<td>15.5</td>
</tr>
<tr>
<td>(Aqueous Layer)</td>
<td>2 : 1</td>
<td>14.1</td>
</tr>
<tr>
<td>(Organic Layer)</td>
<td>3 : 1</td>
<td>5.6</td>
</tr>
<tr>
<td>11</td>
<td>1 : 1</td>
<td>15.9</td>
</tr>
<tr>
<td>(Organic Layer)</td>
<td>2 : 1</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>3 : 1</td>
<td>4.8</td>
</tr>
</tbody>
</table>

**Table 3. Extraction of Chromate**

**AS AN OXIMATE**
interfered by forming emulsions similar to those previously described.
The conclusions arrived at are:-

(i) The Cr$^{3+}$ does not extract under the same conditions as aluminium but that

(ii) The Cr$^{3+}$ precipitates in various forms which would physically interfere with aluminium extraction.

(iii) The Solvent Extraction of Iron (III)

The iron was extracted under the same conditions as for the aluminium and chromium i.e. 50 mls of 0.02M Fe$^{3+}$ was extracted under various conditions of pH and oxine concentration into 25 mls chloroform.

After extraction, the aqueous layers were wet-ashed with HNO$_3$ and fuming HClO$_4$ and eventually prepared for titration with potassium dichromate (Appendix 3). On some samples the organic layer was also analysed.

The results are in table 4.

Discussion: Nearly every result is too high due to the precipitation of the Fe$^{3+}$ and the resultant formation of an emulsion in the organic layer. In some cases large amounts of Fe were extracted as a precipitate and not as a true extraction. In many cases the jet black iron oxinate complex almost completely obscured the liquid-liquid interface, particularly over the pH range 5 - 9.
<table>
<thead>
<tr>
<th>pH</th>
<th>Ox : H₂</th>
<th>Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ratio</td>
<td>%</td>
</tr>
<tr>
<td>3</td>
<td>1:1</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>64.7</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>98.2</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>84.3</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>88.7</td>
</tr>
<tr>
<td>7</td>
<td>1:1 (aq.)</td>
<td>98.1</td>
</tr>
<tr>
<td></td>
<td>1:1 (org.)</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>78.5</td>
</tr>
<tr>
<td>9</td>
<td>1:1 (org.)</td>
<td>93.1</td>
</tr>
<tr>
<td></td>
<td>1:1 (aq.)</td>
<td>94.3</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>28.3</td>
</tr>
<tr>
<td>11</td>
<td>1:1</td>
<td>70.6</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td>3:1 (aq.)</td>
<td>83.3</td>
</tr>
<tr>
<td></td>
<td>3:1 (org.)</td>
<td>83.3</td>
</tr>
</tbody>
</table>

**Table 4.** Extraction of iron(III) as an oxinate.
Conclusions drawn from this are that the iron may interfere with Al (Ox)₃ extraction in two main ways:

(i) The iron extracts to a large extent over the same range as for aluminium.

(ii) The iron forms various precipitates of Fe(OH)₃ and oxinates that will physically interfere with the extraction of aluminium.

(iv) The Solvent Extraction of Nickel (II)

Extractions were carried out on 50 mls 0.02M Ni solution under exactly the same conditions as for the aluminium, chromium and iron.

Atomic absorption spectroscopy was used to analyse for nickel (Appendix 6).

Results are in table 5.

Discussion: Only at pH = 3 were both liquid layers clear of any precipitate or emulsion. It is again clear that interference to an aluminium extraction would come from the precipitation of the Nickel as Ni(OH)₂ or as various oxinate forms.
<table>
<thead>
<tr>
<th>pH</th>
<th>Ox : Ni Ratio</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1:1</td>
<td>Nil</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>3:1 (aq.)</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>3:1 (org.)</td>
<td>33.9</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>44.6</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>57.1</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>84.3</td>
</tr>
<tr>
<td>7</td>
<td>1:1</td>
<td>74.6</td>
</tr>
<tr>
<td></td>
<td>2:1 (aq.)</td>
<td>76.6</td>
</tr>
<tr>
<td></td>
<td>2:1 (org.)</td>
<td>76.8</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>73.8</td>
</tr>
<tr>
<td>9</td>
<td>1:1</td>
<td>41.8</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>91.4</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>92.5</td>
</tr>
<tr>
<td>11</td>
<td>1:1</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>77.1</td>
</tr>
<tr>
<td></td>
<td>3:1 (aq.)</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>3:1 (org.)</td>
<td>27.2</td>
</tr>
</tbody>
</table>

Table 5. Extraction of Nickel as an Oxinate.
(B) STUDY OF COMPLEXING AGENTS FOR IRON

From observing the investigations already made concerning the extractions of aluminium and iron as oxinates it appears that a complexing agent would be successful in removing the interference of iron if it met the following requirements:

(i) The complexing agent should prevent iron from precipitating as Fe(OH)$_3$ under the conditions for aluminium extraction.

(ii) It should prevent iron from forming an oxinate.

(iii) It should not precipitate iron with itself.

It is probable that these requirements would be satisfied by a complexing agent whose iron complex had a greater stability constant than that of the iron-oxinate complex. The Chemical Society's publication of "Stability Constants" gives the values for the iron oxinate complexes as:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Log of equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>not given</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$K_1 = 8.58$ $B_2 = 16.93$ $B_3 = 22.23$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$K_1 = 14.52$ $B_3 = 38.00$</td>
</tr>
</tbody>
</table>

where oxine $\equiv$ HL and the complex is FeL$_n^3$

Consequently, the following complexes were selected for investigation:

$5$
(i) **Tartaric and Citric Acids**

The stability constants for the iron complexes of these are:\(^5\)

\(\text{- Tartaric Acid - } H_2L\)

\[
\begin{align*}
\text{Fe}^{2+} & \quad \log K_2 = 4.85 \\
\text{Fe}^{3+} & \quad \log K_1 = 18.06 \quad \log K_3 = 15.29
\end{align*}
\]

\(\text{Citric Acid - } H_4L\)

\[
\begin{align*}
\text{Fe}^{2+} & \quad \text{for } (\text{Fe}^{2+} + H_2L^2^- \rightleftharpoons \text{Fe} \cdot H_2L) \quad \log K = 2.12 \\
\text{Fe}^{3+} & \quad \text{for } (\text{Fe}^{3+} + HL^3^- \rightleftharpoons \text{Fe} \cdot HL) \quad \log K = 11.85 \\
& \quad \text{for } (\text{Fe}^{3+} + HL^3^- \rightleftharpoons \text{FeL} + H^+) \quad \log K = 9.46 \\
& \quad \log K_4 = 25 \quad \text{for } (\text{Fe}^{3+} + L^- \rightleftharpoons \text{FeL}^{2+})
\end{align*}
\]

Tartaric and Citric acids are both well-known for their ability to keep iron in solution at high pH. A series of extractions were carried out at pH = 9.0 to assess:-

(i) The extraction of aluminium in the presence of tartaric and citric acids to determine any interference from the ligands themselves.

