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SOLVENT EXTRACTION, GAS CHROMATOGRAPHIC,
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METAL FLUOROACETYLACETONATES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Gerald Prescott Morie, B.S., M.Sc.

*****

The Ohio State University
1966

Approved by

[Signature]
Department of Chemistry
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FIELD OF STUDY

Major Field: Analytical Chemistry
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INTRODUCTION

The purpose of this investigation was to study the extraction of various metal ions into benzene using trifluoroacetylacetone. Metal trifluoroacetylacetonates have been successfully eluted by gas-liquid chromatography and it was felt that a combination of solvent extraction and gas chromatography might be effective for the quantitative determination of metals. It was also hoped that information concerning the nature and stability of these metal chelates might be obtained from extraction studies and spectral data.
CHAPTER I

SOLVENT EXTRACTION OF METAL IONS WITH
TRIFLUOROACETYLACETONE AND HEXAFLUOROACETYLACETONE

Historical Review

The extraction of metal ions from aqueous solution into an organic phase requires the use of a substance which will combine with the metal ion to form a neutral species. The first examples of such compounds were those in which the extractable species formed by the association of ions. Among these was Peligot's discovery in 1842 that ether could extract uranium (VI) from nitric acid.¹ The first record of an extraction procedure used in analysis was described by Rothe² in the now classic extraction of ferric chloride from aqueous hydrochloric acid solutions into ether. Since this time, numerous ion association extraction systems

have been described. Morrison and Freiser tabulated extraction data for many of these systems and updated this information with reviews in *Analytical Chemistry*. A new type of extraction system, the metal chelate system, resulted with the introduction of dithizone in 1925. Unlike ion association complexes, for which the chemical equilibria are often quite complicated, the reaction of cations with organic chelating agents to give neutral and less hydrophilic species can usually be described by relatively simple equations. A number of other organic chelating agents such as cupferron and 8-hydroxy-quinoline soon followed dithizone as reagents for the extraction of metal ions. Stary listed nearly a hundred chelating agents which have been used for solvent extraction. In addition, the conditions for the extraction of various metal ions with these reagents are described in this book.

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Among the various chelating agents used in solvent extraction, few have been more widely used than \( \beta \)-diketones. From 1948 to the present, numerous extraction studies have been performed using acetylacetone and thenoyltrifluoroacetone. Acetylacetone extraction data has been collected and summarized in a table in Stary's book. Stary and Hladky have recently reported a systematic study of some thirty \( \beta \)-diketonates in which acetylacetone, benzoylacetone and dibenzoylmethane were compared.\(^7\) Other \( \beta \)-diketones such as furoyltrifluoroacetone,\(^8\) pyrroyltrifluoroacetone,\(^9\) and selenoylacetone\(^10\) have been proposed as extraction reagents. Recent studies indicate that dipivaloylmethane forms quite stable lanthanide complexes.\(^11\) These complexes are soluble in benzene and therefore might be extracted into an organic solvent.


\(^8\)McIntyre, R. T., Berg, E. W., Campbell, P. N., Anal. Chem. 28, 1316 (1956).


Until quite recently, relatively few extraction studies were made using trifluoroacetylacetone. A few United States' patents were granted for various radio-chemical separations with this reagent. Among these is the extraction of plutonium (IV),\textsuperscript{12,13} zirconium,\textsuperscript{14} the separation of actinides from fission products,\textsuperscript{15} and actinium from radium and its decay products.\textsuperscript{16} Tri-fluoroacetylacetone has also been used for the separation of neptunium from plutonium, uranium and fission products\textsuperscript{17} and protactinium from uranium and thorium.\textsuperscript{18}

\textsuperscript{13}Crandall, H., Thomas, J. R., Reid, J. C. (U. S. Atomic Energy Commission) C N 2657 (1945).
\textsuperscript{17}Magnuson, L. (To U. S. Atomic Energy Commission), U. S. Patent 2,830,066 (April 8, 1958).
Several years ago, Larsen and co-workers studied the extraction of zirconium and hafnium using trifluoroacetylacetone. Recently the distribution of scandium trifluoroacetylacetonate between water and various organic solvents was determined and a correlation between the extraction data and the regular solution theory was made.

Since 1963, when it was shown that many metal trifluoroacetylacetonates are volatile enough to be chromatographed by gas-liquid chromatography, increased interest has been shown in solvent extraction studies using this reagent. Since the present investigation was begun, two comprehensive extraction studies have been reported by Scribner et al. In the first study it was found


that copper, iron and aluminum can be extracted from aqueous acetate solutions into chloroform which is 0.1 M with respect to trifluoroacetylacetone. Manganese, nickel, zinc, and magnesium were hardly extracted at all and the extraction of chromium (III) was found to be extremely slow. The second paper described a trifluoroacetylacetone-isobutylamine system. Divalent metals, whose coordination number is greater than four, were extracted when isobutylamine replaced water in the two coordination sites not occupied by trifluoroacetylacetone.

Theory

Solvent extraction is based on the distribution of a solute between two immiscible phases. The Gibbs phase rule,

\[ F = C - P + 2 \]

where \( P \) = number of phases
\( C \) = number of components
\( F \) = degrees of freedom

is therefore applicable as it is for any phase distribution. Thus, a system consisting of two immiscible solvents and one solute has one degree of freedom at constant temperature.
and pressure. Consequently, if the concentration of the solute in one phase is selected, the concentration of the solute in the other phase is fixed. This relationship leads to the Nernst distribution law, which states that the ratio of concentrations of the solute in each phase will be constant at equilibrium. The equilibrium for a solute, $A$, distributed between water, indicated by a subscript $W$, and an organic phase denoted by subscript $O$, is described by:

$$A_W \rightleftharpoons A_O \quad K_d = \frac{m_{A_O}}{m_{A_W}} \approx \frac{[A]_O}{[A]_W}$$  (1.2)

where $m$ indicates molality, brackets indicate molarity, and $K_d$ is the distribution coefficient, a constant independent of total solute concentration. The distribution coefficient, $K_d$, of a compound is often approximately equal to the ratio of its solubility in the organic and aqueous phases.

The distribution ratio, $D$, is a more useful quantity for describing extractions. This is the stochiometric

---

ratio of total metal concentration in the organic phase to that in the aqueous phase, or

\[
D = \frac{C_{M_o}}{C_{M_w}}
\]  

(1.3)

From the analytical chemist's point of view, probably the most useful term which describes extractions is the percent extracted, %E. This involves the ratio of species A in the organic phase to the total amount, or

\[
\%E = \frac{C_{A_o} V_o}{C_{A_o} V_o + C_{A_w} V_w}
\]  

(100)  

(1.4)

where \( V_o \) and \( V_w \) are the volumes of the organic and aqueous phases. Substituting equation 1.3 into equation 1.4 and dividing numerator and denominator by \( V_o \) gives:

\[
\%E = \frac{100 D}{D + \left( \frac{V_w}{V_o} \right)}
\]  

(1.5)

Before 1941, the variables and number of equilibria involved in metal chelate extractions were thought to be so numerous that a simple, quantitative extraction equation could not be derived.\(^{26}\) However, in 1941 Kolthoff and

Sandell developed an equation based on the following equilibria:

\[
\begin{align*}
H^+ + A^- & \rightleftharpoons HA \\
H^{+n} + nA^- & \rightleftharpoons MAn \\
& \text{water} \\
& \text{organic solvent}
\end{align*}
\]

The equilibria involved include the ionization of reagent, HA, considered to be a weak acid, the formation of the chelate, MAn, and the distribution of both of these species between the two phases. The equilibrium constants are given as follows:

\[
K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{dissociation constant} \quad (1.6)
\]

\[
K_f = \frac{[MAn]}{[M^{+n}][A^-]^n} \quad \text{overall formation constant of complex} \quad (1.7)
\]

\[
K_d = \frac{[MAn]}{[MAn]^0_w} \quad \text{distribution of the metal chelate} \quad (1.8)
\]

\[
K_{dA} = \frac{[HA]^0_o}{[HA]^0_w} \quad \text{distribution of the reagent} \quad (1.9)
\]

---

The following equation for the distribution of the metal may be derived;

\[
D = \frac{K_f K_d K_a^n [HA]^o_n}{K_{d_A} [H^+]^n}
\]  
(1.10)

\[
D = \frac{K_f K_d K_a^n [HA]^n_w}{[H^+]^n}
\]  
(1.11)

\[
D = \frac{K' [HA]^n_w}{[H^+]^n}
\]  
(1.12)

Where \( K' = K_d K_a^n K_f \) and the subscript, \( o \), refers to species in the organic phase.

In developing the above equation, it has been assumed that the hydrated metal ion is the only form of the metal with an appreciable concentration in the aqueous phase and the neutral chelate is the only metal containing species in the organic phase. Even though these assumptions have been made, the equation is fairly accurate for most systems and it illustrates several important facts. Namely, the distribution of the metal is a function of two experimental values, the pH and \([HA]^w\), the concentration of reagent in the aqueous phase. Thus, at
a given pH the amount of metal extracted into the organic phase will increase as the reagent concentration in the aqueous phase increases, and at a given reagent concentration the amount extracted will increase as the hydrogen ion concentration decreases. It is also apparent that the distribution also depends on the formation constant of the chelate, the acidity constant of the reagent, and distribution coefficients of chelate and reagent.

Irving and Williams demonstrated that if the reagent concentration in the water is maintained constant, the distribution of the metal in a given system is a function of pH alone. Because of this, curves of percent metal extracted versus pH at constant reagent concentration are of great analytical significance. Using the relationship between equations 1.5 and 1.12,

\[
D = \frac{\%E}{100 - \%E} = K' \frac{[HA]^n}{[H^+]^n} \tag{1.13}
\]

and if \([HA]^n_w\) remains constant

\[
D = \frac{\%E}{100 - \%E} = K'' [H^+]^{-n} \tag{1.14}
\]

where \(K'' = K_f K_d K_a^n [HA]^n_w\).

---

Expressing equation 1.14 in logarithmic form

\[ \log \%E - \log (100 - \%E) = \log K'' - n \log (H^+) = \log K'' + n \text{pH} \tag{1.15} \]

Equation 1.15 describes a family of symmetrical sigmoid curves, the position of which along the pH axis depends only on the magnitude of $K''$ and $n$, and the slope of each at 50% $E$ is determined by the charge on the metal ion. Two of these curves have been calculated and are shown in Figure 1. Experimental curves may vary somewhat from these for several reasons. The concentration of excess reagent may not be constant, equilibrium may not have been attained or hydrolysis of the metal ion may alter the extraction curve.

It is evident that by taking the logarithm of both sides of equation 1.14, a straight line is predicted for a plot of log D versus pH.

The pH value at $\%E = 50$ has been designated as $\text{pH}^{1/2}$ and is given by

\[ \text{pH}^{1/2} = - \frac{1}{n} \log K'' \tag{1.16} \]

The spread of the $\text{pH}^{1/2}$ values is an indication of the separability of given ions in a system.

\[ ^{29}\text{Ibid.} \]
Figure 1
THEORETICAL EXTRACTION CURVES FOR A DIVALENT AND TRIVALENT METAL

○ Divalent metal, pH₂ = 3.0

○ Trivalent metal, pH₁ = 2.0
It is often desirable to separate one metal from another by solvent extraction. The ease of separation with a particular reagent is given by \( \beta \), the separation factor.

\[
\beta = \frac{D_1}{D_2} = \frac{K_{f_1} K_{d_1}}{K_{f_2} K_{d_2}}
\]  

(1.17)

From equation 1.11 it is evident that the extractability of a metal with a given reagent depends on several factors. Other, more subtle factors also influence the extraction of metals, and although a detailed discussion is beyond the scope of this treatise, these factors will be enumerated.

Equation 1.11 indicates that the distribution of a metal with a certain reagent depends on the concentration of the reagent. This is indeed true and high reagent concentration is often employed so that certain metals can be extracted at a low pH.

This equation also shows the dependence of the extraction of a chelate on its overall formation constant. Therefore, a rapid visual comparison of the relative stability of several complexes can be made from extraction curves.
As pointed out previously, the extraction is dependent not only upon $K_d$, but also on the dissociation constant of the reagent.

In many extraction procedures, especially separations, supplementary masking agents are introduced. The masking agent forms water soluble complexes with metals in competition with the extraction agent. Equations showing how masking agents affect the extraction of metals are given in Chapter V.

The nature of the organic solvent also influences the distribution of both reagent and metal chelate. Until recently, solvents were usually selected on the basis of trial and error. In a recent paper,\(^{30}\) distribution coefficients of $\beta$-diketones were explained successfully on the basis of the regular solution theory.

Often, when two reagents are used simultaneously in an extraction study, a synergistic enhancement of the distribution coefficient is observed. This enhancement may be $10^4$ times greater for the combination than it is for either individual reagent.\(^{31}\) This synergistic effect

---


often occurs when a metal's coordination number is more than twice its oxidation state. Thus, a second reagent may replace water in the coordination sphere and result in a less hydrophilic species.

Finally, many extractions are kinetically controlled, a phenomenon that can be either advantageous or undesirable depending on the situation. The rate that equilibrium is attained depends on two factors: (1) the rate of formation of the extractable species and (2) the rate of transfer of this species to the organic phase. The former is usually more important.

Properties of Trifluoroacetylacetone. The synthesis of trifluoroacetylacetone was first described by Staniforth.\textsuperscript{32} It is a colorless liquid with a specific gravity of 1.27 and a boiling point of 107°C.\textsuperscript{33} Since it is decomposed by bases into trifluoroacetic acid and acetone, it cannot be used for extraction from solutions with a pH greater than 8 or 9.

\textsuperscript{32}Staniforth, R. A., Doctoral Dissertation, Ohio State University, 1943.

Like other ketones, acetylacetone and its fluorinated derivatives exhibit keto-enol tautomerism. The electron attracting trifluoromethyl group increases the extent of enolization. The enol content has been estimated to be 76%, 95%, and 100% for acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone respectively.\(^\text{34}\) Hydrogen bonding also occurs so that two forms are possible:

Similarly, two forms of the corresponding chelate can be written:

This is known as the resonance effect and has been used to explain why certain chelates of β-diketones have

greater stability than those of salicylaldehyde. The stability increase results from the contribution of resonance structures of the chelate ring to the structure of the chelate. This resonance may also result in an increased solubility in such solvents as benzene.

Experimental

Apparatus. Activity measurements of all isotopes except thallium-207 were made by integral scintillation counting on a Radiation Instrument Development Laboratory model 49-54 Scaler. The scaler was connected to either a 2 inch by 2 inch Harshaw thallium activated solium iodide crystal or a 5 inch by 4 inch well crystal of the same composition.

This type of instrument is particularly good for the measurement of γ radiation. The γ rays are absorbed by the crystal and produce scintillations which are detected by a photocell, amplifier and recorded. Counting rates as a function of the discriminator setting were obtained for all gamma emitters and the integral and differential gamma spectra were drawn. The discriminator settings, voltage, crystal and gain that were used for

each isotope are given in Table 1. In general, this setting excluded all pulses with energies below the peak of maximum energy.

Periodically, the performance of the scaler was evaluated statistically by means of a chi square test. This test checks the fit of data to the Poisson probability curve and is described in detail in Chase's text.\textsuperscript{36}

The resolving time, $t$, of the apparatus is a function of the electronic scaler and is given by the manufacturer as five micro seconds. Therefore, in order to have a 0.5\% error in counting rates due to resolving time, the counting rate would have to be 60,000 counts per minute. Since no counting rates higher than this were used, corrections for resolving time were unnecessary.

The sample holder for the two inch by two inch crystal consisted of a 1.8 (i.d.) by 5.5 cm. vial fused to a glass jacket. This jacket was fastened over the crystal to insure constant geometry, and to protect the crystal as well. The construction and an illustration

# TABLE 1

## COUNTING CONDITIONS AND PROPERTIES OF RADIOISOTOPES USED

<table>
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<th>Isotope</th>
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<th>Discriminator Setting*</th>
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<td>Chromium-51</td>
<td>27.8d</td>
<td>0.323 γ</td>
<td>2x2</td>
<td>0.80</td>
</tr>
<tr>
<td>Manganese-54</td>
<td>300d</td>
<td>0.835 γ</td>
<td>2x2</td>
<td>1.90</td>
</tr>
<tr>
<td>Iron-59</td>
<td>45.1d</td>
<td>1.10 γ</td>
<td>2x2</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.29 γ</td>
<td>4x5</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.191 γ</td>
</tr>
<tr>
<td>Gallium-68</td>
<td>68M</td>
<td>1.10 γ</td>
<td>4x5</td>
<td>2.25</td>
</tr>
<tr>
<td>Indium-114m-114</td>
<td>114m-49d</td>
<td>0.192 γ</td>
<td>4x5</td>
<td>0.50</td>
</tr>
<tr>
<td>Thallium-207</td>
<td>4.1y</td>
<td>0.765 β⁻</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

*Above settings are for instrument number 364177 (O.S.U. serial number) when set at a gain of 1/16 and 1000 volts for the 2x2 inch crystal and 900 volts for the 4x5 inch.*

**Geiger-Muller Tube.
of this device are presented in an article by Morie, Sweet, and Pitstick.\footnote{37}

Liquid samples were counted in two dram screw-cap vials. Previous workers in this laboratory\footnote{38} have shown that no correction factors need be used for differences in size or geometry of these vials.

Thallium-204 was measured with a Geiger-Mueller counter since it is a beta emitter. The instrument employed was a Hamner Electronics model N-221 scaler equipped with a Tracerlab TGC-2 Geiger-Mueller tube.

Purity checks were made on each isotope with a Radiation Instrument Development Laboratory 200 channel pulse height analyzer. This instrument converts an energy of a gamma ray to an electrical impulse of a discrete energy which is amplified and stored. The gamma spectra of an isotope is then viewed on an oscilloscope or printed on a tape.


\footnote{38} Mencis, I., doctoral dissertation, the Ohio State University, Columbus, Ohio (1963).
A Beckman model G pH meter equipped with either a 40495 Beckman glass electrode or a 31983 Beckman combination glass, silver-silver chloride electrode was used for pH measurements.

A Burrell wrist action shaker was used to agitate the solutions during batch equilibrium studies. Samples were shaken in 60 ml duraglass screw-cap bottles which had a polyethylene cone sealing device in the caps.

Spectrophotometric measurements were made with either a Cary model 14 recording spectrophotometer or a Beckman model D. U. Spectrophotometer equipped with a model 73600 A.C. D. U. power supply.