(ii) The extraction of aluminium and iron together in the presence of tartaric and citric acids.

Gravimetric analysis was carried out on the first set of extractions and atomic absorption spectroscopy was used for the analysis of the second set.

Results for extractions (i) and (ii) are in tables 6 and 7 respectively.
## Table 6. $\text{Al(OH)}_3$ Extracted in the Presence of Tartaric and Citric Acids.

<table>
<thead>
<tr>
<th>Complexing Agent Added</th>
<th>Grams of $\text{Al}_2\text{O}_3$ in Aq. Layer</th>
<th>Grams of $\text{Al}_2\text{O}_3$ in Org. Layer</th>
<th>Total Grams $\text{Al}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0489</td>
<td>0.0013</td>
<td>0.0502</td>
</tr>
<tr>
<td></td>
<td>0.0485</td>
<td>0.0012</td>
<td>0.0497</td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>0.0508</td>
<td>0.0009</td>
<td>0.0517</td>
</tr>
<tr>
<td></td>
<td>0.0507</td>
<td>0.0006</td>
<td>0.0513</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>0.0493</td>
<td>0.0007</td>
<td>0.0500</td>
</tr>
<tr>
<td></td>
<td>0.0509</td>
<td>0.0005</td>
<td>0.0514</td>
</tr>
</tbody>
</table>

## Table 7. Extraction of $\text{Al(OH)}_3$ in the Presence of Iron and Tartaric and Citric Acids.

<table>
<thead>
<tr>
<th>Complexing Agent Added</th>
<th>% Extraction of Aluminium</th>
<th>% Extraction of Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>78.0</td>
<td>94.9</td>
</tr>
<tr>
<td></td>
<td>74.6</td>
<td>90.3</td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>24.7</td>
<td>66.5</td>
</tr>
<tr>
<td></td>
<td>24.7</td>
<td>76.0</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>35.5</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>73.5</td>
</tr>
</tbody>
</table>
### Table 8. Test of Interferences of Al Fe and Oxine by A.A. Spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transmission 1</th>
<th>Transmission 2</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mls. 0.02 M Al diluted to 100 mls.</td>
<td>95.5</td>
<td>85.5</td>
<td>0.0680</td>
</tr>
<tr>
<td>5 mls. 0.02 M Fe diluted to 100 mls.</td>
<td>100.0</td>
<td>100.0</td>
<td>Nil</td>
</tr>
<tr>
<td>5 mls 0.02 M Al + 5 mls 0.02 M Fe /100 mls.</td>
<td>85.5</td>
<td>85.5</td>
<td>0.0680</td>
</tr>
<tr>
<td>5 mls 0.02 M Al + 5 mls 0.1 M Oxine/100 mls.</td>
<td>86.5</td>
<td>85.5</td>
<td>0.0655</td>
</tr>
<tr>
<td>5 mls 0.02 M Fe + 5 mls 0.1 M Oxine/100 mls.</td>
<td>100.0</td>
<td>100.0</td>
<td>Nil</td>
</tr>
<tr>
<td>5 mls. 0.1 M Oxine diluted to 100 mls.</td>
<td>100.0</td>
<td>100.0</td>
<td>Nil</td>
</tr>
</tbody>
</table>

### Table 8a. Absorbance of Aluminium at

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transmission 1</th>
<th>Transmission 2</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mls. 0.02 M Al diluted to 100 mls.</td>
<td>100.0</td>
<td>100.0</td>
<td>Nil</td>
</tr>
<tr>
<td>5 mls. 0.02 M Fe diluted to 100 mls.</td>
<td>41.5</td>
<td>42.5</td>
<td>0.377</td>
</tr>
<tr>
<td>5 mls. 0.02 M Al + 5 mls. 0.02 M Fe /100 mls.</td>
<td>41.5</td>
<td>42.5</td>
<td>0.377</td>
</tr>
<tr>
<td>5 mls. 0.02 M Al + 5 mls. 0.1 M Oxine /100 mls.</td>
<td>100.0</td>
<td>100.0</td>
<td>Nil</td>
</tr>
<tr>
<td>5 mls. 0.02 M Fe + 5 mls. 0.1 M Oxine /100 mls.</td>
<td>42.5</td>
<td>41.5</td>
<td>0.377</td>
</tr>
<tr>
<td>5 mls. 0.1 M Oxine diluted to 100 mls.</td>
<td>100.0</td>
<td>100.0</td>
<td>Nil</td>
</tr>
</tbody>
</table>

### Table 8b. Absorbance of Iron at
Samples were tested by atomic absorption spectroscopy for any interference between the iron, oxine, and aluminium. No interference was noted as can be seen in table 8.

Discussion of Results: Neither tartaric or citric acid was successful in complexing the iron in the presence of oxine under the conditions of operation. In each case the black iron oxinate was formed and extracted with the aluminium.

The results show that the tartaric and citric acids do not interfere with the aluminium oxinate extraction themselves. This is contrary to the results of some other workers\textsuperscript{12,35} who found that tartrate interferes when present in relatively large amounts. It is probable that the concentration of tartrate present in the current work was not high enough to effectively interfere.

However, the extraction of the aluminium was found to be inhibited when iron was present. This was probably due to a selective competition for the limited amount of oxine present. Had enough excess oxine been present it is likely that both the iron and the aluminium would have extracted completely.

(ii) Tiron and Nitrilotriacetic Acid

The stability constants for the iron complexes of these ligands are:\textsuperscript{5}
Tiron (4, 5-Dihydroxybenzene - 1, 3-disculphonic acid) $H_4L$

$$\text{Fe}^{3+} \quad \log K_1 = 20.7 \quad \log K_2 = 15.2 \quad \log K_3 = 11.0$$

for $(\text{Fe}^{3+} + \text{HL}^3- \rightleftharpoons \text{Fe} \text{HL}) \quad \log K = 10.00$

Nitrilotriacetic Acid (N.T.A.) $H_3L$

$$\text{Fe}^{3+} \quad \log K_1 = 15.87$$

for $(\text{Fe}^{3+} + \text{L}^3- + \text{A}^4- \rightleftharpoons \text{Fe LA}^4-) \quad \log K = 31.85$

where $H_2A^- = \text{Tiron}$

Before carrying out a series of extractions, those complexing agents were examined in test-tube quantities for their ability to complex the iron successfully in the presence of oxinate. The pH's of the test-samples were adjusted with dil $\text{NH}_4\text{OH}$ to pH $\geq 9 - 10$ with universal indicator pH papers.

The results of these tests showed that both N.T.A. and Tiron formed iron complexes soluble in aqueous solution at pH $9 - 10$. However, when oxine was added, the black iron oxinate complex formed in the presence of N.T.A. The iron oxinate did not form in the presence of Tiron or of tiron and N.T.A. combined. A pale yellow-green precipitate formed and was taken to be the aluminium oxinate. The above tests were made with each metal by itself and then together.

On the basis of these results the following extractions were carried out:

(i) $\text{Al} + \text{Fe} + \text{Oxine} + \text{N.T.A.} + \text{Tiron}$

(ii) $\text{Al} + \text{Fe} + \text{Oxine} + \text{Tiron}$
(iii) Al + Fe + Tiron
(iv) Al + Tiron

50 mls aliquots of 0.02M solutions of the metals were treated with excess of all of the ligands and the pH adjusted to 9.0. Extraction was made with 25 mls of chloroform.

Samples (iii) and (iv) were run in order to determine whether or not the tiron-metal complexes extract into chloroform themselves.

Atomic absorption spectroscopy was used for analysis.

The results are given in table 9.

**Discussion of Results:** Under extraction conditions emulsions were formed in the first two samples. This resulted in partial extraction of the iron and aluminium. It seems apparent from the results, however, that Tiron greatly retards the extraction of the oxinates of both aluminium and iron under the experimental conditions investigated.

Considering these results, a series of extractions was carried out to investigate the possibility of extracting the aluminium-tiron complex itself. This was shown (table 10) to be unsuccessful over a pH range of 3 - 11.

No previous studies of this nature involving Tiron and N.T.A. have been found.
Table 9. Extraction of aluminium and iron oxalates in the presence of tiron and N.T.A.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Extraction Alum</th>
<th>% Extraction Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>14.3</td>
<td>43.3</td>
</tr>
<tr>
<td>(b)</td>
<td>14.3</td>
<td>43.3</td>
</tr>
<tr>
<td>(c)</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>(d)</td>
<td>Nil</td>
<td>-</td>
</tr>
</tbody>
</table>

See text for identification of samples.
Majumdar and Sen have found that α-picolinic acid can be used to complex iron and chromium so that aluminium hydroxide may be quantitatively precipitated without the corresponding precipitation of iron and chromium. They achieved:

Separation of Al from Fe: pH 5.8 - 6.85
Separation of Al from Cr: pH 6.25 - 7.05

From this it would appear that, if oxine would not complex with iron and chromium under the above conditions of pH, the α-picolinic acid would be a suitable complexing agent for prevention of interferences from iron and chromium in the extraction of aluminium oxinate.

The stability constants of the iron-α-picolinate complexes are:

Pyridine - 2-carboxylic acid (α-picolinic acid). \( \text{HL} \)

\[
\begin{align*}
\text{Fe}^{2+} & : \log K_1 = 4.90 \quad \log K_2 = 4.10 \quad \log K_3 = 3.30 \\
\text{Fe}^{3+} & : \log B_2 = 12.80 \\
\text{for} \ (\text{Fe}^{3+} + 2\text{L}^- + \text{OH}^- & \rightleftharpoons \text{FeL}_2\text{OH}) \quad \log K = 23.84 \\
\text{for} \ (2\text{Fe}^{3+} + 4\text{L}^- + 2\text{OH}^- & \rightleftharpoons \text{Fe}_{2}\text{L}_4(\text{OH})_4) \quad \log K = 50.76
\end{align*}
\]

The following experimental work was carried out:

(a) Iron (II) Complex of α-picolinic acid

Following previous workers the iron was reduced with hydroxylamine hydrochloride and a 10:1 α-picolinic acid:iron(II) concentration ratio was effected:
5 mls each of 0.02M Fe\(^{3+}\) and 0.02M Al solutions were pipetted into beakers and heated until boiling. 5\% hydroxylamine hydrochloride was added dropwise until the solution was colourless. The solution was cooled and 10 mls of a 0.1M solution of picolinic acid were added. Excess oxine solution was then added and the solutions adjusted to the following pH's:

\[
\text{pH 3, 4, 4.5, 5, 5.5, 6.0}
\]

These were then transferred to extraction vessels and extracted once with 10 mls of Chloroform.

Analysis was done by atomic absorption spectroscopy, and the results are given in table 11.

**Discussion of Results**: It is seen that the \(\alpha\)-picolinic acid does not appreciably inhibit the extraction of aluminium oxinate. Unfortunately, however, it does not inhibit, to a large enough degree, the extraction of the Fe (II) - oxinate complex within the pH range considered.

Small scale tests showed that, above pH = 6, the Fe (II) - oxinate started to precipitate, even in the presence of \(\alpha\)-picolinic acid.

(b) Iron (III) Complex of \(\alpha\)-picolinic acid

G. Anderegg\(^1\) gives the pH conditions for the formation of:

\[
2\text{Fe}^{3+} + 4L^- + 20\text{H}^- \rightleftharpoons \text{Fe}_2L_4(\text{OH})_4 \quad \log K = 50.76
\]

as being below pH = 3. Although a pK of -50.76 is a large stability constant for an iron (III) complex, in view of competition for oxine,
### Table 11. Extraction of Al\(^{3+}\) and Fe\(^{2+}\) Oxinates in the Presence of \(\alpha\)-Acolinic Acid.