A Heto constant temperature water bath was used to maintain extraction vials at a constant temperature.

Reagents. All reagents used in this investigation were analytical reagent grade unless otherwise specified. Double distilled demineralized water containing less than one part per million of impurities was used.

Purification of trifluoroacetylacetone and hexafluoroacetylacetone. These two reagents were received in varying degrees of purity and were distilled prior to use. The fraction of trifluoroacetylacetone boiling
between 105-6° was collected and stored in a refrigerator. The infrared spectrum of the compound reproduced in Figure 2 shows no extraneous bands compared to the spectrum reported in the literature.\(^{39}\) The absence of a band at 1800 cm\(^{-1}\) indicated that the trifluoroacetylacetone contained no acidic impurity which is sometimes present and which cannot be removed by distillation.

Hexafluoroacetylacetone was distilled in a closed system so that atmospheric moisture was excluded. The fraction boiling from 65-67° was collected and also stored in a refrigerator.

Standard solutions of trifluoroacetylacetone in benzene (usually 0.25 M) were prepared as follows: about seven ml. of trifluoroacetylacetone were added to a tared weighing bottle from a graduated cylinder and additional reagent was added until the weight reached 9.38 g. The bottle was stoppered and a final weight was obtained. The contents were then transferred to a 250 ml volumetric flask and was followed by several washings with benzene.

The contents were diluted to the mark, mixed and transferred to an amber glass bottle fitted with a polyethylene-seal screw cap.

High purity gallium and indium metal were obtained from Electronic Space Products, Inc., Los Angeles, California. High purity thallic oxide was obtained from B.D.H. Chemicals, Ealing Corporation, Cambridge, Massachusetts.

Indium 114-m, thallium 204, and iron-59 were obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee. Manganese-54, which is accelerator produced, and chromium-51 were obtained from Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania.

Gallium-68 was obtained from a gallium-68 cow supplied by Dr. W. G. Myers. The radiation energies and counting conditions for all radioisotopes used are given in Table 1.

Purification of iron-59. All radioisotopes except iron-59 were received in a very pure state. Iron-59 was contaminated with 0.001 mc of cobalt-60 and 0.0005 mc of manganese-54. These impurities were removed by an anion exchange separation based on the work of Kraus and Nelson.\(^{40}\)

The sample was made 5 molar with hydrochloric acid and $10^{-3}$ M in cobalt and manganese. A 5 cm. column of 0.8 cm. i. d. glass tubing was filled with Dowex 1-x8 resin and rinsed thoroughly with 4 M hydrochloric acid. The sample was introduced on column and the cobalt-60 and manganese-54 was eluted with 4 M hydrochloric acid. The column was then eluted with 0.05 M hydrochloric acid to remove iron-59. By monitoring the activity with a survey meter, the majority of the iron-59 activity was found to be in a 5 ml. volume. A twenty minute count on the multi-channel analyzer showed no evidence of any cobalt-60 or manganese-54.

**Procurement and purification of gallium-68.**

Gallium-68 was obtained from a bench top generator known as a gallium-68 cow which was first described by Green and Tucker.\(^1\) The generator, which was prepared by Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania, consists of a glass column 10 cm. in length, 2.5 cm. in diameter containing 10 grams of chromatographic alumina retained on a fritted glass disc. About one

millicurie of Germanium-68 ($t_\frac{1}{2} = 290$ d) is placed on
the column in a solution of 0.005 M EDTA, the pH of
which is adjusted to 7.0 with dilute sodium hydroxide.
Germanium-68 decays to gallium-68 ($t_\frac{1}{2} = 68$ min) by
electron capture so that secular equilibrium is
established in about twelve hours.

The cow is milked of gallium-68 by pouring 25 ml.
of neutral 0.005 M EDTA solution into the column and
allowing it to pass down the alumina. The germanium-68
is retained on the column while gallium-68 is removed as
an EDTA complex in three to four minutes. The yield is
about 75\% and the product is carrier free.

Because it was impossible to utilize the gallium-
68 in the form of its EDTA complex, a gallium chloride
extraction into isopropyl ether was performed. The
procedure used was similar to the method of Nachtrieb and
Fryxell, \textsuperscript{42} but was modified by Anderson. \textsuperscript{43} Twenty-five
ml. of concentrated hydrochloric acid was added to the
25 ml. of aqueous solution containing gallium-68 in a

\textsuperscript{42} Nachtrieb, N. H., Fryxell, R. E., J. Am. Chem.

\textsuperscript{43} Anderson, W. G., private communication.
100 ml. beaker. This solution was brought to boiling in a hood for a few seconds to expell any germanium-68 as germanium tetrachloride which may have bled from the column. The solution was cooled, poured into a 125 ml. separatory funnel, and 50 ml. of isopropyl ether was added. The funnel was shaken for about two minutes, the contents were allowed to settle and the lower aqueous phase was withdrawn, checked with a survey meter and discarded. Fifty ml. of distilled water were then added to the funnel and the gallium chloride was back-extracted into water. The aqueous phase containing gallium-68 was withdrawn and used in extraction studies. This extraction procedure also eliminated any aluminum that may have been eluted from the alumina column.

Procedure

General extraction procedure. Because one of the objectives of this investigation was to develop practical, analytical methods, aqueous volumes of 25 ml. and organic volumes of 5 ml. were used so that a five fold concentration occurred. Preliminary experiments indicated that if the extractions were to be combined with gas
chromatography, $10^{-2}$ to $10^{-3}$ molar metal solutions would be needed for detection by the thermal conductivity detector. Therefore, $8 \times 10^{-3}$ M metal solutions were used in extraction studies. The benzene and aqueous phases were not pre-saturated because their mutual solubility is negligible.

In general, the following procedure was employed:

Twenty-five ml. portions of standard metal solutions were transferred to extraction bottles. The pH was adjusted with a few drops of 6 M perchloric acid, 6 M sodium hydroxide or 1 M sodium hydroxide. It was possible to adjust the pH directly in the extraction flasks using the combination electrode. The volume of base or acid added was recorded and used in calculating distribution ratios. Sufficient sodium perchlorate was then added if needed to bring the total ionic strength to 0.1. Five ml. portions of 0.25 M trifluoroacetylacetone in benzene were added and caps were immediately placed on the bottles. The bottles were then placed on a shaker and shaken at a medium speed for four hours. The results of a time study, which will be discussed later, indicated that this length of time was necessary for equilibration. Extraction
flasks were then allowed to attain constant temperature in a water bath maintained at 25°C ± 0.5°C.

After equilibration, aliquots were taken for determining distribution ratios, and the aqueous phase of each flask was then poured into a 50 ml beaker. The equilibrium pH of each aqueous phase was measured with a 40495 Beckman glass electrode and saturated calomel electrode. These electrodes seemed to be more accurate and more nearly linear than the combination electrode over the pH change studied. Usually several additional extractions were performed in the pH\(_1/2\) region so that a well defined curve was obtained.

Radiometric measurements were made as follows: Equal volumes of aqueous and organic phases were withdrawn and placed in ten ml. screw cap vials for counting. After making background corrections, and a correction for the decay of the short-lived gallium-68, the distribution ratios were calculated from ratios of activities in the two phases.

Extraction of various elements.—Aluminum. Reagent grade aluminum nitrate nonohydrate, 3.0012 g., was weighed
out, transferred to a one-liter volumetric flask, and the flask was filled to the mark with distilled water.

Because no convenient tracer for aluminum is available, it was necessary to find some method, other than a radiometric one, to follow the extraction of this element. The familiar spectrophotometric method based on the yellow aluminum 8-hydroxyquinolate seemed to be a logical choice and was performed as follows: 44

Aluminum 8-hydroxyquinolate was synthesized and standard solutions of this complex were prepared in benzene.; The absorbance of these solutions obeyed the Beer-Lambert law. One ml. portions of the benzene phase containing aluminum trifluoroacetylacetonate was withdrawn from each extraction flask. This was added to a 100 ml. volumetric flask which contained 2 ml. of a one percent solution of 8-hydroxyquinoline in absolute ethanol. About 0.1 gram of sodium acetate was added to neutralize any excess acid which may have been extracted. The mixture was allowed to stand and was diluted to the mark

with benzene. This ligand exchange reaction in benzene was so slow the absorbance of the solution was still increasing after forty-eight hours so another approach was taken.

Aluminum trifluoroacetylacetonate was synthesized as described in Chapter IV and purified by recrystallization in hexane. Standard solutions were prepared in benzene and portions were taken for gas chromatographic determination. Previous workers have shown that this chelate can be chromatographed without decomposition. Different amounts of the chelate were injected into a chromatograph and a calibration curve based on peak area was obtained. The curve was linear and reproducible over the range investigated. Twenty micro-liter portions of the organic phase were withdrawn from extraction flasks with a syringe and injected into the chromatograph. The percent extraction was obtained from the amount of metal found and the total amount present in both phases.

**Gallium.** High purity (99.99%) gallium metal, 0.5577 grams, was weighed out and dissolved in a minimum amount of perchloric acid. After dissolution, the

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gallium perchlorate was transferred to a one-liter volumetric flask and the flask was diluted to the mark with distilled water. The solution was then transferred to a one-liter polyethylene flask and a few drops of gallium-68 were added. Since gallium-68 has a short half life (68 min.), corrections for the decay of this species were made. The activity of each sample was corrected to the time that the first sample in the series was counted. Two ml. portions of each phase were counted, corrected for background, and distribution ratios for each extraction were calculated from the ratio of specific activity in the organic phase to that of the aqueous phase. Some points on the gallium extraction curve were later checked by the gas chromatographic method described for aluminum.

**Indium.** Solutions of indium were made by dissolving high purity indium metal (0.9185 g) in about ten ml. of perchloric acid. The mixture was heated gently to speed up the reaction rate, cooled and added to a one-liter volumetric flask with copious washings, and the flask was diluted to the mark. The solution was transferred to a one-liter polyethylene flask. Sufficient high specific
activity indium-114 in the form of indium chloride was added to give an adequate counting rate. Again, two ml. portions of each phase were counted and the results were used to calculate distribution ratios.

**Thallium.** Trivalent thallium solutions were prepared from thallic oxide. To a one-liter volumetric flask which contained about 100 ml. of 1 M perchloric acid, 1.8270 grams of Tl$_2$O$_3$ were added. Water which had been previously saturated with bromine was added dropwise until the red color of the bromine remained. This was done to oxidize any thallium (I) which may have been present and usually three to four drops were sufficient. A few drops of high specific activity thallium-204, in the form of thallous chloride was added to a 50 ml. beaker which contained about 20 ml. of 2 M perchloric acid. Bromine water was added until all of the thallium was oxidized. This thallium-204 solution was then added to the thallium solution in the flask and made up to volume. This solution was used immediately in extraction studies. After equilibration, one ml. portions of each phase were taken and placed in glass planchetts. These were counted with a Geiger-Mueller counter.
Additional extractions were attempted with thallium (III) in the presence of pyridine. Extraction flasks were prepared in the usual manner except that one half ml. of pyridine was added to each. Since it was necessary to know the exact volume of each phase for calculating percent extraction values, the distribution of pyridine between benzene and water was investigated and is described in detail later. The new volume of each phase was used in calculating the results. The extraction behavior of thallium (I) was also investigated. Thallium-204 was added to a solution of thallous sulfate. The procedure was the same as that described for Thallium (III) in the absence of pyridine.

Chromium. Chromic nitrate was used to prepare a solution approximately $8 \times 10^{-3}$ M. This solution was standardized spectrophotometrically using the chromate method. To a one-liter volumetric flask containing 160 ml. of 6 M sodium hydroxide, 0.5886 g. of potassium dichromate was added. The flask was diluted to the mark and various aliquots were taken to give solutions

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of the following concentrations:

\[ 4.00 \times 10^{-5} \text{ M} \]
\[ 6.00 \times 10^{-5} \text{ M} \]
\[ 10.00 \times 10^{-5} \text{ M} \]

Ten ml. of the chromic solution to be standardized was then added to a 100 ml. of 3 M sodium hydroxide. About two grams of sodium peroxide were added to oxidize the chromium to chromate and the solution was boiled gently to expel the hydrogen. This solution was transferred to a one-liter volumetric flask and the flask was diluted to the original chromium solution was \( 8.20 \times 10^{-3} \text{ M} \).

A few drops of chromium-51 were added to standard chromic solutions. Extractions of chromium into benzene with trifluoroacetylacetone did not reach equilibrium after several days so other conditions were used. An extraction was attempted in which flasks were shaken while immersed in a water bath maintained at 60°. The reaction was still too slow to be of much practical value. Various substances were added to form a chromic complex which might react faster with trifluoroacetylacetone. When pyridine was added, a relatively rapid extraction
occurred. Therefore, the extraction curve for chromium was obtained when one-half ml. of pyridine had been added to the extraction flasks.

**Manganese (II).** A manganese solution was prepared from a 50% solution of manganese nitrate. The solution was standardized by a colorimetric method. The solution was found to be $7.85 \times 10^{-3}$ M in manganese. Manganese-54 was added and after equilibration, one ml. samples of each phase were counted. Preliminary experiments showed that manganese (II) did not extract, probably because it is hydrated at the two co-ordination sites not occupied by trifluoroacetylacetone. Therefore, one-half ml. of pyridine was added to each extraction flask in order to displace these water molecules.

**Manganese (III).** Several attempts were made to quantitatively oxidize manganese (II) in the presence of trifluoroacetylacetone and extract the product. Sodium peroxide, hydrogen peroxide, sodium bismuthate, and potassium permanganate were tried for this. None of these reagents gave a quantitative conversion, although a rather good yield was obtained with potassium permanganate.

\[47\] Ibid.
Therefore, it was used in a preparative extraction of tris (trifluoroacetylacetonato) manganese (III) described in Chapter IV.

Although an extraction of manganese via the trivalent complex was not successful, it seemed desireable to compare manganese (III) with its nearest neighbors in the periodic table. For this reason, a back-extraction of the manganese (III) complex into water was performed. To a 100 ml. volumetric flask, 0.200 g. of the manganic chelate was added followed by 2.5 g. of trifluoroacetylacetone and sufficient benzene to give 100 ml. of solution. The aqueous phase used in the extractions was 0.1 M in oxalic acid and was adjusted to various pH values as described previously. Five ml. portions of the organic-chelate solutions were added to 25 ml. portions of oxalate solutions and equilibrated for ten minutes. Three ml. portions of the organic phase were taken and the absorbance was read at the 552 m\(\mu\) shoulder exhibited by the manganese (III) complex.

**Iron.** Reagent grade iron wire, 0.4468 g., was dissolved in a minimum amount of perchloric acid with gentle heating. A few drops of iron-59, which had been
purified as described previously, was added to the $8 \times 10^{-3}$ M iron (III) solution in a polyethylene flask. After extraction, one ml. portions of each phase were counted and the distribution ratios were calculated.

**Distribution of pyridine between water and benzene.** It was mentioned previously that pyridine was used in three extraction studies: those of thallium (III), chromium (III), and manganese (II). Because the exact volume of each phase must be known in order to calculate distribution ratios, it was necessary to find which phase the pyridine was in after equilibration. This could have been done by measuring the volume of each phase, but since only 0.5 ml. of pyridine was added, this method was not used. Instead, a gas chromatographic procedure for the separation of pyridine from benzene was used. The separation is shown in Figure 2 and the column and conditions for the separation are listed. Pyridine distributed rather evenly (45% in the benzene phase) over the pH range used for extraction. This was then taken into account when distribution ratios were calculated.
Figure 2

DETERMINATION OF PYRIDINE IN
BENZENE BY GAS CHROMATOGRAPHY

First Peak - Benzene, X_{32}
Second Peak - Pyridine, X_{4}

Column:
  Length: 6 ft.

Liquid Phase: Carbowax-20M
  Wt. %: 20

Support: Red Chromasorb
  Mesh: 30/60

Carrier Gas: Helium
  Rate: 50 ml/min.

Detector: Thermal conductivity

Pressure: 40 psi

Temperatures:
  Column: 115°C
  Detector: 150°C

Injection port: 150°C

Bridge Current: 150 mA

Sample Size: 3 μl
Results and Discussion

**Trifluoroacetylacetone extractions**

**Aluminum.** Nearly quantitative extraction of aluminum occurs in the pH range of 4.5 to 5.5 as shown in Figure 3. An equilibration time study shown in Figure 4 indicated that about four hours is necessary for extraction when no auxiliary complexing agent or buffer is present. Aluminum exists as aluminum hydroxide at the initial pH needed for extraction and therefore this metal extracts rather slowly. This initial pH is higher than the equilibrium pH as shown in Table 2 because trifluoroacetylacetone, a weak acid, migrates to the aqueous phase and also releases hydrogen ions upon chelation with aluminum. Three things were found to increase the rate of extraction of aluminum: (1) Use of larger volumes of organic phase compared with the aqueous phase, (2) use of a buffer that would lower the initial pH so that hydroxide formation is minimized, and (3) use of a complexing agent to keep aluminum in solution and hence speed up its reaction with trifluoroacetylacetone. Equal volumes were not used
Figure 3

EFFECT OF pH ON THE EXTRACTION OF ALUMINUM (III)

Aqueous phase - 25 ml, 8 x 10^{-3}M Aluminum

Organic phase - 5 ml benzene, 0.25 M Trifluoroacetylacetone
Figure 4

EFFECT OF TIME ON THE EXTRACTION OF ALUMINUM (III),
GALLIUM (III), AND INDIUM (III) WITH
TRIFLUOROACETYLACETONE

Organic phase - 5 ml benzene
0.25 M in trifluoroacetylacetone

Aqueous phase - 25 ml

○ 8 x 10^{-3}M Aluminum
□ 8 x 10^{-3}M Gallium
△ 8 x 10^{-3}M Indium

Initial pH - 8
Equilibrium pH - 5
<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.25</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>a</td>
<td>a</td>
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<td>1.01</td>
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<td>a</td>
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<td>1.50</td>
<td>1.50</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>2.05</td>
<td>2.01</td>
<td>0.05</td>
<td>1</td>
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<td>2.60</td>
<td>2.32</td>
<td>0.217</td>
<td>4.16</td>
</tr>
<tr>
<td>3.80</td>
<td>2.51</td>
<td>0.496</td>
<td>9.03</td>
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<tr>
<td>3.20</td>
<td>2.64</td>
<td>0.584</td>
<td>10.46</td>
</tr>
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<td>4.50</td>
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<td>6.02</td>
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<td>3.95</td>
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<td>8.90</td>
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</tr>
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<td>6.51</td>
<td>151</td>
<td>96.29</td>
</tr>
<tr>
<td>12.50</td>
<td>8.06</td>
<td>54.9</td>
<td>91.66</td>
</tr>
</tbody>
</table>

\(^a\) None Detected by the Gas Chromatograph
because it was felt that a concentration step was
desirable for a useful analytical method. Picolinic
acid (pKa = 5.23) was found to be an effective
complexing agent as well as a buffer for the pH range
of optimum extraction. When this auxiliary reagent
was used, complete extraction occurred in fifteen
minutes. This compound also minimized emulsion formation
which sometimes occurred at high pH.