<table>
<thead>
<tr>
<th>pH</th>
<th>% Extraction Aluminum</th>
<th>% Extraction Iron (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>Nil</td>
<td>1.5</td>
</tr>
<tr>
<td>4.0</td>
<td>25.9</td>
<td>6.7</td>
</tr>
<tr>
<td>4.5</td>
<td>58.3</td>
<td>9.5</td>
</tr>
<tr>
<td>5.0</td>
<td>75.7</td>
<td>19.1</td>
</tr>
<tr>
<td>5.5</td>
<td>79.2</td>
<td>45.4</td>
</tr>
<tr>
<td>6.0</td>
<td>96.5</td>
<td>62.7</td>
</tr>
</tbody>
</table>

### Table 12. Tabulation for Calibration Curves for Spectrophotometric Analysis of Aluminium Oxinate in Chloroform.

<table>
<thead>
<tr>
<th>Standard µg/ml Aluminium</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>390 nm</td>
</tr>
<tr>
<td>4.13</td>
<td>0.990</td>
</tr>
<tr>
<td>3.30</td>
<td>0.790</td>
</tr>
<tr>
<td>2.48</td>
<td>0.585</td>
</tr>
<tr>
<td>1.65</td>
<td>0.391</td>
</tr>
<tr>
<td>0.82</td>
<td>0.194</td>
</tr>
</tbody>
</table>
it is of little consequence as aluminium oxinate does not extract at all below pH = 3.

Attempts were made to find suitable conditions for both the extraction of aluminium oxinate and the formation of the above iron (III) - \(\alpha\)-picolinate complex. No success was achieved. A range of pH values from 1 to 11 and a range of picolinic acid:iron (III) ratios of from 1:1 to 20:1 were tried to no avail. Not only was the picolinic acid unsuccessful in preventing the precipitation of \(\text{Fe(OH)}_3\) but it was also unsuccessful in preventing the formation of iron oxinate.

(iv.) Ethylenediamine - NNN'NN' - tetra - acetic acid

Stability constants for iron - E.D.T.A. complexes are:\(^5\)

\[
\begin{align*}
\text{Fe}^{2+} & \quad \log K_1 = 14.33 \\
\text{Fe}^{3+} & \quad \log K_1 = 25.1
\end{align*}
\]

Small-scale tests over a pH range of 3 - 11 and various metal:ligand ratios gave the following results:-

(i) E.D.T.A. does not prevent the precipitation of \(\text{Fe(OH)}_3\) in the pH range for aluminium oxinate extraction.

(ii) E.D.T.A. does not prevent the formation and precipitation of the iron oxinate complex.

(iii) E.D.T.A. prevents the precipitation of \(\text{Al(OH)}_3\) and subsequently the formation and precipitation of aluminium oxinate.
Because of these findings, no further work was carried out with E.D.T.A.

Claassen\textsuperscript{6} also found that E.D.T.A. could not successfully remove the interference of iron from aluminium oxinate extraction. However, they found no interference from the E.D.T.A. in the extraction of the aluminium oxinate itself, although they only obtained this extraction with difficulty.

(v) Thioglycollic Acid

A series of small-scale tests over various pH ranges and various ligand-metal ratios of both Fe (II) and Fe (III) gave the following results:-

(i) Success in preventing the formation of hydrated iron oxide precipitates.

(ii) No success in preventing the formation of iron oxinates.

This is consistent with work done by previous researchers\textsuperscript{6,12,35} so no further work was carried out with thioglycollic acid.

(vi) 1,10-Phenanthroline

Similar results were obtained for ortho-phenanthroline as were obtained for thioglycollic acid. Consequently no further work was attempted with this complexing agent.
However, contrary to the above results, Sprain and Banks\textsuperscript{36} have successfully used ortho-phenanthroline to remove the interference of iron (as iron (II)) from aluminium oxinate extraction.

\textbf{(vii) Potassium Cyanide}

A number of workers\textsuperscript{6,12,31,21,4,25} have used potassium cyanide either by itself or in conjunction with another complexing agent in order to prevent iron (II) from complexing with oxine, in aluminium extraction research.

A series of tests over a pH range of 7 - 11 were carried out to determine whether or not potassium cyanide prevented the formation of iron (II) oxinate. These were successful.

However, before investigating extractions in the presence of potassium cyanide, a new method of analysis had to be found since atomic absorption spectroscopy requires the vapourisation of solutions and is therefore unsafe for cyanide solutions.

A spectrophotometric method involving the measurement of the absorbance of the organic extract at 390 m\textmu was found to be suitable.

However, due to complications arising in the calibration of this method, no further investigations were carried out with potassium cyanide. A discussion of these complications is given in Part C. of the Experimental Section.
(c) EXTRACTION AND SPECTROPHOTOMETRIC ANALYSIS

For this work a Hitachi 101 U.V.-Visible Spectrophotometer was used.

In order to free the chloroform from any acidic decomposition products which destroy the aluminium oxinate complex, the purifying method of Gentry and Sherrington\textsuperscript{12} was used. For reclamation of chloroform after extraction the method of Moeller\textsuperscript{28} was used followed by that of Gentry and Sherrington\textsuperscript{12} (Appendix 4).

**Calibration Curve:** Gentry and Sherrington\textsuperscript{12} used a calibration curve of standard solutions prepared from pure aluminium oxinate dried at 140\textdegree{}C. A known weight of this salt was dissolved in chloroform and aliquotted to suitable volumes.

In the present work pure aluminium oxinate was prepared by a standard analytical method (see Appendix 5) and the following standards were made up:

0.1407 g aluminium oxinate was dissolved in chloroform and diluted to 100 mls in a volumetric flask. A 10 ml aliquot was accurately pipetted and diluted to 100 mls. Further aliquots of 25, 20, 15, 10 and 5 mls were diluted to 50 mls.

The absorbances of these standards were read and plotted against concentration of aluminium.

Since the absorption peak of aluminium oxinate is at a maximum from 385 m\textmu{} to 410 m\textmu{} readings were taken at three wavelengths - 390, 395 and 400 m\textmu{.}
Beer's Law was obeyed in each case as may be seen from table 12 and Fig. IV.

**Preliminary Extractions:** The concentration range for aluminium determination was very small - 0-5 μg/ ml Al - necessitating the following precautions:-

(i) All reagents, including buffers, were pipetted directly into the separating funnels.

(ii) Na₂SO₄ was added to the separated organic extract so as to remove any turbidity due to water droplets.

(iii) Blank samples containing distilled water in place of aluminium solution were carried through.

(iv) All buffers and reagents were filtered before making up to the final volume. This was found to be particularly valuable with the pH 9.35 buffer as traces of Fe(OH)₃ were found in the filter paper after filtration.

The following extractions were made:-

1. 2 mls 0.0015 M Al + 5 mls 0.005 M Oxine + 25 mls buffer
2. " " 10 " "
3. " " 15 " 
4. 2 mls distilled H₂O 5 " "
5. " " 10 " "
6. " 15 " "

Fig. 4. Calibration curves for spectrophotometric analysis of aluminium oxinate.
The standard aluminium solution was prepared by dissolving a known weight of spectrographically pure aluminium wire in a minimum of dilute hydrochloric acid and diluting to volume. This was analysed gravimetrically. Aliquots were taken from an 0.02M Al solution to make the 0.0015M Al solution.

The oxine reagent was prepared by dissolving pure oxine in 20 mls glacial acetic acid and diluting to 1000 mls to make 0.1M Oxine. The 0.005M solution was diluted from this.

The buffer solution was prepared by dissolving 100 g of ammonium chloride in distilled water, adding 100 mls 15M NH$_4$OH and diluting to 1 litre. This gave a pH of 9.35 which is suitable for the aluminium oxinate extraction requirements.

The extraction was effected with 4 x 5 ml portions of chloroform and made to a final volume of 25 mls. Na$_2$SO$_4$ was then added, shaken, allowed to stand for a while, and then a sample was decanted for measurement of absorbance.

For this work a final result of 3.312 $\mu$g/ml of aluminium is equivalent to 100% extraction.

Results are given in tables 13 (a) (b) and (c).

Discussion of Results: Values for percentage extraction were observed ranging from 106% to 113.8%. The error involved here was suspected to arise from one or more of the following possibilities:
<table>
<thead>
<tr>
<th>Sample</th>
<th>Abs. of Epi.</th>
<th>Abs. of Oil</th>
<th>Absorbance</th>
<th>μg/ml Al</th>
<th>% Ext.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.855</td>
<td>0.020</td>
<td>0.835</td>
<td>3.51</td>
<td>106.0</td>
</tr>
<tr>
<td>2.</td>
<td>0.875</td>
<td>0.025</td>
<td>0.850</td>
<td>3.58</td>
<td>108.2</td>
</tr>
<tr>
<td>3.</td>
<td>0.885</td>
<td>0.027</td>
<td>0.868</td>
<td>3.62</td>
<td>109.3</td>
</tr>
</tbody>
</table>

**Table 13 a. Absorbance at 390 μm.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Abs. of Epi.</th>
<th>Abs. of Oil</th>
<th>Absorbance</th>
<th>μg/ml Al</th>
<th>% Ext.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.820</td>
<td>0.017</td>
<td>0.801</td>
<td>3.58</td>
<td>108.1</td>
</tr>
<tr>
<td>2.</td>
<td>0.840</td>
<td>0.023</td>
<td>0.817</td>
<td>3.66</td>
<td>110.5</td>
</tr>
<tr>
<td>3.</td>
<td>0.850</td>
<td>0.025</td>
<td>0.825</td>
<td>3.69</td>
<td>111.5</td>
</tr>
</tbody>
</table>

**Table 13 b. Absorbance at 395 μm.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Abs. of Epi.</th>
<th>Abs. of Oil</th>
<th>Absorbance</th>
<th>μg/ml Al</th>
<th>% Ext.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.780</td>
<td>0.019</td>
<td>0.761</td>
<td>3.64</td>
<td>109.9</td>
</tr>
<tr>
<td>2.</td>
<td>0.800</td>
<td>0.022</td>
<td>0.778</td>
<td>3.71</td>
<td>112.0</td>
</tr>
<tr>
<td>3.</td>
<td>0.815</td>
<td>0.025</td>
<td>0.790</td>
<td>3.77</td>
<td>113.2</td>
</tr>
</tbody>
</table>

**Table 13 c. Absorbance at 400 μm.**

*See text for identification of samples.*
These possible sources of error were considered as follows:

(i) Reagent Impurities: These are automatically taken care of by carrying through a blank sample with each experimental sample. No source of error can arise from the aluminium solution itself since it is spectrographically pure aluminium wire and contains no other metals.

(ii) Volumetric Equipment: This was all thoroughly cleaned with chromic acid. Some of the older equipment was replaced with new equipment which was also cleaned with chromic acid before use.

(iii) Calibration Errors: These could arise in three main ways:

(a) Error in the molarity of the standard aluminium solution.

(b) Error in the preparation of the aluminium oxinate.

(c) Error in the dilution and preparation of the final standards.

These were investigated as follows:
(a) Fresh solutions of aluminium were prepared. The new and old solutions were both analysed gravimetrically (Appendix 1). At least three separate analyses were carried out and results showed that the analysis of the 0.0015M aluminium solution previously in use was correct.

(b) Various other methods of precipitating an aluminium oxinate solution were investigated.\textsuperscript{15,16,40} The method previously used\textsuperscript{22} was found to be the best and gave analytical results comparable with the results from (a) above. It was taken for granted that, having been prepared by an analytical method, the aluminium oxinate would be in a suitably pure state for preparing calibration standards from (Appendix 5).

(c) The main source of error in the dilution of the standard solution would probably arise due to the volatility of chloroform. Whilst several workers\textsuperscript{12,27,28} have used chloroform with apparent success, Bolleter\textsuperscript{4} recommends the use of trichlorethylene due to its lower volatility. In support of the use of chloroform, fresh calibration curves were prepared on three more occasions and in each case the plots were exactly the same as those already shown in figure IV. For each new calibration curve prepared, a series of extractions were made. All the results were similar, if not the same, as those shown in tables 13 (a) (b) and (c). Consequently, it appears that the source of error for the high percentage extractions does not lie with the preparation of the calibration curve.
(iv) Sodium Sulphate Contamination: Previous workers have used various means of removing moisture droplets from a separated organic extract. In some cases the anhydrous \( \text{Na}_2\text{SO}_4 \) was added to the extract itself\(^{12,23,26}\) in some cases the extract was filtered directly into the optical cell\(^{4,6,11}\) and, in other cases, no precautions were described.\(^{20,25,36,42}\)

In view of these approaches, a series of extractions were carried out as follows:

(i) No precaution taken for moisture.
(ii) \( \text{Na}_2\text{SO}_4 \) added to remove moisture.
(iii) The above samples were then filtered and re-read to check for any difference.

For this series, 2 mls of 0.0015M Al solution were added to 5 mls of 0.005M Oxine solution, followed by 25 mls pH = 9.35 buffer solution. Corresponding blanks were prepared and the extractions made. The results are given in table 14.