If the extraction curve in Figure 4 is compared
with the theoretical trivalent curve, both similarities
and differences can be found. The initial slope for
each is nearly the same, but the aluminum curve is more
rounded at the top. This is probably due to hydroxy
complex formation which was not considered in the
theoretical curve. The gradual decrease in extraction
above pH 5.5 is probably due to the slow reaction of
trifluoroacetylacetone with aluminum hydroxide.

The upper concentration limit of this extraction
is shown in Table 3. The lower limit was not checked
since Graham and Seaborg demonstrated that the
distribution coefficient is independent of concentration
### TABLE 3

**CONCENTRATION STUDY**

<table>
<thead>
<tr>
<th>Metal Ion Concentration</th>
<th>Trifluoroacetyl-Acetone Concentration</th>
<th>Extraction Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$8 \times 10^{-3} \text{M}$</td>
<td>0.25M</td>
<td>99.90</td>
</tr>
<tr>
<td>$1.2 \times 10^{-2} \text{M}$</td>
<td>0.25M</td>
<td>85.75</td>
</tr>
<tr>
<td>$1.6 \times 10^{-2} \text{M}$</td>
<td>0.25M</td>
<td>71.40</td>
</tr>
<tr>
<td>$1.6 \times 10^{-2} \text{M}$</td>
<td>1.00M</td>
<td>93.00</td>
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<tr>
<td>Gallium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$8 \times 10^{-3} \text{M}$</td>
<td>0.25M</td>
<td>99.90</td>
</tr>
<tr>
<td>$1.2 \times 10^{-2} \text{M}$</td>
<td>0.25M</td>
<td>78.50</td>
</tr>
<tr>
<td>$1.6 \times 10^{-2} \text{M}$</td>
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<td>63.45</td>
</tr>
<tr>
<td>$1.6 \times 10^{-2} \text{M}$</td>
<td>1.00M</td>
<td>75.15</td>
</tr>
<tr>
<td>Indium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrier Free</td>
<td>0.25M</td>
<td>99.90</td>
</tr>
<tr>
<td>$8 \times 10^{-5} \text{M}$</td>
<td>0.25M</td>
<td>99.89</td>
</tr>
<tr>
<td>$8 \times 10^{-4} \text{M}$</td>
<td>0.25M</td>
<td>99.89</td>
</tr>
<tr>
<td>$8 \times 10^{-3} \text{M}$</td>
<td>0.25M</td>
<td>99.60</td>
</tr>
<tr>
<td>$1.2 \times 10^{-2} \text{M}$</td>
<td>0.25M</td>
<td>50.90</td>
</tr>
<tr>
<td>$1.6 \times 10^{-2} \text{M}$</td>
<td>0.25M</td>
<td>20.45</td>
</tr>
<tr>
<td>$1.6 \times 10^{-2} \text{M}$</td>
<td>1.00M</td>
<td>35.20</td>
</tr>
</tbody>
</table>
so long as the solubility of the species in the organic solvent is not exceeded.\textsuperscript{48}

**Gallium.** Extraction of gallium ($pH_{1/2} = 1.90$) occurs at a lower pH than aluminum as shown in Figure 5. Because of its similarities to aluminum, namely reaction with hydroxide, it too requires about four hours for complete extraction. Table 4 shows the initial pH that is necessary for a given equilibrium pH when no buffer is present. No buffer was found to be satisfactory for gallium extractions. All of those investigated, even acetate, complexed gallium so well that extraction was slower than it was with no buffer present.

The concentration range is also shown in Table 3. Emulsion formation was also a problem in gallium extractions and occasionally it was necessary to centrifuge extraction flasks.

**Indium.** Nearly quantitative extraction of indium occurs from pH 4.4 to at least 7.0 and the curve closely resembles the theoretical extraction curve. This group three metal also required about four hours to reach

Figure 5

EFFECT OF pH ON THE EXTRACTION OF GALLIUM (III)

Aqueous phase - 25 ml, $8 \times 10^{-3} \text{M}$

Gallium

Organic phase - 5 ml benzene, 0.25 M

Trifluoroacetylacetone
### TABLE 4

**EXTRACTION OF GALLIUM (III)**

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
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<td>~ 1</td>
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<td>99.9</td>
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<tr>
<td>12.00</td>
<td>6.75</td>
<td>289.0</td>
<td>98.30</td>
</tr>
</tbody>
</table>

^a None detected by the gas chromatograph
Figure 6

EFFECT OF pH ON THE EXTRACTION OF INDIUM (III)

Aqueous phase - 25 ml, $8 \times 10^{-3} \text{M}$ Indium

Organic phase - 5 ml benzene, 0.25 M Trifluoroacetylacetone
### TABLE 5

**EXTRACTION OF INDIUM (III)**

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
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<td>0.45</td>
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<td>0.80</td>
<td>0.80</td>
<td>$4.39 \times 10^{-3}$</td>
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</tr>
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<td>1.22</td>
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<td>$4.18 \times 10^{-3}$</td>
<td>0.08</td>
</tr>
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<td>1.50</td>
<td>1.61</td>
<td>$5.88 \times 10^{-3}$</td>
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<td>1.75</td>
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<td>5.90</td>
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<td>99.38</td>
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<td>11.90</td>
<td>6.01</td>
<td>985.8</td>
<td>99.49</td>
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<td>12.20</td>
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<td>610.8</td>
<td>99.05</td>
</tr>
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<td>12.50</td>
<td>11.52</td>
<td>0.550</td>
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<tr>
<td>13.00</td>
<td>13.00</td>
<td>0.298</td>
<td>5.62</td>
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</table>
equilibrium. Because the convenient tracer, indium-114 was available, indium was singled out for further kinetic study. A re-plot of the data from the time study shown in Figure 4 indicated that no simple order kinetics occurred. This is probably due to the fact that indium hydroxide is initially present and this three phase system is rather complicated. In addition, the pH changed markedly in the equilibration study and preliminary experiments showed that the rate is pH dependent.

Another series of extractions, in which the pH was adjusted before the indium was added, were carried out. The initial pH was adjusted to 3.5 in order to minimize hydrolysis of indium and the pH change during the extraction. A plot of the logarithm of the indium concentration in the aqueous phase versus time gives a straight line indicating a first-order or pseudo-first-order reaction. The rate constant, k, was found to be 0.0462 min\(^{-1}\) at this pH. It is possible that the reagent is in high enough concentration to remain effectively constant. This pseudo-first-order behavior is not unusual in extraction studies.

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INFLUENCE OF EQUILIBRATION TIME ON THE EXTRACTION OF INDIUM WITH TRIFLUOROACETYLACETONE

Aqueous phase - 25 ml adjusted to pH 3.5

Organic phase - 5 ml benzene, 0.25 M in Trifluoroacetylacetone
The rate determining step for the overall extraction process has not been determined. However, a few extractions were repeated using chloroform as a solvent and results did not vary appreciably from the benzene extractions. This would seem to indicate that the rate determining step would be the rate of formation of the indium complex and not the rate of transfer of this species to the organic phase.

Emulsion formation in indium extractions was more prevalent than with any other metal studied. Because the molarity of metal solutions was kept constant, the total weight of indium was greater than aluminum. This weight was probably approaching the solubility limit of the chelate in benzene and resulted in emulsion formation. However, after these turbid extraction vessels were centrifuged, they yielded results comparable to indium extractions in which there was no emulsion formation.

Both high and low indium concentration ranges were studied (Table 3) and complete extraction occurred all the way down to carrier free indium as might be expected.

Thallium. Although thallium is a group three metal, its chemistry is quite different than the other
members of this group. Specifically, thallium (III) is quite unstable with respect to the following reaction:

\[ \text{Tl}^{+3} + 2 \text{e} \rightarrow \text{Tl}^{+1} \quad E_0 = 1.25 \text{ V} \]

Because of this, and because the solubility product of thallic hydroxide is \(1.5 \times 10^{-44}\), some difficulty was anticipated in the extraction of thallium (III). However, since the extraction of this species with acetylacetone was reported, work was begun with trifluoroacetylacetone. Essentially no thallium (III) was extracted. This is probably due to the fact that spontaneous reduction to thallium (I) occurs. Moeller and Cohen have stated in an oxine extraction of thallium (III) that some additional complexing agent, which would stabilize the higher oxidation state, would appear to be essential for the extraction of this ion. Stary and Hladky reported the extraction of thallium (III) with acetylacetone and no mention was made of an additional

---


complexing agent. It appears from the chemistry of this ion that some additional complexing agent is in fact necessary, but that it was not reported in this paper.

Two approaches were then taken in order to extract thallium: Extraction of thallium (III) with trifluoroacetylacetone in the presence of other complexing agents and extraction of thallium (I). The results of the latter study are given in Table 6. It is evident that this is an extremely poor extraction. The results of this study with thallium (I) are comparable to those obtained with several other reagents.

The above results indicated that the best approach was probably the use of an additional complexing agent. Acetate, tartrate, and ethylenediamine all complexed thallium (III) so well that no extraction was obtained. A weaker complexing agent, pyridine was tested and the results are shown in Figure 8. It is probable that a rather complicated system exists here as indicated

TABLE 6

EXTRACTION OF THALLIUM (I)

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
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<tr>
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<td>2.54</td>
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<tr>
<td>13.00</td>
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<td>3.66</td>
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a_TRACE
Figure 8

EFFECT OF pH ON THE EXTRACTION
OF THALLIUM (III)

0.25 M Trifluoroacetylacetone

Aqueous phase - 25 ml, 0.5 ml pyridine
added, $8 \times 10^{-3}$ M Thallium

Organic phase - 5 ml benzene, 0.25 M
Trifluoroacetylacetone
<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
</tr>
</thead>
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<td>1.01</td>
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<td>2.40</td>
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<td>0.939</td>
<td>17.85</td>
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<td>3.373</td>
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<td>3.58</td>
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<td>7.58</td>
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by the unusual extraction curve. The extraction is far from complete, but isotope dilution might be used or successive extractions could be made in order to obtain quantitative results.

Chromium. It was recently reported that chromium (III) reacts too slowly with trifluoroacetylacetone to be very useful in an extraction procedure. It was felt that some means of overcoming this kinetic effect might be found so chromium was included in this study.

First extractions of chromium (III) into benzene were attempted in order to see if the extraction was slow when this solvent was used. It was indeed slow; so slow that chromium was less than 50% extracted after twenty-four hours shaking. The first approach taken to speed up the reaction was extraction at an elevated temperature. An apparatus was devised whereby extraction flasks could be shaken under water. The water bath was maintained at 60°C and several extractions at various pH increments were performed. None of these exceeded

60% extraction after four hours shaking. In addition, emulsion formation was extremely dense.

The slow reaction of chromium (III) with various complexing agents is well known. This phenomenon is attributed to the relatively inert polynuclear hydroxy complexes of chromium which are present in aqueous media. With this in mind, several possible conditions that might speed up the rate were considered. (1) A chromium (III) solution containing trifluoroacetylacetone might be refluxed to accelerate the reaction. McKaveney and Freiser used this route to extract chromium with acetylacetone. However, it was felt that this procedure considerably complicated the extraction and it was not attempted. (2) A solution of chromium might be heated in the presence of chloride in order to form one of the green aque-chloro complexes which might react quickly with the reagent. This was briefly pursued, but no extraction of chromium occurred.


Brandt and Heveran used this method in order to extract chromium with acetylacetone into carbon bisulfide.\textsuperscript{58} The success of this method may be due to the fact that the aquo-chloro chromium (III) complex is slightly soluble in carbon disulfide. (3) Chromium (IV) could be reduced in the presence of the reagent thus avoiding oxy-bridge formation, or (4) the extraction of chromium (II) might be attempted. However, neither of these routes seemed promising and were not pursued further.

It seemed that if chromium (III) were complexed to a ligand and were not present as a polynuclear hydroxy complex, it might react faster. Several nitrogen donor ligands such as ethylenediamine, triethylene tetramine, and pyridine were tested for this purpose. Of these, only pyridine gave any positive results, and for a different reason than originally intended. The results of the extraction of chromium with pyridine-trifluoroacetylacetone mixtures are shown in Figure 9. The extraction was quite clean and

\textsuperscript{58} Brandt, W. W., Heveran, J. E., 142 ed ACS Meeting, Atlantic City, New Jersey, 1962.
Figure 9

EFFECT OF pH ON THE EXTRACTION OF CHROMIUM (III)

0.25 M Trifluoroacetylaceton

Aqueous phase - 25 ml with 0.5 ml pyridine added, $8 \times 10^{-3}$ M Chromium

Organic phase - 5 ml benzene, 0.25 M Trifluoroacetylaceton
TABLE 8

EXTRACTION OF CHROMIUM (III)

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
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<td>0.02</td>
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</tr>
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<td>2.60</td>
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<td>0.81</td>
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<td>2.10</td>
<td>0.101</td>
<td>2.10</td>
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<td>4.00</td>
<td>3.39</td>
<td>2.509</td>
<td>34.80</td>
</tr>
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<td>3.62</td>
<td>9.911</td>
<td>67.88</td>
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<td>4.39</td>
<td>81.77</td>
<td>94.56</td>
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<td>10.00</td>
<td>7.02</td>
<td>20.34</td>
<td>80.10</td>
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</table>
was complete in slightly over an hour. The optimum amount of pyridine was found to be about 0.5 ml. as indicated from Table 8. The final product was found to be the simple 3:1 chelate since its visible spectra and gas chromatographic retention time were identical to those of chromium trifluoroacetylacetonate.

On the other hand, several differences were apparent in the chromium extraction which indicated that pyridine did more than complex chromium in the aqueous phase. Unlike the other metals studied, the extraction dropped off rapidly above pH 6.4 and initially a cloudy green substance appeared in the organic phase. An extraction flask in which more than 99% of the chromium had been extracted at pH 5.5 was re-adjusted to pH 7.0 and shaken for one hour. The percent extraction remained constant as it did in a similar experiment at pH 8.0. This indicates that the chromium chelate is stable at these higher pH values, but that the mechanism by which it was transferred to the organic phase did not occur. Because of this, it was thought that the process might involve some chromium-pyridine intermediate which is initially extracted into the organic phase, where it reacts with trifluoroacetylacetone.
### TABLE 9

**EFFECT OF PYRIDINE CONCENTRATION ON EXTRACTION OF CHROMIUM WITH TRIFLUOROACETYLACETONE**

<table>
<thead>
<tr>
<th>Ml. Pyridine Added</th>
<th>Percent Extraction After One Hour</th>
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<td>0.05</td>
<td>75.22</td>
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<tr>
<td>0.12</td>
<td>79.30</td>
</tr>
<tr>
<td>0.25</td>
<td>88.02</td>
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<tr>
<td>0.50</td>
<td>97.38</td>
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<tr>
<td>2.00</td>
<td>88.69</td>
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### TABLE 10

**EXTRACTION OF CHROMIUM (III) WITH PYRIDINE**

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
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<tr>
<td>3.50</td>
<td>3.80</td>
<td>0.011</td>
<td>0.21</td>
</tr>
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<td>4.50</td>
<td>4.38</td>
<td>0.038</td>
<td>0.71</td>
</tr>
<tr>
<td>5.00</td>
<td>4.89</td>
<td>0.057</td>
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<tr>
<td>5.50</td>
<td>5.40</td>
<td>2.695</td>
<td>35.02</td>
</tr>
<tr>
<td>6.20</td>
<td>6.04</td>
<td>8.888</td>
<td>63.99</td>
</tr>
<tr>
<td>10.00</td>
<td>10.20</td>
<td>0.072</td>
<td>1.25</td>
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<tr>
<td>11.50</td>
<td>11.70</td>
<td>0.062</td>
<td>1.10</td>
</tr>
</tbody>
</table>

75
In order to check for the above process, an extraction of chromium into benzene with pyridine alone was attempted. The results of this experiment are shown in Table 9. The extraction is far from clean and may not even be an extraction in the true sense of the word. The chromium appears to be present in the form of a green, colloidal emulsion suspended in the organic phase. Nevertheless, when some of this material was added to a benzene solution of trifluoroacetylacetone, the purple color of the chromium chelate appeared. This information supports the proposed "extraction via ligand exchange". To the author's knowledge, no previous extractions involving this type of phenomena have been reported. Soon after these results were obtained, Scribner found that chromium (III) could be quickly extracted into butanol. However, spectral and gas chromatographic evidence indicated that something other than the simple 3:1 chelate had formed.

At this point it seemed that some rate data might give additional proof to the proposed mechanism.

These data are given in Appendix I and none of the steps seemed to obey any simple order kinetics. From these results, it is evident that the reaction of trifluoroacetylacetone with the chromium-pyridine intermediate is complete in ten minutes. This was determined by following the appearance of the 560 μ peak. Since the extraction employing both pyridine and trifluoroacetylacetone was only 40% complete in 15 minutes, the exchange step was not rate-controlling. It was thought that the extraction with pyridine would occur at about the same rate or somewhat faster than the combined extraction. However, it proved to be slower, about 30% complete in 15 minutes. This fact does not disprove the suggested mechanism, since any chromium that is extracted reacts with trifluoroacetylacetone and equilibrium is shifted for the pyridine step.

**Manganese (III).** Even though several attempts to oxidize manganese (II) to manganese (III) and subsequently extract the trivalent complex failed, it seemed desireable to include this species in a comparative study. Therefore, a back-extraction of the manganese (III) complex was done with certain modifications. The
concentration was chosen so that the absorbance of the complex could be obtained without dilution. Additional trifluoroacetylacetone was added to the organic phase so that total concentration was 0.25 M as it was in previous extractions. Due to the disproportionation of manganese (III),

\[
2 \text{Mn}^{+3} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Mn}^{+2} + \text{MnO}_2 + 4 \text{H}^+ \quad K = 10^9
\]

oxalate ion was added to the aqueous phase.