Observation of these results suggest the following conclusions:

(a) No contamination or interference is arising from the \( \text{Na}_2\text{SO}_4 \).
(b) If care is taken when separation of the extract is made no water should be present. The results show that it does not matter whether or not precautions are taken to remove water from the extract.
(c) There is practically no variation in results over the region of wavelengths investigated.
(d) The accuracy of the analytical conditions in use is supported by the quadruplicate results shown.
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Na₂SO₄ Present or Absent</th>
<th>Concentration of Extract.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3400 μg</td>
</tr>
<tr>
<td>1. Filtered</td>
<td>Absent</td>
<td>1.70</td>
</tr>
<tr>
<td>Unfiltered</td>
<td></td>
<td>1.70</td>
</tr>
<tr>
<td>2. Filtered</td>
<td></td>
<td>1.74</td>
</tr>
<tr>
<td>Unfiltered</td>
<td></td>
<td>1.73</td>
</tr>
<tr>
<td>3. Filtered</td>
<td>Present</td>
<td>1.74</td>
</tr>
<tr>
<td>Unfiltered</td>
<td></td>
<td>1.73</td>
</tr>
<tr>
<td>4. Filtered</td>
<td></td>
<td>1.73</td>
</tr>
<tr>
<td>Unfiltered</td>
<td></td>
<td>1.72</td>
</tr>
</tbody>
</table>

Concentration is in μg/ml of Aluminium.

1.66 μg/ml Al = 100% Extraction.

**Table 14. Investigation of Moisture Interference in the Spectrophotometric Determination of Aluminium Oxinate.**
For further work the absorbance was read at only 390 m\(\mu\).

The use of Na\(\text{SO}_4\) was continued as a precaution against moisture in the extract.

(v) The Aluminium Oxinate Absorbance Peak: Errors could possibly be present if one or more of the following changes occurred in the U.V. absorption peak of aluminium oxinate:

(i) A darkening of the yellow chloroform solution due to photodecomposition of the oxinate would cause the absorbance reading at 390 m\(\mu\) to be greater.

(ii) A shift of the wavelength of the peak can occur due to acetic acid being extracted into the chloroform layer. Other workers\(^{26,29,38}\) have noted this phenomena.

(iii) Interference may possibly be caused by excess oxine ligand being extracted into the chloroform.

The investigation of these situations was as follows:

(i) To prevent photodecomposition of the samples they were read on the spectrophotometer as soon as practicable after extraction. If any delay occurred the samples were placed in a dark cupboard. These were considered satisfactory precautions.\(^{12,26,27,28,42}\)

(ii) The extractions were made at a pH of 9.35 and consequently, any acetic acid in the system should remain in the aqueous layer and so not interfere with the absorption peak.\(^{4,27,42}\)

(iii) The possibility of interference from the extraction of excess ligand was investigated by gradually increasing the ligand concentration until it was far in excess of that needed for
complete extraction of aluminium. The following series of extractions were carried out:

2 mls of 0.0015M Al were treated with various amounts of oxine starting at 5 mls of 0.005M oxine solution. 25 mls of buffer pH = 9.35 solution were added and the system was extracted once with exactly 25 mls of chloroform. Corresponding blanks were carried through.

When a levelling out of the quantity of extracted aluminium was reached the ligand:metal ratio was taken to an extreme of 1000:1 to observe any ill effects.

The results may be seen in table 15.

From these studies it may be seen that:-

(a) Excess ligand has no ill effect upon the actual extraction of the aluminium oxinate.

(b) The extraction of aluminium oxinate under the conditions of investigation levelled out at approximately 119% extraction. This occurred with 5 mls of 0.1M oxine solution which is 167:1 ligand:metal ratio.

With complete extraction achieved there remain two possibilities that may account for the high percentage extraction.

1. There is some, as yet unexplained, distortion of the absorption peak for aluminium oxinate. This requires an inspection of spectra of the samples.
<table>
<thead>
<tr>
<th>Orine Present</th>
<th>Corrected Absorbance</th>
<th>mg lill Aluminium in Solution</th>
<th>% Extraction Aluminium</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mls. 0.005M Orine</td>
<td>0.422</td>
<td>3.73</td>
<td>112.7</td>
</tr>
<tr>
<td>10 mls. &quot;</td>
<td>0.420</td>
<td>3.77</td>
<td>113.0</td>
</tr>
<tr>
<td>15 mls. &quot;</td>
<td>0.413</td>
<td>3.62</td>
<td>111.2</td>
</tr>
<tr>
<td>20 mls. &quot;</td>
<td>0.333</td>
<td>2.47</td>
<td>114.9</td>
</tr>
<tr>
<td>25 mls. &quot;</td>
<td>0.393</td>
<td>2.91</td>
<td>113.2</td>
</tr>
<tr>
<td>30 mls. &quot;</td>
<td>0.440</td>
<td>3.33</td>
<td>117.3</td>
</tr>
<tr>
<td>5 mls. 0.1M Orine</td>
<td>0.930</td>
<td>3.79</td>
<td>114.6</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.926</td>
<td>3.76</td>
<td>113.5</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.941</td>
<td>3.92</td>
<td>117.2</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.924</td>
<td>3.74</td>
<td>113.0</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.924</td>
<td>3.74</td>
<td>113.0</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.930</td>
<td>3.72</td>
<td>113.7</td>
</tr>
<tr>
<td>10 mls. &quot;</td>
<td>0.945</td>
<td>3.93</td>
<td>116.7</td>
</tr>
<tr>
<td>20 mls. &quot;</td>
<td>0.947</td>
<td>3.94</td>
<td>119.0</td>
</tr>
<tr>
<td>30 mls. &quot;</td>
<td>0.915</td>
<td>3.75</td>
<td>113.6</td>
</tr>
</tbody>
</table>

**Table 15. Investigation for Interference, in the Extraction of Al(OH)$_3$, from Large Excess of Orine Reagent.**
2. Beer's Law is possibly not obeyed in the experimental conditions being used. This requires a set of calibration standards to be prepared under actual experimental extraction conditions.

Both of these were investigated:

1. The spectra investigated are shown in Fig. V.
   Spectrum (a) has two peaks, one at 250 \( \mu \) and one at 320 \( \mu \). At 390 \( \mu \) this spectrum, which is an oxine blank, has zero absorbance.
   Spectrum (b) is a sample of aluminium oxinate extracted under experimental conditions and so it contains excess oxine extracted with it. This spectrum contains the aluminium oxinate absorption peak at 385 - 410 \( \mu \) and both of the peaks present in the oxine spectrum.
   Spectrum (c) is a sample of pure aluminium oxinate dissolved in chloroform. The peak that is present at 320 \( \mu \) in both of the two previous spectra is absent in this spectrum.
   This is probably the cause of the error that is under investigation.