The tris (oxalato) manganese (III) complex is rather stable and it was added to retard the disproportionation. On the other hand, information indicated that this complex would not be more stable than the trifluoroacetylacetonate. The results of this study are shown in Figure 9. An extraction curve which agrees well with the theoretical trivalent curve was obtained. However, it is felt that some disproportionation of manganese (III) occurred or some of the manganic oxalate complex was reduced to the manganous complex so that the equilibrium was shifted in favor of

---

\text{Taube, H. J., J. Am. Chem. Soc., 70, 3928 (1948).}
Figure 10

EFFECT OF pH ON THE EXTRACTION
OF MANGANESE (III)

Aqueous phase - 25 ml, 0.1 M in oxolate ion

Organic phase - 5 ml benzene $4 \times 10^{-3}$M in Manganese (III) Trifluoroacetylacetone and 0.25 M in Trifluoroacetylacetone
TABLE 11

EXTRACTION OF MANGANESE (III)

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Absorbance Ratio</th>
<th>Percent Extraction</th>
</tr>
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<td>1.40</td>
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<tr>
<td>2.00</td>
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<td>0.918</td>
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<td>0.514</td>
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<td>3.03</td>
<td>0.555</td>
<td>13.537</td>
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<tr>
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<td>4.11</td>
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<td>0.690</td>
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<td>7.00</td>
<td>5.90</td>
<td>0.660</td>
<td>32.99</td>
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<tr>
<td>8.30</td>
<td>6.00</td>
<td>0.660</td>
<td>32.99</td>
</tr>
<tr>
<td>11.00</td>
<td>6.95</td>
<td>0.655</td>
<td>32.03</td>
</tr>
</tbody>
</table>

81
the aqueous phase. This would account for the lower extraction (86%) compared to other trivalent ions. Since the main objective of this study was to compare the extraction of manganese (III) to chromium (III) and iron (III), it was successful. The pH falls between iron and chromium indicating the trend in stability is Fe > Mn > Cr. It was later suggested that pyrophosphate ion might stabilize manganese (III) better than oxalate ion. A few extractions in the 4 to 6 pH range were repeated with 0.1 M pyrophosphate ion in the aqueous phase and the manganese (III) remained nearly completely in the organic phase.

**Manganese (II).** The extraction of manganese (II) has been attempted with trifluoroacetylacetone and only a small trace could be extracted. Preliminary studies indicated that a synergistic effect occurred when various amines were added. Pyridine was chosen because it had been used successfully in chromium extractions. The results of this extraction study are shown in Figure 11 and Table 11. Complete extraction was

---

Figure 11

EFFECT OF pH ON THE EXTRACTION OF MANGANESE (II)

Aqueous phase - 25 ml water and 0.5 ml pyridine, $8 \times 10^{-3} \text{M}$ Manganese

Organic phase - 5 ml benzene, 0.25 M Trifluoroacetylacetone
### TABLE 12

**EXTRACTION OF MANGANESE (II)**

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.20</td>
<td>0.001</td>
<td>0.02</td>
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<tr>
<td>2.05</td>
<td>2.08</td>
<td>0.001</td>
<td>0.02</td>
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<tr>
<td>4.10</td>
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<td>0.233</td>
<td>4.37</td>
</tr>
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<td>4.25</td>
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</tr>
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<td>42.43</td>
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<td>513.4</td>
<td>99.11</td>
</tr>
<tr>
<td>6.90</td>
<td>5.87</td>
<td>351.1</td>
<td>98.67</td>
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<tr>
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<td>5.90</td>
<td>567.0</td>
<td>99.12</td>
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<tr>
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<td>5.95</td>
<td>665.2</td>
<td>99.28</td>
</tr>
<tr>
<td>10.50</td>
<td>7.05</td>
<td>501.1</td>
<td>99.00</td>
</tr>
</tbody>
</table>
attained in fifteen minutes. The slope of the extraction curve is a little greater than that expected for a divalent metal.

It was originally thought that pyridine replaced two molecules of water on the coordination sphere of manganese. However, chemical analysis of the product indicates that the molecule consists of one manganese atom, two trifluoroacetylacetone molecules, and one molecule each of pyridine and water. More details concerning this species are given in Chapter IV. The resulting species is less hydrophilic and is therefore extracted. A higher pH is required for extraction ($\text{pH}^* = 4.5$) for this divalent metal than for trivalent metals. This is to be expected since the overall stability constant of the divalent manganese would be smaller than that of a more highly charged ion.

Iron. Quantitative extraction of iron occurs from pH 1.5 to 6.0 as shown in Figure 12. The time necessary for equilibrium passes through a minimum around pH 2.5. The extraction is rather slow at low pH, probably because the reagent is not ionized appreciably. The extraction requires about four hours
Figure 12

EFFECT OF pH ON THE EXTRACTION OF IRON (III)

0.25 M Trifluoroacetylacetone
8 x 10^{-3} M Iron

Aqueous phase - 25 ml, 8 x 10^{-3} M Iron

Organic phase - 5 ml benzene, 0.25 M Trifluoroacetylacetone
<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>Distribution Ratio</th>
<th>Percent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
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<td>190.5</td>
<td>97.44</td>
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<tr>
<td>1.00</td>
<td>0.52</td>
<td>247.4</td>
<td>98.01</td>
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<tr>
<td>1.20</td>
<td>0.67</td>
<td>1351</td>
<td>99.63</td>
</tr>
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<td>1.30</td>
<td>0.77</td>
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<td>10.80</td>
<td>4.00</td>
<td>3031</td>
<td>99.</td>
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<td>11.20</td>
<td>5.52</td>
<td>2261</td>
<td>99.79</td>
</tr>
<tr>
<td>0.30</td>
<td>0.30</td>
<td>0.882</td>
<td>15.0</td>
</tr>
</tbody>
</table>
at high pH because the reaction with hydrated ferric oxide is slow. Complete extraction is obtained in about fifteen minutes at pH 2.5, and if picolinic acid is used as a buffer and auxiliary complexing agent, a rapid extraction (15 minutes) is possible at pH 5.5.

Iron forms the most stable complex of the metals studied with trifluoroacetylacetone and thus extracts at a lower pH. This is useful because at low pH, iron can be separated from many other metals such as aluminum, chromium or manganese. Such a separation is described in Chapter V. The intense color of the complex is also useful for spectrophotometric work.

**Extraction Studies of Iron With Hexafluoroacetylacetone**

Soon after hexafluoroacetylacetone was first synthesized, the following reaction was found to occur.

\[
\text{CF}_3\text{C-CH}_2\text{C-CF}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{CF}_3\text{O-C-CH}_2\text{O-C-CF}_3
\]
This product seems unlikely, but chemical analysis and infrared spectral data have shown that it is quite stable.62

Because of this unusual behavior, it was felt that the compound would not be very useful in extractions from aqueous solutions. Nevertheless, a literature search showed that several metal hexafluoroacetylacetonates had been prepared by precipitation from aqueous media.63 Evidently, the reaction with the metal forced the hydrolysis reaction in the reverse direction. Hence, it was thought that the reaction with a metal ion in an extraction might also reverse this equilibrium and result in complete extraction.

Preliminary experiments with iron and hexafluoroacetylacetone were encouraging. The red color of the iron chelate quickly appeared in the organic phase. However, when the extraction flasks were allowed to stand over night, the color in the benzene phase faded completely. But when the benzene phase containing the


63 Ibid.
red, iron chelate was removed from the extraction flask containing water, it was stable for at least one week. The absorbance at 450 m\(\mu\) was checked daily for one week and remained constant during this time. A similar experiment with copper gave the same results so a more detailed study of this phenomena was made.

The fading seemed to be slower if less concentrated metal solutions were used. Therefore, an iron (III) solution containing 4 mg of iron per liter was spiked with iron-59 and used in this study. The concentration of hexafluoroacetylacetone in benzene was 0.25 M and ten ml. of each phase was used.

To eliminate a time lapse when extraction flasks were transferred to and from a shaker, they were shaken by hand. A rate of one inversion per second was used.

The results of these experiments are shown in Figure 13. The extraction passes through a maximum and then decreases. The decrease seems to be a first order reaction as shown by the log \([Fe]\) versus time plots. It is also evident that the rate of decomposition is accelerated at a low pH. The extraction
Figure 13

EFFECT OF TIME ON THE EXTRACTION OF IRON WITH HEXAFLUOROACETYLACETONE

△ pH 3.8
○ pH 1.8
□ pH 2.8
increases at pH 3.8 for about 30 minutes at which time it also reaches a maximum and then recedes. Hardly any extraction occurs below pH one, probably because the rate of decomposition of the complex is faster than the extraction. Similarly, no extraction could be obtained from basic media. Therefore, in order to see what happens in more acidic or basic media, some iron complex was withdrawn from an extraction flask which had been adjusted to pH 3.0. Ten milliliters of this benzene solution containing the iron complex was then placed in a flask containing ten ml. of aqueous solution which had been adjusted to the desired pH. It was found that the iron chelate left the organic phase more rapidly at pH 1.0 than it did from a solution of pH 1.85. Furthermore, the decomposition was almost too fast to measure in a more basic solution of pH 8 or 9. The first order rate constants for the disappearance of iron in the organic phase were 0.192 min\(^{-1}\) and 0.398 min\(^{-1}\) for pH 2.80 and 1.85 respectively.

A possible explanation of the above results is given as follows: Hydrolysis of hexafluoroacetylacetone occurs. In solutions ranging in pH from 1.8 to 3.4 the
extraction occurs more quickly than the hydrolysis, thus the initial build-up. Moreover, it is felt that the hydrolysis is acid or base catalyzed. This would account for the increased decomposition in acidic or basic solutions. This seems reasonable since many hydrolysis reactions are acid or base catalyzed. In addition, it is in agreement with the results obtained by Gilman. He stated that freshly distilled hexafluoroacetylacetone could be placed in contact with water and nothing happened. However, when a drop of sodium hydroxide was added the dihydrate immediately precipitated.

The use of hexafluoroacetylacetone for extractions, although quite interesting, seems to be of limited practical value and with the exception of a few experiments described later, was not pursued further.

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CHAPTER II

CALCULATION OF STABILITY CONSTANTS

FROM EXTRACTION DATA

Historical Review

The first record in which solvent extraction was used to determine stability constants precedes the better known potentiometric work of Bjerrum. In a classic investigation of the complex formation between $\text{Hg}^{+2}$ and $\text{X}^-$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) Morse made use of the fact that $\text{HgX}_2$ molecules are soluble in toluene. From the distribution of mercury between toluene and water as a function of $[\text{X}^-]$ he calculated the concentration of $\text{HgX}^+$ and $\text{HgX}_2$ and subsequently, constants for the formation of $\text{HgX}^+$.

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Connick and McVey studied the nature of the zirconium (IV) species which exists in aqueous solution by means of two phase distribution equilibria. The zirconium was partially extracted into a benzene-thenoyltrifluoroacetone solution and the formulas and stabilities of the zirconium containing species in the aqueous phase were deduced from the variation of the distribution ratio as a function of the aqueous solution composition.

It was not until 1950 that the stability of a metal chelate was determined using solvent extraction. In this year, Rydberg developed equations for the thorium acetylacetone system and calculated step-wise stability constants for all four species. This study was quite comprehensive and only two assumptions were made: (1) No charged species are present in the organic phase and (2) no hydrolysis of the metal ion occurs. Both of these assumptions are valid for this particular system. In the following years Rydberg made several

---

studies in which additional equilibria, including hydrolysis, were included in the final equation.\textsuperscript{5,6}

Krishen and Freiser calculated the stability constants for acetylacetone complexes of aluminum, beryllium, copper, gallium, hafnium, and other metals using extraction data.\textsuperscript{7} They used very high reagent concentrations and were therefore able to neglect hydrolysis of the metal ions. In general, the results obtained in their study agree well with constants that were calculated from potentiometric data.

Theory

In order to write an equation which can be used to calculate successive stability constants, it is necessary to list all of the equilibria involved. All of the equations will be written for a trivalent metal and a ligand which is a monoprotic acid.

The stepwise formation of the chelate can be expressed by the following equation:


\[ M^{+3} + A^- \rightleftharpoons MA^{+2} \quad k_1 = \frac{[MA^{+2}]}{[M^{+3}] [A^-]} \quad (2.1) \]

\[ MA^{+2} + A^- \rightleftharpoons MA_2^+ \quad k_2 = \frac{[MA_2^+]}{[MA^{+2}] [A^-]} \quad (2.2) \]

\[ MA_2^+ + A^- \rightleftharpoons MA_3^- \quad k_3 = \frac{[MA_3^-]}{[MA_2^+] [A^-]} \quad (2.3) \]

and the overall stability constant, \( \beta_3 \), is defined by:

\[ \beta_3 = k_1 k_2 k_3 \quad (2.4) \]

The ionization of the reagent, trifluoroacetyl-acetone, is expressed in the usual manner.

\[ HA \rightleftharpoons H^+ + A^- \quad K_a = \frac{(H^+)[A^-]}{[HA]} \quad (2.5) \]

Concentration is indicated by brackets and activity is denoted by parenthesis.

The distribution of the metal chelate between the two phases is expressed by the distribution coefficient.

\[ MA_{3w} \rightleftharpoons MA_{3o} \quad K_d = \frac{[MA_3^+]}{[MA_3]} \quad (2.6) \]
Likewise, the distribution of the reagent is given by:

\[
HA_w \rightleftharpoons HA_o \quad K_{dAA} = \frac{[HA_o]}{[HA_w]} \quad (2.7)
\]

Often, competing reactions such as hydrolysis are important and these may be expressed in the usual form.

\[
M^{+3} + HOH \rightleftharpoons M(OH)^{+2} + H^+ \quad (2.8)
\]

\[
k_{h1} = \frac{[M(OH)^{+2}]}{[M^{+3}]} \left(\frac{[H^+]}{[H^+]^2}\right)
\]

\[
M(OH)^{+2} + HOH \rightleftharpoons M(OH)^{+} + H^+ \quad (2.9)
\]

\[
k_{h2} = \frac{[M(OH)^{+}]}{[M(OH)^{+2}]} \left(\frac{[H^+]}{[H^+]^2}\right)
\]

The distribution ratio is defined as the total concentration of metal in any form in the organic phase over the total concentration of metal in the aqueous phase, or:

\[
D = \frac{C_{M_o}}{C_{M_w}} \quad (2.10)
\]
Assuming that the only form of metal in the organic phase is the neutral chelate and that no additional complexes are present in the aqueous phase:

\[
D = \frac{[MA_3]}{[M^{+3}] + [MA_2^+] + [MA_3^+] + [M(OH)^{+2}]} \ldots
\]

\[
+ \frac{[M(OH)_2^+] + [M(OH)_3^-]}{}
\]

(2.11)

All concentrations in the organic phase are indicated by a subscript, \( o \). All other terms carry no subscript and refer to concentrations in the aqueous phase. Since the pH used in all calculations was lower than the pH at which the metal hydroxide would precipitate, this term may be dropped. Substituting equations 2.1, 2.2, 2.3, 2.8, and 2.9 into equation 2.11 gives:

\[
D = \frac{[MA_3]}{[M^{+3}] + k_1 [M^{+3}] [A^-] + k_1 k_2 k_3 [M^{+3}] [A^-]^2} \ldots
\]

(2.12)

\[
+ k_1 k_2 k_3 [A^-]^3 + \frac{k_{h1} [M^{+3}]}{(H^+)} + \frac{k_{h1} k_{h2} [M^{+3}]}{(H^+)^2}
\]
Factoring for $[M^+3]$

\[
D = \frac{[MA_3]}{[M^+3]} \frac{[MA_3]}{o} \frac{1}{(1 + k_1 [A^-] + k_1 k_2 [A^-]^2 + k_1 k_2 k_3 [A^-]^3)^3} \ldots
\]

\[
= \frac{k_{h1}}{(H^+)} + \frac{k_{h1} k_{h2}}{(H^+)^2}
\]

(2.13)

Combining equations 2.1, 2.2, and 2.3 gives:

\[
[M^+3] = \frac{[MA_3]}{k_1 k_2 k_3 [A^-]^3}
\]

(2.14)

This can be substituted into equation 2.13.

\[
D = \frac{[MA_3]}{o} \frac{k_1 k_2 k_3 [A^-]^3}{[MA_3]} \frac{1}{(1 + k_1 [A^-] + k_1 k_2 [A^-]^2 + k_1 k_2 k_3 [A^-]^3)^3} \ldots
\]

\[
+ \frac{k_{h1}}{(H^+)} + \frac{k_{h1} k_{h2}}{(H^+)^2}
\]

(2.15)

But

\[
\frac{[MA_3]}{o} = \frac{[MA_3]}{w} = K_d
\]
Therefore:

\[ D = \frac{K_d k_1 k_2 k_3 [A^-]^3}{1 + k_1 [A^-] + k_1 k_2 [A^-]^2 + k_1 k_2 k_3 [A^-]^3} \ldots \]

\[ + \frac{k_{h1}}{(H^+)} + \frac{k_{h1} k_{h2}}{(H^+)^2} \]

Multiplying both sides of equation 2.16 by the denominator gives:

\[ D + k_1 [A^-] D + k_1 k_2 [A^-]^2 D + k_1 k_2 k_3 [A^-]^3 D \ldots \]

\[ + \frac{k_{h1} D}{(H^+)} + \frac{k_{h1} k_{h2}}{(H^+)^2} \]

\[ D = K_d k_1 k_2 k_3 [A^-]^3 \]

Factoring the terms containing \( k_1 k_2 k_3 [A^-]^3 \) and rearranging gives:

\[ D = \frac{(K_d - D) k_1 k_2 k_3 [A^-]^3}{1 + k_1 [A^-] + k_1 k_2 [A^-]^2 + \frac{k_{h1}}{(H^+)} + \frac{k_{h1} k_{h2}}{(H^+)^2}} \]

Solving equation 2.5 for \([A^-]\) gives:

\[ [A^-] = \frac{K_a [HA]}{(H^+)} \]
and substituting this into equation 2.18 gives:

\[
D = \frac{(K_d - D) k_1 k_2 k_3 [HA]^3 K_a^3}{(H^+)^3 + k_1 [HA] K_a (H^+)^2 + k_1 k_2 [HA] K_a^2 (H^+)} + k_{h_1}(H^+)^2 + k_{h_1}k_{h_2}(H^+)
\]

Multiplying both sides of equation 2.19 by the denominator and then dividing by \(k_1 k_2 k_3\) yields:

\[
(K_d - D) [HA]^3 K_a^3 = \frac{D(H^+)^3}{k_1 k_2 k_3} + \frac{D k_1 HA K_a (H^+)^2}{k_1 k_2 k_3} \quad \ldots
\]

\[
\frac{D k_1 k_2 [HA] K_a^2 (H^+)}{k_1 k_2 k_3} \quad + \quad \frac{D k_{h_1}(H^+)^2}{k_1 k_2 k_3} \quad + \quad \frac{D k_{h_1}k_{h_2}(H^+)}{k_1 k_2 k_3}
\]

Cancelling and combining common terms gives:

\[
(K_d - D) [HA]^3 K_a^3 = \frac{D}{k_1 k_2 k_3} (H^+)^3 + k_{h_1}(H^+)^2 \quad \ldots
\]

\[
+ k_{h_1} k_{h_2}(H^+) + \frac{D [HA] K_a (H^+)^2}{k_2 k_3} + \frac{D [HA]^2 K_a^2 (H^+)}{k_3}
\]

For convenience, the following substitutions can be made.
Then:

\[
(K_{d-D}) [HA]^{3} K_{a}^{3} = L_{1} D \left\{ (H^{+})^{3} + k_{h1} (H^{+})^{2} \right\} \\
+ k_{h1} k_{h2} (H^{+})^{2} + L_{2} D [HA] K_{a} (H^{+})^{2} + L_{3} D [HA]^{2} K_{a}^{2} (H^{+})
\]

Equation 2.22 now contains three unknowns, \( L_{1} \), \( L_{2} \), and \( L_{3} \) and is in a form that may be solved by third order determinants. This equation may be solved for the unknowns by using three different values for \( D \) at three known hydrogen ion activities and \( [HA] \) values.

As was pointed out in Chapter I, there is an approximate relationship between the distribution ratio and pH for a given chelate system. This relationship is linear for log \( D \) versus pH and can therefore be used as a smoothing curve for experimental data which may then be used in equation 2.22. The reason for this linear relationship is explained below.
The distribution ratio can be simplified to include only the metal ion in the aqueous phase by assuming that the other species in the aqueous phase are negligible.

\[ D = \frac{[MA_3]^o}{[M^{+3}]} \]  \hspace{1cm} (2.23)

recalling that

\[ [M^{+3}] = \frac{[MA_3]}{\beta_3 [A^-]^3} \]

substitution into equation 2.23 gives:

\[ D = \frac{[MA_3]^o \beta_3 [A^-]^3}{[MA_3]^w} = K_d \beta_3 [A^-]^3 \] \hspace{1cm} (2.24)

and

\[ [A^-] = \frac{K_a [HA]}{(H^+)} \]

Therefore

\[ D = \frac{K_d \beta_3 K_a^3 [HA]^3}{(H^+)^3} \] \hspace{1cm} (2.25)
and since

$$K_{d_{HA}} = \frac{[HA]}{[HA]}$$

$$D = \frac{K_d \beta_3 K_a^3 [HA]_o^3}{K_d^3 (H^+)_o^3} = \frac{K' [HA]_o^3}{(H^+)_o^3}$$

(2.26)

where

$$K' = \frac{K_d \beta_3 K_a^3}{K_d^3_{HA}}$$

For simplicity, all of the constants in equation 2.26 are combined into one constant.

Rearranging equation 2.26 and taking the logarithm of both sides:

$$\log \frac{D}{[HA]_o^3} = \log K' + 3 \text{pH} \quad (2.27)$$

Thus if the logarithm of the fraction, $$\frac{D}{[HA]_o^3}$$, is plotted versus the pH, a straight line with a slope of three (for a trivalent metal) should result. If the reagent concentration in the organic phase changes very slightly, it can also be included in the
constant. Under these conditions, a plot of the logarithm of the experimental value of $D$ versus $pH$ should be a straight line. These plots can then be made and in so doing the experimental data is effectively smoothed. The values for the distribution ratios at various pH values can be obtained from such a graph and substituted into equation 2.22 for stability calculations.

A value for $K_a$, the acidity constant for trifluoroacetylacetone, was obtained using conditions similar to those used for stability constant work. A spectrophotometric method was used in this experiment.

The equation for the ionization of trifluoroacetylecetone is:

$$K_a = \frac{(H^+)[A^-]}{[HA]} \quad (2.28)$$

The term $\bar{\varepsilon}$, the apparent molar absorptivity is defined as:

$$\bar{\varepsilon} = \frac{A}{C_A} \cdot 1$$

$$C_A = [A^-] + [HA] \quad (2.29)$$

$$\bar{\varepsilon} = A^+/(A^-) + [HA] \cdot 1$$
Where \( A_+ \) is the total absorbance resulting from both species

\[
l = \text{the length of the cell} \tag{2.30}
\]

\[
A_+ = A_A + A_{HA}
\]

and

\[
\varepsilon C_A = \varepsilon_A \left[ A^- \right] + \varepsilon_{HA} \left[ HA \right] = \varepsilon \left[ A^- \right] + \varepsilon \left[ HA \right] \tag{2.31}
\]

where \( \varepsilon_A \) is the molar absorptivity of the basic form and \( \varepsilon_{HA} \) is the molar absorptivity of the acidic form.

Rearranging:

\[
\varepsilon \left[ A^- \right] - \varepsilon_A \left[ A^- \right] = \varepsilon_{HA} \left[ HA \right] - \varepsilon \left[ HA \right] \tag{2.32}
\]

Factoring yields

\[
(\varepsilon - \varepsilon_A) \left[ A^- \right]_{HA} = (\varepsilon_{HA} - \varepsilon) \tag{2.33}
\]

or

\[
\varepsilon = \varepsilon_{HA} - \left\{ (\varepsilon - \varepsilon_A) \left[ A^- \right]_{HA} \right\} \tag{2.34}
\]

changing signs and substituting for \( \left[ A^- \right]_{HA} \) gives:

\[
\varepsilon = \varepsilon_{HA} + (\varepsilon_A - \varepsilon) \frac{K_a}{[H^+]}. \tag{2.35}
\]
Equation 2.35 is in the form of a straight line with a slope equal to $K_a$.

**Experimental**

The apparatus, reagents, and procedure used in extraction studies have been given in Chapter I. Nonetheless, some of the experimental techniques which are particularly pertinent to stability constant calculations will be reviewed.

All extraction flasks were equilibrated in a constant temperature bath at $25^\circ C$ and were adjusted to 0.1 ionic strength with sodium perchlorate. Equilibrium pH measurements were made with a Beckman 40495 glass and saturated calomel electrode.

The distribution ratios used in stability constant calculations were taken from plots of log D versus pH. This helped to smooth or average the data which was used for these calculations.

The procedure for determining the acidity constant is similar to a procedure described by Guter and Hammond.\(^8\)

---

An aqueous solution of trifluoroacety lacetone was prepared and the concentration was adjusted so the absorbance maximum could be read without further dilution. A solution which was about $1 \times 10^{-4}$ molar in trifluoroacety lacetone resulted. After the concentration range was established, a $2 \times 10^{-4}$ molar trifluoroacety lacetone solution was prepared. Sufficient sodium chloride was added to this solution to give an ionic strength of 0.2. Fifty ml. aliquots of this solution were pipetted into 100 ml. beakers and the pH was adjusted with sodium hydroxide or hydrochloric acid. These solutions were then transferred to 100 ml. volumetric flasks followed by copious washings. The flasks were then diluted to the mark, mixed and brought to constant temperature in a water bath maintained at 25°C. Portions of these solutions were placed in one cm. silica cells and the absorbance was read at 290 μ. After this was done, approximately 50 ml. volumes of the solutions were poured into 50 ml. beakers and the equilibrium pH was carefully recorded.

The molar absorptivity of the basic form was calculated using the absorbance of a basic solution of
trifluoroacetylacetone. The acidity constant was calculated from a plot of $\bar{\varepsilon}$ versus $(\varepsilon_A - \bar{\varepsilon})/(H^+)$ as described in the theory section of this chapter.

It is necessary to know the concentration of reagent in the aqueous phase for use in equation 2.22. This was calculated using the total amount of reagent, the amount bound to metal, and the distribution data reported by previous workers.

Results and Discussion

Determination of the Acidity Constant of Trifluoroacetylacetone

The acidity constant for this reagent was calculated because previous values were obtained under different conditions. The logarithm of the constant was found to be 8.7 in 75 percent dioxane. A value of 6.3 in aqueous medium was reported by Reid and Calvin.


However, this value is the thermodynamic value extrapolated to zero ionic strength.

The ultraviolet spectrum of trifluoroacetylacetone is shown in Figure 14. The acidity constant was calculated from the spectrophotometric data at 25°C and 0.1 ionic strength. The value of the constant taken from the slope of Figure 15 was $6.7 \times 10^{-7}$.

Stability Constants for Various Metal Trifluoroacetylacetonates

Aluminum. The successive stability constants for aluminum trifluoroacetylacetonate were calculated using equation 2.22. Distribution ratios used in the calculations were taken from a plot of the logarithm of the distribution ratios versus the pH shown in Figure 16. The value used for the distribution coefficient was 500. This was the region in which the distribution ratio remained fairly constant and was thought to be equal to the distribution coefficient. This is because the species other than the fully formed chelate, $MA_3^-$, become insignificant as the pH is increased. If no other competing reactions occurred,
Figure 14

ULTRAVIOLET SPECTRUM OF TRIFLUORO-
ACETYLACETONE IN WATER
Figure 15

DETERMINATION OF $K_a$ FOR TRIFLUOROACETYLACETONE

117
Slope $= 6.86 \times 10^{-7}$

\[
\frac{\varepsilon_0 - \bar{\varepsilon}}{\left( H^+ \right) \times 10^9}
\]
the distribution ratio would remain constant from this particular pH on. However, hydroxy complex formation becomes more important at higher pH values and this tends to reduce the distribution ratio. The quantity, 500, was checked later by recalculating the distribution coefficient at widely different pH values from the stability constants obtained. Since the distribution coefficient, $K_d$, is a constant, consistent values for $K_d$ should be obtained over the entire pH range if accurate values for all terms were used. When this was done, values very near 500 were obtained for the distribution coefficient and these values are shown in Table 14. The value which differed the greatest was 515, a variation of about three percent. The value used for the acidity constant was $6.86 \times 10^{-7}$ as mentioned previously. The equilibrium constants for the hydrolysis of aluminum were taken from the literature. The values used were the most recent ones obtained under conditions similar to those used in this study. The logarithm of the values used were $-5.02^{12}$ and $-8.06^{13}$ for $k_{h1}$ and $k_{h1}k_{h2}$ respectively.

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Using the data described above, values of 5.00, 3.83, and 3.23 were obtained for the logarithms of $k_1$, $k_2$, and $k_3$ respectively. No other values for the stability constants have been reported for aluminum trifluoroacetylacetone complexes. Acetylacetone, a less acidic ligand, forms stronger complexes with aluminum. The constants reported by Izatt et. al.\textsuperscript{14} are 8.6, 7.9, and 5.8 for log $k_1$, log $k_2$, and log $k_3$.

**Gallium.** This metal forms a very stable complex with trifluoroacetylacetone as it does with acetylacetone. Again, equation 2.22 was used and 500 was taken as the value of the distribution coefficient. This also proved to be a valid constant as shown by re-calculation of the distribution coefficient from the stability constants at different pH values. The results are shown in Table 14. The hydrolysis constants used were, log $k_{h1} = 2.92$\textsuperscript{15} and log $k_{h2} = 3.46$\textsuperscript{16}


Again, these values were the latest ones reported for conditions similar to those in this study. Distribution ratios were taken from a plot of log D versus pH as shown in Figure 16. All other experimentally determined values in equation 2.22 were obtained as described previously.

The successive stability constants obtained from the calculations were 5.84, 5.22, and 3.87 for log $k_1$, log $k_2$, and log $k_3$ respectively. There is very little data available that can be compared with these results. The constants for gallium acetylacetonate are log $k_1 = 9.5$, log $k_2 = 8.4$, and log $k_3 = 5.7$. Gallium forms more stable complexes with both ligands than the other group III B metals.

**Indium.** The distribution ratio for indium reached a plateau at 950 so this was taken as the distribution coefficient. This value was re-calculated from the stability data at other pH values and very close agreement was obtained as shown in Table 14.

---

Figure 16

EFFECT OF pH ON THE DISTRIBUTION RATIO
OF ALUMINUM, GALLIUM, AND INDIUM

○ Aluminum
□ Gallium
△ Indium
◊ Theoretical trivalent ion
### Table 14

**Calculation of the Distribution Coefficient from Stability Constants**

<table>
<thead>
<tr>
<th>Aluminum</th>
<th>Gallium</th>
<th>Indium</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>K&lt;sub&gt;d&lt;/sub&gt;</td>
<td>pH</td>
<td>K&lt;sub&gt;d&lt;/sub&gt;</td>
</tr>
<tr>
<td>3.01</td>
<td>490</td>
<td>1.92</td>
<td>512</td>
</tr>
<tr>
<td>3.95</td>
<td>505</td>
<td>3.11</td>
<td>510</td>
</tr>
<tr>
<td>6.51</td>
<td>515</td>
<td>4.95</td>
<td>505</td>
</tr>
</tbody>
</table>

124
The values for the distribution ratio at various pH increments were taken from a graph of the experimental values shown in Figure 16. The hydrolysis constants obtained under similar conditions are $-4.4^{18}$ and $-3.9^{19}$ for the logarithm of $k_{h_1}$ and $k_{h_2}$ respectively. All other quantities used in the calculations were obtained as described above.

Indium forms a more stable complex with trifluoroacetylacetone than aluminum. The constants for the indium chelate are 5.65, 4.27, and 3.29 for log $k_1$, log $k_2$, and log $k_3$. The slightly greater stability of the indium complex over the aluminum complex is reversed when acetylacetone is the ligand. The constants for the indium acetylacetonates are 8.0 for log $k_1$, 7.1 for log $k_2$, and 5.2 for log $k_3$. This fact is consistent with the extraction behavior of these metals with both ligands. At present, this fact is unexplained.

---


Iron. This metal is extracted at very low pH and it follows that the stability of the iron trifluoroacetylacetonate complex will be quite high. The distribution ratio for iron is shown separately in Figure 17 since the distribution is higher for iron than for the other metals studied. Distribution ratios at several pH increments were used in calculations. The distribution ratio leveled off at 2400 so this value was used as the distribution coefficient. Recalculation of the distribution coefficient from stability data indicated that this figure was correct. Iron is extracted at such a low pH that hydrolysis is unimportant. However, calculations were made to determine whether hydrolysis should be considered. The constants used in these calculations were -3.05 for log $k_{h_1}$ and 6.31 for log $k_{h_1} k_{h_2}$.\(^{20}\)

The stability of the iron complex is quite high compared to the group III B metal complexes. The stability constants obtained are log $k_1 = 7.08$,

Figure 17

EFFECT OF pH ON THE DISTRIBUTION RATIO OF IRON

- Iron
- Theoretical trivalent ion
log $k_2 = 6.75$, and log $k_3 = 4.51$. There is some information available which serves as a check on these results. Scribner found that if ethylenediaminetetraacetic acid is present in an aqueous solution of iron adjusted to pH 5.0 to 5.5, the extraction of iron with trifluoroacetylacetone takes about thirty days. It is therefore reasonable that the stability of the trifluoroacetylacetone complex is quite similar to the stability of the iron EDTA complex at pH 5.5. The logarithm of the overall conditional constant of the iron EDTA complex at this pH is 18.2. The overall stability constant obtained for iron trifluoroacetylacetone is 18.34. The conditional constant at pH 5.5 was calculated from the stability constant and the fraction of free trifluoroacetylacetone present as the anion. The logarithm of the value obtained was 17.57. At this pH more of the iron would be present in the EDTA complex than in the trifluoroacetylacetone

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21 Scribner, W., Private communication.

complex. However, the latter is extracted into benzene so the equilibrium is shifted.

**General discussion of stability constant data.**
The constants obtained using extraction data are probably not as accurate as ones obtained using potentiometric measurements. This is due in part to the greater number of variables present and also to the limited accuracy of some of the measurements. However, for systems which are very slightly water soluble, a potentiometric method could not be used in aqueous medium. Therefore, solvent extraction offers a convenient means of obtaining stability data for special cases such as the trifluoroacetylacetone system.