2. The following calibration curve was prepared by extraction of aluminium oxinate into chloroform under actual experimental conditions:
   1, 2, 3, 4 and 5 mls of 0.0015M aluminium solution were treated with 5 mls of 0.1M oxine solution each and extracted once with exactly 25 mls of chloroform. This was then repeated. The absorbances were read at 390 \( \mu \) in 0.5 cm cells.
Fig. 5 - Spectra (U.V.) of Aluminium Oxinate.
TABLE 16. TABULATION FOR FIGURE 6.
(a) Calibration curve prepared under actual experimental conditions.
(b) Calibration curve prepared by dissolving pure Al(Ox)$_3$ in CHCl$_3$. 

![Graph showing absorbance vs. mg/ml Aluminium](image-url)
The results are given in table 16 and Fig. VI. A standard calibration prepared from pure aluminium oxinate dissolved in chloroform has been plotted on the same chart for comparison with the calibration curve in situ.

**Discussion of Results:** It is observed after detailed investigation that Beer's law holds for the absorption of U.V. light by aluminium oxinate under the experimental conditions used.

However, an appreciable difference is observed between the slopes of a calibration curve prepared under experimental conditions and one prepared from pure reagents. This is enough to account for almost 20% error when measuring percentage of extraction, bearing in mind the amounts of aluminium involved.

Examination of the spectra of aluminium oxinate and of oxine indicate that this difference in calibration methods is due to the presence of excess oxine in the experimentally prepared calibration samples.

Consequently it can be advised from this and other work\(^4,26,42\) that calibration curves be prepared under actual experimental conditions if absolute analysis is required. If only comparative analysis is required there is no need for a calibration curve.
PART III

CONCLUSION
PART III

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A detailed study of the solvent extraction of aluminium oxinate has been made. The extraction chemistries of oxinates of iron, chromium, and nickel have also been investigated.

The main aims of this project have been to:-

(i) Find the conditions for complete extraction of aluminium oxinate.

(ii) Investigate methods for analysis of the extract, particularly with regard to trace quantities.

(iii) Investigate the removal of interferences from iron, chromium, and nickel.

The following results have been obtained:

(i) Complete extraction of aluminium oxinate was obtained over a pH range of 5 - 11. For extraction to be complete over the whole of this range it is necessary to add the oxine ligand to the aluminium solution before adjusting the pH. The aluminium is precipitated as the oxinate and extracted as such. If this procedure is not followed, and extraction is made using a chloroform solution of oxine, aluminium hydroxide precipitates in the pH range of 6 - 8 and interferes with the extraction of aluminium as oxinate.
The extraction can be made with either one accurately measured volume of chloroform or with a number of consecutive extractions that are combined and diluted to an exact volume. Either method is suitable as one extraction effects complete extraction. (Extractability of aluminium oxinate at pH = 9.35 is \( \frac{1}{1 + 2.09 \times 10^{-6}} \) \{see theory\}).

If the concentration of the extract is to be measured, say, in mg/ml Al, one extraction is ample. However, if the total aluminium in the extract is to be measured, e.g. by back-extraction followed by gravimetric determination, then the multi-extraction method is necessary since small droplets of chloroform sometimes float on the surface of the aqueous layer and these will be extracted by a multi-extraction system.

During the course of this work, extractions were carried out in the pH 9 - 11 range in preference to the lower range in the vicinity of pH \( \approx 5 \). The reasons for this preference are:

(a) In the pH range of 9 - 11 the Al(Ox)_2 is completely precipitated. Consequently the extraction is more easily and more quickly effected as the precipitate merely dissolves in the chloroform. An extraction time of 30 - 60 seconds was required whereas extractions of aluminium with a chloroform solution of oxine may require up to 10 minutes of agitation.

(b) In the lower pH range, buffering is usually effected with acetic acid/ammonium acetate buffers. The ill effect of acetic acid upon the absorption peak of aluminium oxinate \( ^{26,29,38} \) eliminates the use of spectrophotometry for analysis of this extract unless special precautions are taken (the extract can be
washed with water but this could possibly result in partial re-extraction of the aluminium oxinate into the aqueous layer used for washing). In higher pH ranges ammonia/ammonium chloride buffers are usually used and these have no effect on the absorption peak of aluminium oxinate at 390 m\(\mu\). Any acetic acid present would remain in the aqueous layer at higher pH's.

(c) Okura\(^{33}\) has pointed out that, in low-acidity solutions, aluminium ions undergo polymerisation to polynuclear hydroxo-aquo complexes with aluminium atoms probably linked to one another with diol bridges as in:

\[
\left[ (\text{H}_2\text{O})_{2}\text{Al}\left\{\text{H}_{2}\text{O}\right\}_{2}\text{Al}\left\{\text{H}_{2}\text{O}\right\}_{2}\text{Al}\left\{\text{H}_{2}\text{O}\right\}_{2}\text{Al}\left(\text{H}_2\text{O}\right)_{2} \right]^{4+}
\]

It seems likely that a series of polynuclear ions with different degrees of polymerisation, ranging from monomer to colloidal hydrated alumina, exist in solution in equilibrium.

A study of oxine extractions also carried out by Okura\(^{33}\) showed that these high molecular weight aluminium ions are not extracted. It was shown that only aluminium ions with a degree of polymerisation at or very close to unity may be determined by extraction. These workers claim that the application of this extraction method
reveals that many current colorimetric methods involve changes in the form of aluminium during the course of determination.

Consequently, it is safer to avoid this type of aluminium polymer by extracting at higher pH's.

(ii) Suitable methods for analysis of the organic extract were found for a wide range of aluminium concentrations.

For concentrations in the range of 0.027 g of aluminium, the extract was re-extracted with 10 M HCl and a gravimetric Al₂O₃ determination carried out.

For trace amounts in the region of 75 μg of aluminium, spectrophotometric measurement of the absorbance of the organic extract at 390 μm was found to be most suitable. Associated problems can be seen more clearly by reading the experimental section of this work.