All stability constants reported are for 25°C adjusted to 0.1 ionic strength with sodium perchlorate. All constants were calculated using hydrogen ion activity and concentration for all other species. Therefore, the constants reported are mixed constants according to Sillen's
nomenclature\textsuperscript{23} or hybrid constants according to Watter's.\textsuperscript{24}

The stability constants obtained are summarized in Table 15. The order of decreasing stability is Fe > Ga > In > Al. When the logarithm of the overall stability constant is graphed versus pH\textsubscript{2}, a straight line results as shown in Figure 18. This is predicted by equation 2.27. If the distribution ratios for two species, A and B, are equated at the pH of fifty percent extraction, then

\[
\log D = \log K'_{A} + n \log \frac{\beta_{3A} K_{a}}{K_{dHA}} = \log K'_{B} + n \log \frac{\beta_{3B} K_{a}}{K_{dHB}}
\]

or

\[
\log \frac{K_{dA} \beta_{3A} K_{a}^3}{K_{dHA}} - \log \frac{K_{dB} \beta_{3B} K_{a}^3}{K_{dHB}} = n \log \frac{\beta_{3B}}{\beta_{3A}}
\]

Therefore

\[
(\log K_{dA} + \log \beta_{3A}) - (\log K_{dB} - \log \beta_{3B})
\]

\[
= n \log \frac{\beta_{3B}}{\beta_{3A}}
\]


\textsuperscript{24}Watters, J. I., "Systematic Methods for Equilibria Calculations in the Titration of Polybasic Acids".
TABLE 15

STABILITY CONSTANTS OF SOME METAL TRIFLUOROACETYLACETONATES

<table>
<thead>
<tr>
<th></th>
<th>Aluminum</th>
<th>Gallium</th>
<th>Indium</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log k_1$</td>
<td>5.00</td>
<td>5.84</td>
<td>5.65</td>
<td>7.08</td>
</tr>
<tr>
<td>$\log k_2$</td>
<td>3.83</td>
<td>5.22</td>
<td>4.27</td>
<td>6.75</td>
</tr>
<tr>
<td>$\log k_3$</td>
<td>3.23</td>
<td>3.87</td>
<td>3.29</td>
<td>4.51</td>
</tr>
<tr>
<td>$\log \beta_3$</td>
<td>12.06</td>
<td>14.93</td>
<td>13.21</td>
<td>18.34</td>
</tr>
<tr>
<td>$pH_{1/2}$</td>
<td>3.00</td>
<td>1.95</td>
<td>2.75</td>
<td>0.60</td>
</tr>
</tbody>
</table>
And if the difference between $\log K_{dA}$ and $\log K_{dB}$ is small compared to the difference between $\log \beta^3_{3A}$ and $\log \beta^3_{3B}$

$$\log \beta^3_{3A} - \log \beta^3_{3B} = n \text{pH}_2B - n \text{pH}_2A \quad (2.39)$$

$$\Delta \log \beta^3 = n \Delta \text{pH}_2 \quad (2.40)$$

Figure 18 is a useful aid in predicting the relative stability of metal complexes containing the same ligand. Chromium (III) and manganese (III) are placed on the graph according to $\text{pH}_2$. The approximate stability constant can then be obtained for these metals. This is particularly useful because it would be quite difficult to calculate the stability constants for these metals. There are probably several, rather complicated, equilibria involving pyridine which should be considered in the chromium extraction. The maximum extraction of manganese (III) is probably not valid for reasons already pointed out. Therefore, for these situations, the approximation technique is especially useful.
Figure 18

RELATIONSHIP BETWEEN THE LOGARITHM OF THE OVERALL STABILITY CONSTANT FOR TRIFLUOROACETYLACETONE COMPLEXES AND THE $\text{pH}_{\frac{1}{2}}$ (PH OF 50 PERCENT EXTRACTION)

○ - Calculated values
□ - Estimated values
It was previously mentioned that the stability of aluminum, gallium, indium or iron complexes has not been studied heretofore. Moreover, no stability studies have been made on any trifluoroacetylacetonates in aqueous media. The only stability constants reported for this ligand are for the nickel and copper complexes and this work was done in 75% dioxane. Therefore, no direct comparison of the results obtained with any literature value is possible.
CHAPTER III

GAS CHROMATOGRAPHIC STUDIES OF METAL TRIFLUOROACETYLACETONATES

Historical Review

Since its introduction in 1952\(^1\) gas liquid partition chromatography has been used with great success for the analysis of complex organic mixtures. The separation and analysis of inorganic compounds has lagged behind that of organic compounds. For some time inorganic separations were confined to gases such as oxygen and nitrogen. It was not until 1959 that the potential of this technique was investigated for possible metal analysis. This delay was probably due to the limited volatility and thermal stability of most compounds containing metals. The first attempts

to apply gas chromatography to metal analysis were made by Wachi\(^2\) and Freiser\(^3\) who reported the use of volatile metal halides and by Floutz\(^4\) and Duswalt\(^5\) who studied metal acetylacetonates. Unfortunately, the transition metal halides are reactive toward most organic liquid phases commonly in use and are also quite easily hydrolyzed so anhydrous conditions must be used. Additional work has been done with these compounds\(^6\) and Juvet and Wachi recommended the use of inorganic fused salts as stationary liquid phases for the analysis of inorganic compounds.\(^7\) Recently a simple method for titanium was reported by Sievers, Wheeler, and Ross.\(^8\) The titanium in a bauxite sample was placed in a tube

with carbon tetrachloride. The tube was sealed and heated so that the titanium was converted to titanium tetrachloride. The tube was broken in the injection port and the resulting peak could be related to the amount of titanium present.

It appeared that some of the metal acetylacetonates might be eluted by gas chromatography more successively than the metal halides. The beryllium, aluminum (III), and chromium (III) acetylacetonates were particularly well suited for this.

Unfortunately, many of the other acetylacetonates that have been studied are not volatile enough to be chromatographed without decomposition.

In 1963, Moshier et al.\textsuperscript{11} and Sievers\textsuperscript{12} showed that substitution of fluorine in the ligands significantly

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increases the vapor pressure of metal acetylacetonates. These fluorinated derivatives can be chromatographed at lower column and injection port temperatures than the parent compounds. In more detailed studies,\textsuperscript{13,14} trifluoroacetylacetonato complexes of beryllium (II), aluminum (III), indium (III), chromium (III), iron (III), copper (II), rhodium (III), zirconium (IV), and hafnium (IV) were successfully eluted.

A number of detectors were investigated and a few quantitative determinations of these metal chelates soon followed this initial work. Hill and Gesser\textsuperscript{15} reported that the beryllium, aluminum, and chromium complexes of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone could be determined within ten percent using a flame ionization detector.


Brandt and Heveran also used the flame detector for trace amounts of chromium. An argon ionization detector has been used and Juvet and Durbin explored the possibility of using a flame photometer as a detector for metal chelates.

It was suspected rather soon after the introduction of these fluorinated reagents that electron capture would be rather effective for the detection of fluorene containing chelates. This is indeed true as indicated by studies made by Ross and co-workers. Albert made a comparative study of electron capture and flame ionization detectors for several metal chelates.

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Schwarberg, Moshier, and Walsh made a careful study of several trifluoroacetylacetonates using the thermal conductivity detector.\textsuperscript{23} An overall mean error of 2 percent based on calibration data indicated the feasibility of this technique for metal chelate analysis.

A recent study indicates that the rare earth complexes with the ligand, dipivaloylmethane are volatile and thermally stable.\textsuperscript{24} Several of these complexes have been eluted through a chromatographic column without decomposition. Two studies, which did not involve gas chromatography, but which are related have been made. In the first of these, Berg and Truemper obtained vapor pressure-temperature data for various metal $\beta$-diketone chelates.\textsuperscript{25} This data was then used in fractional sublimation studies and separations of several metal chelates.\textsuperscript{26}

\textsuperscript{23}Schwarberg, J. E., Moshier, R. W., Walsh, J. H., Talanta, 11, 1213 (1964).

\textsuperscript{24}Eisentrout, K. J., Sievers, R. E., J. Am. Chem. Soc. 87, 5254 (1965).


Theory

Although gas chromatography is somewhat empirical, several workers have elucidated some of the theory involved in this technique. The theory of gas chromatography can be found in several books on the subject and is covered quite thoroughly in the one by Purnell. 27

Two techniques for checking the efficiency of chromatographic columns were used. The development of these two techniques is given in the text by Dal Nogare and Juvet. 28 The first gives the number of theoretical plates in a column as:

\[ N = 2\pi (h. X/A)^2 \]  \hspace{1cm} (3.1)

and the second by:

\[ N = 16 \left( \frac{X}{Y} \right)^2 \]  \hspace{1cm} (3.2)

where:

\[ N = \text{number of theoretical plates}; \]

\[ h = \text{peak height}; \]

\[ X = \text{peak width at half height}; \]

\[ Y = \text{chromatographic band width}; \]

\[ A = \text{cross-sectional area of column}; \]

\[ h. = \text{hatched line - peak height}; \]

\[ X. = \text{hatched line - peak width}; \]

\[ Y. = \text{hatched line - chromatographic band width}; \]

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\[ Y. = \text{hatched line - chromatographic band width}; \]

\[ A. = \text{cross-sectional area of column - peak width}; \]

\[ h. = \text{hatched line - peak height}; \]

\[ X. = \text{hatched line - peak width}; \]

\[ Y. = \text{hatched line - chromatographic band width}; \]

\[ A. = \text{cross-sectional area of column - peak height}; \]

\[ h. = \text{hatched line - peak height}; \]

\[ X. = \text{hatched line - peak width}; \]
\[ X = \text{distance from starting point to peak maximum}; \]
\[ A = \text{area}; \]
\[ y = \text{width of peak at base}. \]

It was pointed out previously that one of the most stringent requirements placed on gas chromatography for metal analysis is that of volatility. This requirement may be met easier than it might first appear. The vapor pressure work of Berg and Truemper indicates that many metal chelates can be eluted by gas chromatography at temperatures where they exhibit about one millimeter pressure. However, many metal chelates need to be heated to rather high temperatures in order to attain this vapor pressure. Some of these tend to decompose at such temperatures and are therefore not applicable to gas chromatographic analysis.

Relatively few studies have been concerned with the reasons that certain compounds are volatile. However, several factors such as low polarity, covalent bonding, and the absence of external hydrogen bonding

---

are usually associated with volatile compounds. Many beta diketonates, especially the trifluoroacetyl-acetonates and hexafluoroacetylacetonates meet these requirements and can be eluted by gas chromatography.

Another requirement is that of thermal stability. This is more important for the less volatile compounds because the temperature must be increased in order to chromatograph them. It is interesting to note that thermal stability of these complexes does not parallel the thermodynamic stability of these metal chelates at all. For example, the nickel acetylacetonate complex, which has a higher stability constant than the cobalt complex,\textsuperscript{30} decomposes at $230^\circ\text{C}$ while the latter sublimes at $120^\circ\text{C}$.\textsuperscript{31} For quantitative work the metal complexes should be stable enough to be eluted by gas chromatography without decomposition.

A third requirements is that the metal complex or ligand does not react with the liquid phase, solid support, column or detector. Similarly the metal ion


should probably be in its normal oxidation state so that oxidation or reduction does not occur in the chromatograph. Compounds that are coordinatively saturated with the ligand probably have a better chance of being eluted. This is probably because compounds such as this do not have an additional site for the liquid phase to attach.

Finally, in order to use gas chromatography for metal analysis, a preliminary step is needed in order to get the metal ion into the chelated form. It would of course be desirable if this step were quantitative, or at least reproducible. The stability constants calculated earlier indicate that the reaction of the metal ion with the ligand will be complete. However, these complexes precipitate from aqueous solution when present in an appreciable concentration. Thus extraction of these complexes into an organic solvent is a logical preliminary process. Beta-diketones have been used in the extraction of metal ions and many of the resulting chelates meet the other requirements listed. Thus the fluorinated acetylacetonates seem to be promising reagents for metal analysis.
Experimental

Apparatus. An F and M model 720 gas chromatograph with a thermal conductivity detector containing W-1 tungsten filaments was used. The chromatograph was connected to a Brown-Honeywell one mv. recorder. The chromatograph was modified by placing a piece of 4 mm (o.d.) pyrex tubing 7 cm in length into the injection part. This aided in preventing any reaction of the chelates with the hot metal walls and eliminated any decomposition that might have been catalyzed by the wall. In addition, it was useful in that the glass tubes could be removed periodically and checked for decomposition. Before the investigation was begun, the slide wire was cleaned and the recorder was lubricated and checked with a potentiometer.

A few studies were made with a flame ionization detector and an electron capture detector. The instrument used was a F and M model 700 gas chromatograph equipped with a model 700 electrometer. This instrument was used as a dual column instrument with dual flame detectors or as a single column, single detector electron capture instrument. A double-throw triple pole
switch was placed on the input of the recorder so that it could be used with either instrument. A conversion kit was installed on the oven temperature control of the model 700. This was connected to the temperature controls of the model 720 so that temperature programming of the model 700 was possible.

Helium was used as the carrier gas for all studies with the thermal conductivity detector. Either helium or nitrogen was used with the flame detector. A mixture of five percent carbon dioxide in argon was used for both carrier gas and purge with the electron capture detector. All carrier gases were passed through tubes containing Drierite before the gas entered the instrument. Hydrogen and air were used as fuel and oxygen supply for the flame detector. A tygon tube was placed on the effluent of the instrument and the opposite end was extended to the top of a fume hood. This prevented any tritium which may have escaped from the detector from eluting into the laboratory.

Hamilton syringes were used for sample injection. Ultra violet spectra were obtained with a Cary model 14 recording spectrophotometer. A Perkin-Elmer infrared cord was used to obtain infrared spectra.
Preparation of Chromatographic Columns. Since previous investigations showed that some decomposition of the chelates occurs if they come in contact with the hot metal walls of the column, glass columns were used. A form which aided in bending columns to fit the chromatograph oven was constructed. The form for the model 720 chromatograph consisted on a half inch board covered with quarter inch asbestos and a brass cylinder covered with asbestos as shown in Figure 19. In order to construct a column, a 90° bend was made about three inches from one end of a 7 mm (o.d.) piece of pyrex tubing and the bend end was inserted in a hole in the board. The brass cylinder was then preheated and the tubing was heated with two Fisher burners fastened together. The tubing was wrapped around the cylinder as it was heated. When the approximate length was attained, this operation was stopped and the tubing was allowed to cool. It was then removed from the form and a 90° bend was made so that the two ends were parallel and about three inches apart. The ends were cut off if necessary and fire polished.

The form for the 700 instrument was quite similar. A 1000 ml. crystalization dish which was about 6 inches
Figure 19

FORM USED IN PREPARATION

OF GLASS COLUMNS
A brass cylinder with a 4-inch diameter is mounted on a asbestos board. The cylinder has a 7.0 mm hole located 1.5 inches away. The asbestos board is described as a 1/2-inch board. The tubing is 7.0 mm pyrex.
in diameter was covered with asbestos. This was placed on a laboratory stool, covered with asbestos and a weight was placed on the form to secure it. A ring clamp was fastened on the stool so that it extended upwards. A rubber stopper with a 6 mm hole in it was placed in the clamp and one end of a 6 mm (i.d.) glass tube which was to be used as a column was inserted in this stopper. The free end of this tube was held and was wrapped around the form as the column was heated with two Fisher burners.

Early in this investigation it was found that silanization of the solid support and column reduced tailing and more symmetrical peaks resulted. Therefore, all column packings used in this study were silanized by refluxing the material with a ten percent solution of hexamethyldisilazane in petroleum ether for one hour as described by Bohemen, et. al.\(^\text{32}\)

The liquid phase was then applied to the solid support as follows: A given weight of the liquid phase was dissolved in chloroform in an evaporating dish

which contained a known amount of silanized solid support, usually glass beads. The chloroform was then evaporated on a steam bath in a hood and then the mixture was stirred to insure even distribution and uniform coating.

Because the columns were helix-shaped and the coated support was somewhat sticky because of the relatively low surface area of glass beads, conventional methods for filling columns failed. The following procedure was found to be the most effective method for filling the columns. A piece of silanized glass wool was placed in the column so that about one cm. extend out of the column. This portion was turned back over the outside of the column and a piece of vacuum tubing was placed over the end of the column so that it held the glass wool in place. The vacuum tubing was connected to a 500 ml. trap, a needle valve, and a vacuum pump. A small funnel was placed on the opposite end of the column with tygon tubing. The column packing was added to the funnel, the vacuum pump was turned on, and a vibra-tool was used to agitate the packing so that it was distributed evenly.
Stainless steel Swedglock fittings which had been previously widened with a 7 mm drill were placed on the column followed by nylon front and back ferrules. The column was fastened on the instruments with the Swedglock fittings and tested for leaks with a soap solution.

**Chromatographic columns**

The following columns were used successfully:

1. A pyrex glass column four feet in length containing 1 percent SE-30 silicon grease on 60 to 80 mesh glass beads.

2. A silanized pyrex glass column four feet in length containing 0.5 percent DC-710 silicone oil on 60 to 80 mesh silanized glass beads.

3. A column six feet in length which contained the same packing as number two.

4. Two glass columns (one for the model 720 and one for the 700 instrument) containing 0.5 percent DC-550 oil on 60 to 80 mesh silanized glass beads.

**Reagents.** Hexamethyldisilazane was obtained from Analabs, Inc. and was used without further purification. All silicone oils, DC-550, DC-710, and
SE-30 and glass beads were obtained from Wilkins Scientific Company. All other reagents have been described in previous chapters and the syntheses of the chelate are described in Chapter IV.

**Operating procedures.** In preliminary studies metal trifluoroacetylacetonates were dissolved in benzene prior to injection into the chromatograph. Column temperatures were usually about $125^\circ$ to $135^\circ$, the same range in which most of the chelates melt. Some decomposition of some of the chelates seemed to occur above $150^\circ$. The injection port and detector temperatures were about $25^\circ$ higher than the column temperature.

A chelate might decompose and yield a product which is volatile and appear as a well defined peak. Therefore, in addition to the visual inspection of the glass lined injection port, a second check for decomposition was made. A large portion of the chelate was injected into the chromatograph and the eluent was collected in a cooled glass tube as the peak emerged. This was either dissolved in hexane and check by ultraviolet spectroscopy or was mixed with potassium
bromide and its infrared spectrum was obtained. All of the chelates on which quantitative work was done gave identical spectra before and after elution.

The quantitative gas chromatography work is described in Chapter V, the analysis section.

Results and Discussion

The chromatogram showing the separation of aluminum, gallium, and indium is given in Figure 20. The conditions are given with the figure and are optimum for this combination of chelates on this particular column. Attempts to reduce the time for the elution by increasing the temperature or flow rate resulted in an overlap of the solvent and aluminum peaks. The higher temperature could be used if only gallium and indium were present and the results are shown in Figure 20. This is probably about the maximum temperature that can be used when indium is present. When the column temperature was increased to 150° and the injection port to 170°, a residue was found in the glass liner of the injection port after several injections containing indium had been made. When the conditions that are listed with Figure 21 were used no
Figure 20

GAS CHROMATOGRAPHIC SEPARATION
OF ALUMINUM TRIFLUOROACETYLACETONATE
GALLIUM TRIFLUOROACETYLACETONATE AND
INDIUM TRIFLUOROACETYLACETONATE

Column:

Length: 3.5 ft.
I.D.: 7 mm.

Liquid Phase: DC-550 Silicone oil
Wt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: Helium
Rate: 75 ml/min.

Detector: Thermal conductivity
Pressure: 40 psi

Temperatures:

Column: 128°C
Detector: 150°C

Injection port: 150 °C
Bridge Current: 150 MA
Sample Size: 20 µl
Figure 21

GAS CHROMATOGRAPHIC SEPARATION OF
GALLIUM TRIFLUOROACETYLACETONATE
AND INDIUM TRIFLUOROACETYLACETONATE

Column:

Length: 3.5 ft.
I.D.: 7 mm.

Liquid Phase: DC-550 Silicone oil
Wt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: Helium
Rate: 75 ml/min.

Detector: Thermal conductivity
Pressure: 40 psi

Temperatures:
Column: 140°C
Detector: 165°C

Injection Port: 165°C

Bridge Current: 150 MA

Sample Size: 20 µl
decomposition of any of the chelates resulted. This was confirmed by a visual inspection of the injection port liner and by comparison of the infrared spectrum of each chelate before and after elution.

The separation of aluminum and iron by gas chromatography is shown in Figure 22. Again careful checks were made for decomposition. A very thorough check was made for iron because this trifluoroacetyl-acetonate seemed to leave a residue in the injection port according to Sievers. However, soon after work was begun on iron, other workers found that little or no decomposition of the iron chelate occurred. These workers also developed an accurate quantitative method for iron based on gas chromatography.

Aluminum and chromium can also be separated by gas chromatography as shown in Figure 23. These two metals form the most volatile chelates studied and no evidence of decomposition occurred. The conditions are

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Figure 22

GAS CHROMATOGRAPHIC SEPARATION OF ALUMINUM TRIFLUOROACETYLACETONATE AND IRON TRIFLUOROACETYLACETONATE

Column:
Length: 3.5 ft.
I.D.: 7 mm.

Liquid Phase: DC-550 Silicone oil
Wt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: Helium
Rate: 75 ml/min.

Detector: Thermal conductivity
Pressure: 40 psi

Temperatures:
Column: 128°C
Detector: 150°C

Injection port: 150°C

Bridge Current: 150 MA
Sample Size: 20 μl
GAS CHROMATOGRAPHIC SEPARATION OF ALUMINUM TRIFLUOROACETYLACETONATE AND CHROMIUM TRIFLUOROACETYLACETONATE

Column:

Length: 3.5 ft.
I.D.: 7 mm.

Liquid Phase: DC-550 Silicone oil
Wt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: Helium
Rate: 75 ml/min.

Detector: Thermal conductivity
Pressure: 40 psi

Temperatures:

Column: 128°C
Detector: 150°C
Injection port: 150°C

Bridge Current: 150 MA
Sample Size: 20 µl
also listed for this separation and are also optimum for the column used. The efficiency of the column was calculated using the chromium peak. Using equation 3.1, a value of 175 theoretical plates was obtained for the column. Equation 3.2 gave an answer of 164 theoretical plates. Thus, the column is not very efficient, but is quite satisfactory for the separations studied.

Quantitative work on all the above metals was performed. However, this aspect of gas chromatography has been included in Chapter V where quantitative analytical methods based on extraction and gas chromatography are described.

Attempts to separate other combinations of metal chelates were also made. It was found that column number four would separate iron and chromium at a temperature of about 115°C. However, the resulting peaks broadened and if such a separation were desired, another column should probably be used.

The gas chromatographic behavior of several other metal complexes was studied. The tris (trifluoroacetyl-acetonato) vanadium (III) complex was eluted reasonably
well. The preparation of the complex is described in Chapter IV and the elution by gas chromatography is shown in Figure 24. Probably the most unusual feature about this peak is its broad shape. No evidence of decomposition of the chelate could be found, but it is felt that oxidation to the vanadyl complex occurred. This may occur before the injection is made, in the injection port, or on the column. The gas chromatographic behavior of the trifluoroacetylacetonato complexes of manganese (III) and cobalt (III) was also studied. Both of these species left some residue in the injection port indicating they decompose somewhat. Therefore, rather than to attempt to chromatograph these in the trivalent oxidation state, it may be better to elute them as divalent trifluoroacetylacetonato-amine adducts.  

Previous workers indicated that detectors which are normally more sensitive than the thermal conductivity detector might be useful in detecting traces of metals. A question remained however, as to the feasibility of a quantitative extraction of a minute amount of metal  

Figure 24

GAS CHROMATOGRAPHIC ELUTION OF VANADIUM (III) TRIFLUOROACETYLACETONATE

Column:
Length: 3.5 ft.
I.D.: 7 mm.

Liquid Phase: DC-550 Silicone oil
Wt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: Helium
Rate: 75 ml/min.

Detector: Thermal conductivity
Pressure: 40 psi

Temperatures:
Column: 128°C
Detector: 150°C

Injection port: 150°C
Bridge Current: 150 MA

Sample Size: 20 µl
with subsequent gas chromatographic analysis. For this reason work was begun using a flame ionization detector and electron capture detector. A description of these detectors can be found in the book by Dal Nogare and Juvet.\textsuperscript{36}

Solutions of the metal chelates were prepared and dilutions were made until the approximate lower limit of detection by flame detector was reached. Then aqueous solutions of aluminum and chromium in this same concentration range were prepared and extractions into a $2.5 \times 10^{-2}$M solution of trifluoroacetylacetone in benzene were made as previously described. Quantitative extraction were obtained, but when benzene was used, the solvent peak tailed across the entire chromatogram. Several extractions of aluminum and chromium were repeated using carbon disulfide. This proved to be an ideal solvent for the flame detector. A chromatogram showing the separation of 4 PPM of aluminum and 2 PPM of chromium is shown in Figure 25. Additional work with this detector indicates that it should be applicable.

DETECTION OF ALUMINUM AND CHROMIUM
WITH THE FLAME IONIZATION DETECTOR

Sample: 2.16 PPM of Aluminum and
1.0 PPM of Chromium in carbon disulfide

Column: 3.5 ft.
I.D. 6 mm.

Liquid Phase: DC-550 Silicone oil
Wgt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: Helium
Rate: 75 ml/min.

Detector: Flame Ionization

Flow Rates
Hydrogen: 60 ml/min.
Air: 600 ml/min.

Temperatures
Column: 128°C
Detector: 150°C
Injection Port: 150°C

Range Setting: 1
for traces of aluminum and chromium in the range of 2 PPM to at least 10 PPM.

A similar procedure was performed with benzene solutions of the chelates using an electron capture detector. When the concentration reached the lower limit of detection, aqueous solutions of aluminum and chromium were prepared in this concentration range. Extractions into benzene which was $2.5 \times 10^{-4}$ M in trifluoroacetylacetone were made. These seemed to be quantitative also and the excess reagent did not seem to adversely affect the detector. A chromatogram of the aluminum and chromium complexes is shown in Figure 26. The original aqueous concentration of aluminum and chromium was 20 to 40 PPb respectively. Therefore, this method seems applicable for as little as 10 PPb of aluminum and chromium.

A marked improvement in symmetry of peaks occurred after the solid support and glass beads had been silanized prior to use. This involved the reaction of hexamethyldisilazane with the terminal hydroxy groups on the glass as shown below:
DETECTION OF ALUMINUM AND CHROMIUM
WITH THE ELECTRON CAPTURE DETECTOR

Sample: 10 PPb aluminum and 40 PPb chromium in benzene

Column: 3.5 ft.
I.D.: 6 mm.

Liquid Phase: DC-550 silicone oil
Wgt. %: 0.5

Support: Glass beads
Mesh: 60-80

Carrier Gas: 95% argon, 5% carbon dioxide
Flow Rate: 75 ml/min.

Purge Gas: 95% argon, 5% carbon dioxide
Detector: Electron capture
Pulse Rate: 15/second
Range: $10^2$

Temperatures
Column: 128°C
Detector: 150°C
Injection Port: 150°C
The procedure for applying this has been described by Bohemen et. al.\(^{37}\)

"Lightly loaded columns" which contain less than one percent of the liquid phase have been used for high boiling substances\(^{38-40}\) and were selected for this study. General purpose columns usually contain solid supports coated with ten to twenty percent liquid phase. A lightly loaded column has a very thin layer of liquid phase. By use of such columns, it is possible to elute substances at lower temperatures because the species being chromatographed spends relatively less time in the liquid phase.


CHAPTER IV

SYNTHESIS AND INFRARED SPECTROSCOPY STUDY OF VARIOUS METAL-BETA-DIKETONE CHELATES

Historical Introduction

Metal-acetylacetonates were prepared in the early years of metal chelate work.\(^1\) Numerous syntheses for these compounds have been reported and many of these are given in "Inorganic Syntheses".\(^2\)

Many metal-trifluoroacetylacetonates are prepared by methods that are nearly identical to those for the acetylacetonates. However, some of these fluorinated derivatives have been prepared by somewhat different methods with good results.\(^3,4\)

\(^3\) Berg, E. W., Truemper, J. T., J. Phys. Chem. 64, 487 (1960).
Hexafluoroacetylacetone, as pointed out previously, reacts with water so syntheses of metal chelates of this ligand are usually performed in non-aqueous media. Ethanol, acetone, and carbon tetrachloride have been used as solvents for the synthesis of hexafluoroacetylacetonates.\(^5\)\(^-\)\(^9\)

In recent years a number of papers which deal with the vibrational spectra of metal acetylacetonates and metal complexes of related beta-diketones have appeared.\(^10\)\(^-\)\(^13\)


\(^12\) Bellamy, L. J., Spicer, G. S., Strickland, J. D. H., ibid, 1952, 4653.

The literature concerning the infrared spectrum of acetylacetone has been summarized by Cotton. The spectrum of the compound indicates that it exists largely in the enol form and that there is considerable hydrogen bonding.

The infrared spectra of the chelates has also been reviewed by Cotton. At that time, there seemed to be some uncertainty in assignments of bands at about 1580, 1520, and 1380 cm⁻¹. Since the appearance of this review, Nakomoto et al. examined a number of acetylacetonates and observed that the band in the 480 to 420 cm⁻¹ region shifts to higher frequency if the metal is changed in the order of complex stability: Co (II) < Ni (II) < Cu (II). It was suggested that this band might be the metal-oxygen stretching mode and calculations verified this prediction.

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Experimental

Preparation of Metal Chelates

Most of the chelates included in this study have been prepared previously. Melting points for these complexes which agreed within ± 1°C of the literature value were obtained. Two of the complexes, gallium and indium hexafluoroacetylacetonate, have not been made prior to this study and their composition was determined by chemical analysis. Yields are only reported for compounds which have not been made previously or for improved synthesis of complexes which were previously made by other methods. A large number of these chelates were used in a comparative infrared spectroscopy study while others were used in initial gas chromatographic work.

**Aluminum acetylacetonate.** This compound was obtained from Aldrich Chemical Company and was re-crystallized from 95% ethanol.

**Aluminum trifluoroacetylacetonate.** This aluminum complex was synthesized by a method described for
aluminum acetylacetonate. This involved the addition of a neutral aqueous solution of trifluoroacetylacetone to an aqueous solution of aluminum (III). After filtering and drying the white precipitate, the complex was recrystallized from hexane. This product proved to be identical to that prepared previously.

**Aluminum hexafluoroacetylacetonate.** Pierce Chemical Company supplied aluminum hexafluoroacetylacetone and it was used without further purification.

**Gallium acetylacetonate.** Gallium metal (99.99% pure) was obtained from Electronic Space Products, Inc., Los Angeles, California. Half a gram was dissolved in 10 ml. of perchloric acid with gentle heating. The pH of this solution was adjusted to about three and a neutral solution of the acetylacetone was added. After a one hour digestion and cooling, the white precipitate of gallium acetylacetone was filtered and recrystallized from 95% ethanol.

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17 Arch, A., Young, R. C., Inorg, Syn. 2, 17 (1946).

**Gallium trifluoroacetylacetonate.** A procedure identical to that described for gallium acetylacetonate was used. However, an alternate method based on extraction was found to be easier and resulted in a better yield. A hundred ml. of solution containing 0.25 g of dissolved gallium was placed in a 200 ml. extraction bottle. Fifty milliliters of benzene containing about four grams of trifluoroacetylacetone was added, the pH was adjusted with sodium hydroxide and the extraction was performed as previously described. The benzene solution was allowed to evaporate at room temperature and the product was recrystallized from hexane. The weight of product obtained was 1.20 grams for a yield of 34 percent.

**Gallium hexafluoroacetylacetone.** Because hexafluoroacetylacetone reacts with water, a non-aqueous media was chosen for this preparation. Gallium metal (0.5 grams) was dissolved in hydrochloric acid which contained a few drops of nitric acid. This gallium chloride solution was neutralized, evaporated to dryness, and the product was dissolved in 100 milliliters of ethyl ether. Six grams of hexafluoroacetylacetone was
added and the solution was heated gently for a few minutes. The ether was evaporated and the white chelate was recrystallized from hexane. The theoretical composition of \( \text{Ga(C}_5\text{H}_6\text{O}_2\text{F}_6)_3 \) is 26.14% C and 49.65% F. Found: 25.05% C and 48.15% F. The complex melted at 84°C and the yield was 9%.

**Indium acetylacetonate.** Indium metal (99.99%) was dissolved in perchloric acid and the method described for gallium acetylacetonate was used to prepare this complex.

**Indium trifluoroacetylacetonate.** The extraction method that was developed for the preparation of gallium trifluoroacetylacetonate was applied to this metal chelate also.

**Indium hexafluoroacetylacetonate.** Indium metal (0.5 grams) was dissolved in nitric acid with gentle heating. The solution was evaporated to dryness and indium nitrate was placed in 100 ml. of absolute ethanol. The ethanol was heated to boiling to dissolve the indium nitrate. When dissolution had occurred, six grams of hexafluoroacetylacetone was added and the solution was
stirred and allowed to evaporate to dryness at room temperature. The product was recrystallized from hexane and 0.35 grams of material which contained 23.62% carbon and 45.38% fluorine were obtained. The theoretical carbon and fluorine values for In(C₅H₀F₆)₃ are 24.52% C and 46.65% F. The melting point of the chelate is 79°C.

The extractable manganese (II) complex. This complex was prepared in an extraction procedure in an attempt to determine the composition of the species that was extracted. About two grams of manganese sulfate was placed in a 200 milliliter extraction bottle and about 100 milliliters of water was added. The pH was adjusted to about six and a benzene solution that contained three grams of trifluoroacetylacetone and two grams of pyridine was added. The benzene layer was allowed to evaporate at room temperature and the material was then dried under reduced pressure for one hour. The results of an analysis were: 39.06% C and 2.90% H. The theoretical composition of Mn(C₅H₄O₂F₃)₂Py is 40.50% C and 2.94% H. If one molecule of water is included in this complex the theoretical analysis is: 39.40% C and 3.30% H.
Manganese (III) trifluoroacetylacetonate.

This complex was prepared in order to follow the back-extraction of manganese (III). About two grams of manganese sulfate was placed in a 200 milliliters extraction bottle containing 100 milliliters of water. The pH was adjusted to about six and 50 milliliters of benzene solution containing three grams of trifluoroacetylacetone was added. The flask was shaken so that some of the trifluoroacetylacetone would partition into the aqueous phase. Potassium permanganate was added, the lid was placed on the bottle, and the two phases were mixed so that any of the manganic complex that formed was immediately extracted. After two or three minutes of shaking, the benzene layer containing the complex was removed. After evaporation of the benzene, the product was re-crystalized from hexane.

Cobalt trifluoroacetylacetonate. Some of this complex was prepared by a method similar to that described for manganese (III) trifluoroacetylacetonate. Hydrogen peroxide was used as the oxidizing agent and the extraction flask was opened to release the hydrogen
that was given off. The dark green organic layer containing the complex was withdrawn and the solvent was allowed to evaporate.

**Vanadium (III) trifluoroacetylacetonate.** An aqueous solution of vanadium (III) was prepared by reduction of vanadyl by a procedure described in Chapter I. Portions of this vanadium (III) solution were placed in 60 milliliter extraction flasks and solutions of trifluoroacetylacetone in benzene were added and the maroon vanadic complex was extracted.

**Chromium and iron trifluoroacetylacetonates.** These two complexes were taken from several extraction flasks. The benzene was allowed to evaporate and the metal chelates were recrystallized from hexane.

**Infrared spectra of metal chelates.** The spectra were obtained using a Perkin-Elmer model 337 spectrophotometer. Potassium bromide disks were used as the medium for the measurements.

**Results and Discussion**

There has been some uncertainty in several infrared band assignments of metal beta-diketone
complexes. A few attempts have been made to relate the frequency of certain bands to the relative stability of these complexes. However, some inconsistencies have appeared in this work. It was the purpose of this study to compare various infrared bands of several beta-diketonates of known stability. The infrared spectrum of trifluoroacetylacetone is shown in Figure 27.

**Aluminum complexes.** The infrared spectra of aluminum acetylacetonate, aluminum trifluoroacetylacetone, and aluminum hexafluoroacetylacetone are shown in Figures 28 through 30. The location of important bands is given in Table 16. The frequency of the band in the 400-500 cm\(^{-1}\) region increases going from hexafluoroacetylacetone to acetylacetone. Nakomoto et. al. made calculations that indicate this region is characteristic of the metal-oxygen stretching frequency.\(^{19}\) The infrared data obtained is consistent with the stability of these aluminum complexes mentioned in Chapter II.

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Figure 27

INFRARED SPECTRUM OF TRIFLUOROACETYLACETONE
Figure 28

INFRARED SPECTRUM OF ALUMINUM ACETYLACETONATE
Figure 29

INFRARED SPECTRUM OF ALUMINUM TRIFLUOROACETYLACETONATE
Figure 30

INFRARED SPECTRUM OF ALUMINUM HEXAFLUOROACETYLA CETONATE
TABLE 16

COMPARISON OF FREQUENCY OF INFRARED BANDS OF KNOWN STABILITY CONSTANTS OF METAL β-DIKETONE COMPLEXES

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>C=\cdots C Stretch, cm⁻¹</th>
<th>C=\cdots O Stretch, cm⁻¹</th>
<th>M=\cdots O Stretch, cm⁻¹</th>
<th>Log β₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum acetylacetonate</td>
<td>1590</td>
<td>1545</td>
<td>490,425</td>
<td>22.3</td>
</tr>
<tr>
<td>Aluminum trifluoroacetyl-</td>
<td>1635</td>
<td>1540</td>
<td>425</td>
<td>12.06</td>
</tr>
<tr>
<td>acetonate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum hexafluoro-</td>
<td>1654</td>
<td>1636</td>
<td>421</td>
<td></td>
</tr>
<tr>
<td>acetylacetonate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gallium acetylacetonate</td>
<td>1575</td>
<td>1525</td>
<td>445</td>
<td>23.6</td>
</tr>
<tr>
<td>Gallium trifluoroacetyl-</td>
<td>1625</td>
<td>1545</td>
<td>431</td>
<td>14.93</td>
</tr>
<tr>
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<tr>
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<td>420</td>
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<tr>
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<tr>
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<tr>
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<td>418</td>
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Table 16 also indicates that the carbonyl stretching frequency decreases as the stability of the metal chelate increases. As the energy of the metal-oxygen bond decreases, electrons are pulled from this region and are more abundant in the carbon oxygen double bond.

The energy of the carbon-carbon double bond increases in the same direction as that of the carbon oxygen double bond. This probably occurs for the same reason that the carbon-oxygen bond increases in energy with decreasing chelate stability. It would probably be better to designate these bonds as C=O and C=C because of the resonance effect in these chelates.