Atomic absorption spectroscopy was found unsuitable for measuring the trace aluminium. Even when the organic extract itself was sprayed into the flame (this enhances the sensitivity of aluminium) the method was not as sensitive as the measurement of the absorbance of U.V. light. Atomic Absorption spectroscopy was too sensitive to measure the larger amounts of aluminium without previously diluting the samples. Consequently, Atomic Absorption spectroscopy was found to be most suitable for analysis of the concentration range between the trace level and the larger level.
(iii) In an attempt to remove the interference of iron in the extraction of aluminium oxinate, the extraction of aluminium and iron together in the presence of oxine and the following ligands was investigated:

- Tartaric Acid
- Citric Acid
- 4, 5-Dihydroxybenzene - 1, 3-disulphonic acid (Tiron)
- Nitrilotriacetic Acid
- $\alpha$-Picolinic Acid
- Ethylenediamine-tetra-acetic Acid
- Thioglycollic Acid
- 1, 10-Phenanthroline
- Potassium Cyanide

No appreciable success was obtained although some of these may stand further investigation (see experimental section).
APPENDIX
The analytical methods used throughout this study are as follows:

1. **Precipitation of Aluminium Hydroxide**

A solution containing about 0.1 g of aluminium in 200 mls of water was taken and to it was added 5 g of pure ammonium chloride and a few drops of methyl red indicator (0.2% alcoholic solution). This solution was heated until just boiling. Pure dilute ammonia solution (1:1) was added dropwise until the colour of the solution changed to a distinct yellow. The solution was boiled for one or two minutes and filtered at once through a suitable quantitative filter paper (Whatman 541). The precipitate was washed thoroughly with hot 2% ammonium chloride solution made neutral with dilute ammonia solution to methyl red. The paper containing the precipitate was placed in a previously ignited silica or platinum crucible, dried, charred, and ignited for 10-15 minutes at 1200°C in a muffle furnace until constant weight was achieved. For weighing purposes the sample was firstly cooled in a suitable dessicator and then weighed as $\text{Al}_2\text{O}_3$.

$$\text{Al}_2\text{O}_3 \times 0.52913 \equiv \text{Al}$$
2. **Determination of Chromium**

A solution of chromium, that had been freed of organic materials by wet-ashing with concentrated HNO$_3$ and fuming with HClO$_4$, was taken (see text of thesis). To this was added 100 mls distilled water and 50 mls of 25% H$_2$SO$_4$.

This solution was then heated to boiling and 5 mls of 0.1N AgNO$_3$ followed by 50 mls 10% ammonium persulphate solution were added. The solution was then boiled for 20 minutes and then cooled thoroughly.

This solution was then titrated against 0.1N ferrous ammonium sulphate solution and back-titrated against 0.1N potassium dichromate solution. Sodium diphenylamine sulphonate was used as an indicator and 10 mls of phosphoric acid were added before the titration commenced.

\[
1 \text{ ml } N\text{-Fe}^{2+} \equiv 0.01734 \text{ g Cr.}
\]

3. **Determination of Iron**

A solution of iron (III) in about 5-6 N HCl was taken and heated to boiling. A solution of concentrated stannous chloride (30 g SnCl$_2$ 2H$_2$O in 100 mls conc. HCl, diluted to 200 mls) was added dropwise until the iron solution was colourless. The iron (III) was then satisfactorily reduced to iron (II).

After cooling the solution rapidly and thoroughly it was diluted to about 250 mls with distilled water. 10 mls of saturated mercuric
chloride was then added so as to oxidise any excess stannous chloride in the solution.

The solution was titrated with 0.1 \( \text{N} \ K_2\text{Cr}_2\text{O}_7 \) after previously adding 20 mls of 25% \( \text{H}_2\text{SO}_4 \) and 5 mls of phosphoric acid. Sodium diphenylamine sulphonate was used as an indicator.

\[ 1 \text{ mls N-K}_2\text{Cr}_2\text{O}_7 \equiv 0.05585 \text{ g Fe.} \]

4. **Purification of Chloroform**

To purify chloroform from any acidic decomposition products it is necessary to extract the chloroform with an equal volume of a solution that is 2 M with respect to both ammonium chloride and ammonia solution. Repeat this and then wash the chloroform three times with distilled water. Store overnight over calcium chloride and then distill, collecting the fraction at \( 61.15^\circ C \). Add 2% \( \text{V/V} \) absolute ethanol to prevent photodecomposition.

To reclaim used chloroform, extract it with 10 M hydrochloric acid, repeat, wash three times with distilled water and then carry out the previous purification procedure.

5. **Preparation of Aluminium Oxinate**

To a warm solution (70-80°C), very slightly acid with \( \text{HCl} \) or \( \text{H}_2\text{SO}_4 \) and containing not more than the equivalent of 0.05 g Al per 100 mls, add a slight excess of the reagent (5% solution of oxine...
in 2N acetic acid), allowing 1 ml for each 3 mg of aluminium present.

Slowly add 2 N ammonium acetate solution until a precipitate forms (if one has not already formed), and then add 25 mls more for each 100 mls of solution present, in order to ensure complete precipitation. If the supernatant liquid is yellow, enough reagent has been added. Allow the liquid to stand for an hour without further heating, and collect the precipitate in a sintered-glass crucible.

Wash the precipitate well with cold water and dry at 120-140°C. The dried precipitate has the composition Al(C₉H₆O₃N)₃ and contains 5.87% aluminium.

6. Atomic Absorption Spectroscopy

The methods used involved an Atomic Absorption Spectrophotometer model AA3 from Techtron Pty. Limited.

The following operating conditions were used:

<table>
<thead>
<tr>
<th>Element</th>
<th>Absorption Wavelength (Å)</th>
<th>Flame Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>3092</td>
<td>Nitrous Oxide and Acetylene</td>
</tr>
<tr>
<td>Iron</td>
<td>2483</td>
<td>Air/Acetylene</td>
</tr>
<tr>
<td>Nickel</td>
<td>2320</td>
<td>Air/Acetylene</td>
</tr>
</tbody>
</table>

The methods used involved spraying of aqueous solutions into the flame. The spraying of organic extracts directly was investigated and tried but to no appreciable extent.
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ACKNOWLEDGMENTS

The author wishes to thank Mr. F. M. Hall for suggesting the overall outline of the project and for his guidance and discussion throughout. He would also like to express his appreciation to other members of the academic staff and research students of the Wollongong University College Chemistry Department for their help and advice. Appreciation is also expressed to the technical staff at the College.

The author is indebted to the Australian Iron & Steel Pty. Ltd., Port Kembla, for financing much of this project.

The author is also indebted to the patience and encouragement shown by his fiancee.