Gallium complexes. The spectra of the three gallium complexes are shown in Figures 31 through 33. The region characteristic of the metal-oxygen stretch again indicates that the energy of this band increases with chelate stability. For some reason, the intensity of this band for gallium hexafluoroacetylacetonate is rather weak.

The frequency of the C=O band is 1525, 1545, and 1625 cm$^{-1}$ for the acetylacetone, trifluoroacetyl-
Figure 31

INFRARED SPECTRUM OF GALLIUM ACETYLACETONATE
Figure 32

INFRARED SPECTRUM OF GALLIUM TRIFLUOROACETYLACETONATE
Figure 33

INFRARED SPECTRUM OF GALLIUM HEXAFLUOROACETYLACETONATE
acetone and hexafluoroacetylacetone complexes respectively. The frequency of the C\cdots C stretch increases similarly. Again, the order of chelate stability is in the opposite direction just as it was for the aluminum complexes.

**Indium complexes.** The spectra of these three complexes are shown in Figures 34 through 36. The frequency of the metal oxygen band is greater for the acetylacetone complex than it is for the trifluoroacetylacetone complex. This band does not appear in the indium hexafluoroacetylacetonate spectrum, probably because it is still lower in energy and is beyond the range of the instrument.

The other two bands listed in Table 16, the C\cdots O and C\cdots C stretching frequencies, increase in energy with greater fluorine substitution. Again, this is reasonable since the electrons are pulled into the ligand when trifluoromethyl groups are present.

**Spectra of the extractable manganese (II) complex.** The spectrum of the manganese (II) species that was extracted is presented in Figure 37. The chemical analysis of this species was given previously and might apply to either \( \text{Mn} \left( \text{C}_5\text{O}_2\text{H}_4\text{F}_3 \right)_2 \cdot \text{Py} \) or
Figure 34

INFRARED SPECTRUM OF INDIUM ACETYLACETONATE
Figure 35

INFRARED SPECTRUM OF INDIUM TRIFLUOROACETYLACETONATE
Figure 36

INFRARED SPECTRUM OF INDIUM HEXAFLUOROACETYLACETONATE
Figure 37

INFRARED SPECTRUM OF THE MANGANESE (II) TRIFLUOROACETYLACETONE–PYRIDINE COMPLEX
Mn\((\text{C}_\text{5} \text{O}_2 \text{H}_4 \text{F}_3\) \_ \ • \ \text{Py}\ • \ \text{H}_2\text{O}\). It is evident from the band at 3500 cm\(^{-1}\) that water is present in the complex. This is probably attached to the coordination sphere of the complex. However, the complex was prepared by extraction from water and it may simply contain moisture.

**General comparison and discussion.** In addition to the comparison of metal complexes containing the same metal but different ligands, other comparisons can also be made. Perhaps the most obvious is a comparison of different complexes containing the same ligand. This comparison of the metal oxygen stretch follows the expected trend with a few exceptions. On the other hand, the trend breaks down somewhat for the other two bands listed in Table 16. Therefore, it may not be possible to compare the energy of these vibrations to the stability of the chelates. Indeed, Bellamy and Branch concluded that no simple relationship exists between the C–O stretching frequency and stability of a series of acetylacetonates.\(^{20}\) However, Holtzclaw

and Collman and West and Riley state that the order of carbonyl stretching frequency is the same as the stability order if the highest band near 1600 cm\(^{-1}\) is selected as the C=O stretching band. However, Nakamoto has shown by calculations that this is the C=C stretching band. The frequency order of this stretch for some divalent metal acetylacetonates is:

\[
\begin{align*}
\text{Pd} &< \text{Cu} < \text{Zn} < \text{Ni} < \text{Co} \\
1570 &< 1580 < 1592 < 1598 < 1601 \text{ (cm}^{-1}\text{)}
\end{align*}
\]

and the stability constants obtained by potentiometric titration are:

\[
\begin{align*}
\text{Pd} &> \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} \\
\log k_1 &> k_2 27.1 > 14.93 > 10.38 > 9.51 > 8.81
\end{align*}
\]

\[\text{Holtzclaw, H. F., Collman, J. P., J. Am. Chem. Soc. 79, 3318 (1957).}\]


Thus, rather than a correlation in the same direction, with the exception of zinc, just the opposite situation is found, i.e. an increase in frequency as the stability constant decreases.

Nakamoto states that it is more reasonable to compare the metal-oxygen stretching frequencies with stability constants. For a series of divalent metal acetylacetonates the order is:²⁵

\[
Pd > Cu > Ni > Zn \quad Co
\]

\[
464 \quad 455 \quad 452 \quad 422 \quad 422
\]

Thus, the order of the metal-oxygen stretching frequencies is the same as the order of stability constants as shown previously. However, the magnitude of the frequency shifts does not match that of stability constants.

Applying this concept to some trivalent metals, Nakamoto and co-workers found the following order:²⁶

\[
Al > Co > Cr > Fe
\]

\[
490 \quad 466 \quad 459 \quad 434
\]


This of course indicates that the iron-oxygen band is relatively weak. However, Izatt et al. reported there are indeed stability constants for iron and aluminum which show that iron forms a more stable chelate. The logarithm of the overall stability constant for iron acetylacetonate is 26.2 and 22.3 for the aluminum complex.\textsuperscript{27} This would indicate that if this is the region in which the metal-oxygen stretch appears, it cannot be used unambiguously for all situations.

It was pointed out in Chapter I that there is evidence of resonance in the chelate ring. Furthermore, Calvin and Wilson suggested that the metal-oxygen band is involved in the resonance system.\textsuperscript{28} If this is true, \( \pi \) electrons as well as \( d \) electrons from the metal might tend to be more or less localized in the chelate ring of stable chelates. In other, weaker chelates, the \( \pi \) electrons may be more localized in the ligand.

\footnotesize

In conclusion, it would seem that one might be able to compare the metal-oxygen stretching frequency and stability of complexes containing similar metals, such as copper and nickel. However, this relationship should probably be used with discretion when comparing metals which are different in nature.
CHAPTER V

ANALYTICAL METHODS BASED ON SOLVENT EXTRATION AND GAS CHROMATOGRAPHY

Historical Introduction

A historical review of quantitative determinations of several metals using solvent extraction and gas chromatography will necessarily be quite brief because this study is the first record of the combination. However, a procedure for the determination of a single metal, chromium, has been reported previously. The chromium was present as a green aquochloro complex and was extracted into carbon disulfide with acetylacetone. A portion of the extract was taken, injected into a gas chromatograph equipped with a flame ionization detector and the chromium was determined quantitatively.

---

1 Brandt, W. W., Haveran, J. E., 142nd American Chemical Society Meeting, Atlantic City, New Jersey, 1962.
Soon after a portion of the author's work was submitted for publication, Moshier and Schwarberg presented an analytical method for aluminum, copper, and iron using a combination of these techniques.²

Experimental

The apparatus and reagents used and procedure for the extraction of the metal ions have been described previously.

Chromatographic Calibration Curves. Because hydrogen ions are released from the ligand upon chelation, the initial pH was adjusted to a higher value than the equilibrium pH. In order to obtain a calibration curve for each metal, the initial pH of each 25 ml. aqueous phase was adjusted to a value between 7.5 and 9.5. After injection of the samples, the equilibrium pH was checked to see that it was in the range of optimum extraction (pH 4.5 to 5.5). Calibration curves were made by plotting the milligrams of metal originally in the aqueous phase versus the area of the chromato-

Figure 38

GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR ALUMINUM TRIFLUOROACETYLACETONATE
BASED ON THE AMOUNT OF ALUMINUM
IN THE AQUEOUS PHASE

Chromatographic conditions are listed with Figure 20
Figure 39

GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR GALLIUM TRIFLUOROACETYLACETONATE
BASED ON THE AMOUNT OF GALLIUM
IN THE AQUEOUS PHASE

Chromatographic conditions are listed in Figure 20.
Milligrams gallium / 25 ml.
Figure 40

GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR INDIUM TRIFLUOROACETYLACETONATE
BASED ON THE AMOUNT OF INDIUM
IN THE AQUEOUS PHASE

Chromatographic conditions are
listed with Figure 20
A r e a, cm²

Milligrams indium / 25 ml.
Figure 41

GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR IRON TRIFLUOROACETYLACETONATE
BASED ON THE AMOUNT OF IRON
IN THE AQUEOUS PHASE

Chromatographic conditions are listed with Figure 22
Area, cm²

Milligrams iron / 25 ml.
Figure 42

GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR CHROMIUM TRIFLUOROACETYLACETONATE
BASED ON THE AMOUNT OF CHROMIUM
IN THE AQUEOUS PHASE

Chromatographic conditions are listed with Figure 23
Area, cm²

Milligrams chromium / 25 ml.
graphic peak. Areas were measured by using peak height times width at half peak height for all metals except indium. A planimeter was used to measure the areas of indium peaks. Reproducible, linear calibration curves were obtained for each metal over the range studied. These calibration curves are given in Figures 38 through 42. These figures illustrate relative response and sensitivity and are not presented for actual use. The curves were found to shift slightly due to small variations in conditions. For this reason a few points on each calibration curve were repeated each day that a series of unknowns were analyzed.

**Spectrophotometric working curve for iron.** Since iron trifluoroacetylacetonate is intensely colored, a spectrophotometric determination of iron in the benzene layer was also studied. The complex showed a broad maximum at 440 μ. Using the same ratio of organic to aqueous phase as described previously, a spectrophotometric working curve was obtained. The Beer-Lambert law was obeyed over the range of 0.2 to 2.4 parts per million of iron originally in the aqueous phase.
Figure 43

SPECTROPHOTOMETRIC WORKING CURVE
FOR IRON

Note: Absorbance of the iron (III) trifluoroacetyleacetone complex in benzene is given. Concentration of iron in the aqueous phase is given on the abcissa.
Chromatographic Determination of Metals in Synthetic Mixtures

Mixtures of aluminum, gallium, and indium.

Known volumes of aluminum, gallium, and indium solutions were pipetted into extraction flasks to give a total volume of 25 ml. Solutions contained from one to four milligrams of aluminum, five to nine milligrams of gallium, and ten to twenty-five milligrams of indium. The total concentration of metal ions never exceeded $8 \times 10^{-3}$ M. Solutions were adjusted to a pH between 7.5 and 9.5 and 5 ml. portions of 0.25 M trifluoroacetylacetone in benzene were added. After four hours shaking, the flasks were allowed to stand and 20 µl samples of the organic layer were withdrawn with a syringe and injected into the chromatograph. The equilibrium pH of the solutions should be 4.5 to 5.5. If emulsion formation occurred during equilibration, the extraction bottles were centrifuged before a sample was taken for gas chromatographic analysis. The chromatograph was maintained at 128°C.

Mixtures of iron and aluminum. Various volumes of solutions containing one to three milligrams of
aluminum and four to eight milligrams of iron were pipetted into extraction flasks to give total volumes of 25 ml. Solutions were adjusted to a pH between 7.5 and 9.5 and 5 ml. portions of 0.25 M trifluoroacetylace-tone in benzene were added. The flasks were shaken for four hours and 20 μl samples of the organic layer were withdrawn and injected into the chromatograph which was maintained at 128°C.

Mixtures of aluminum and chromium. The procedure used was similar to that described for aluminum and iron except three to eight milligrams of chromium were present instead of iron. Also, 0.5 ml. of pyridine was added so the extraction of chromium would occur. The pyridine acted as a buffer so the initial pH was adjusted to about 5.5.

Determination of iron by spectrophotometry and aluminum by gas chromatography. Various volumes of standard aluminum and iron solutions were transferred into extraction flasks to give a total volume of 25 ml. The aluminum was present in two to four milligram amounts, but only 0.2 to 2.4 parts per million of iron was present. The remainder of the procedure was identical
to that described for the chromatographic determination of iron and aluminum with the exception that a 3.0 ml. portion of the organic phase was placed in a one centimeter silica cell and the iron was determined by spectrophotometry at 440 μm.

Separation of iron from aluminum by solvent extraction. Extraction flasks again contained 25 ml. of solution. Aluminum was in the same concentration as described previously and iron was present in either milligram or microgram quantities. The pH was adjusted to a value between 1.5 and 2.0 and iron was determined by either gas chromatography or spectrophotometry. Each extract was checked by gas chromatography, but no aluminum was found.

Interference Studies

Aluminum, gallium, and indium. The effect of diverse ions on the method was studied by adding known quantities of various salts to solutions containing two milligrams of aluminum, five milligrams of gallium, and ten milligrams of indium. The molar concentration of each ion added was originally a hundred, twenty-five or ten times that of gallium. All metal ions
were added as nitrates and diverse anions were added as either sodium or potassium salts.

**Aluminum and iron.** Possible interfering ions were added to solutions containing two milligrams of aluminum and six milligrams of iron. The molar concentration of each ion added was originally a hundred times that of iron. If significant interferences occurred, the concentration of the interfering ion was decreased until the error was reduced to a value less than five percent.

In order to reduce the interference resulting when copper or nickel was present, picolinic acid was added. To extraction flasks containing two milligrams of aluminum, six milligrams of iron and either 70 milligrams of copper or 157 milligrams of nickel, 1.10 grams of picolinic acid was added.

**Aluminum and chromium.** Various ions were added to solutions containing two milligrams of aluminum and six milligrams of chromium in twenty-five milliliters. Again the initial molar concentration was a hundred times that of chromium. The concentration of any species
that interfered at this concentration was reduced until the error of the determination was reduced to a reasonable value.

Determination of aluminum and iron in a nickel-copper alloy. A 1.400 g. sample of National Bureau of Standards Alloy, 162A, was placed in a 100 ml. beaker and dissolved in ten ml. of hot concentrated perchloric acid. After dissolution of the sample, about 25 ml. of distilled water was added. The solution was then filtered through Whatman Blue Line filter paper to remove the silica. The precipitate was washed thoroughly with distilled water and the filtrate and washings were diluted to the mark in a 100 ml. volumetric flask. Twenty-five ml. aliquots of each solution were transferred to extraction flasks. A three and a half mole ratio of picolinic acid per mole of copper and nickel was added to each flask. The pH was brought to about 5.5 with six molar and one molar sodium hydroxide. The remainder of the procedure was the same as that used for the synthetic mixtures.
Determination of aluminum and chromium in a steel sample. Samples weighing about 0.35 grams were placed in hundred ml. beakers. About 10 ml. of hydrochloric acid were added and the mixtures were warmed gently. A few drops of nitric acid were added to each beaker to convert all of the iron to the ferric state. Boiling was avoided because it is necessary to know the approximate concentration of acid in order to perform the isopropyl ether extraction of iron which followed.\(^3\)

After the sample was dissolved, the solution was allowed to cool and it was transferred to 125 ml. separatory funnel equipped with a teflon stopcock. The beaker which formerly contained the sample was then washed about five to seven times with one ml. portions of distilled water and these were added to the separatory funnel. About 50 ml. of isopropyl ether was added to the funnel and the mixture was shaken by hand for about two minutes. The contents were allowed to settle and the lower aqueous layer was removed. It was found that some

of the iron still remained so the aqueous solution was transferred to a new separatory funnel, followed by equal washings with hydrochloric acid and water. The remaining iron was extracted again, and a third and final extraction was made to further insure that no iron remained.

After the above extractions were performed, the solution was bright green in color, due to the formation of an aquo-chloro chromium complex. Attempts were made to extract this species with trifluoroacetylacetone after neutralizing the acid, but no extraction could be obtained. Therefore, the hydrochloric acid solution evaporated nearly to dryness and about five ml. of nitric acid was added and the solution was heated very gently until the faint purple color of chromic nitrate appeared. If the final heating was too vigorous, the solution became yellow indicating that chromium was oxidized to chromate. If this happened, it was easily corrected upon the addition of a few milligrams of sodium bisulfite.

The solution and subsequent washings were transferred to an extraction flask. The pH was adjusted
to about three to four with six molar or one molar sodium hydroxide and one half ml. of pyridine was added. This brought the pH to about 5.5, the proper range of the extraction. Usually, at this point, the volume of the aqueous phase was about 25 ml. and five milliliters of trifluoroacetylacetone in benzene was added and the extraction was performed as it was previously.

Results and Discussion

Aluminum, gallium, and indium determination. A series of eight extractions, each containing two mg. aluminum, five mg. of gallium, and ten mg. of indium in 25 ml. followed by chromatographic separation and determination was checked for precision. The following formula was used to calculate the standard deviation, $S$, for a series of samples.

$$ S = \sqrt{\frac{\sum_{i=1}^{N} (X_i - m)^2}{N - 1}} $$(5.7)

Where $X$ is the value of individual samples;

$m$ is the mean;

$N$ is the number of samples.
The relative standard deviation was 1.98%, 2.48%, and 5.21% for aluminum, gallium, and indium respectively. The precision of the chromatographic procedure alone was checked by making a series of ten injections from one of the aluminum extractions. The relative standard deviation was 1.03% for three mg. of aluminum in 25 ml. The chromatogram for the separation was shown in Chapter III.

The results for a series of synthetic unknowns are given in Table 17. The mean relative error was 2.32%, 2.34%, and 5.20% for aluminum, gallium, and indium respectively. The entire method was checked for interferences by various ions. The results of this study are given in Table 18. The table indicates that the only species studied which interfere significantly are tartrate, copper, and nickel. Tartrate seems to complex the metals so strongly that very little extraction occurs. Copper extracts in preference to some of the group three metals, and nickel seems to form a green precipitate which exhibits an infrared spectrum similar to nickel trifluoroacetylacetonate.
TABLE 17

Analysis of Aluminum, Gallium, and Indium Mixtures

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<th>Found, mg.</th>
<th>Absolute error, mg.</th>
<th>Rel. error, %</th>
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</tr>
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<tr>
<td>15.00</td>
<td>14.50</td>
<td>0.50</td>
<td>3.00</td>
</tr>
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<td>5.00</td>
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<td>5.70</td>
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<tr>
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<td>16.50</td>
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<td>5.70</td>
</tr>
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<td>23.75</td>
<td>1.25</td>
<td>5.00</td>
</tr>
<tr>
<td>25.00</td>
<td>23.75</td>
<td>1.25</td>
<td>5.00</td>
</tr>
</tbody>
</table>
TABLE 18

**EFFECT OF DIVERSE IONS ON THE ANALYSIS OF ALUMINUM, GALLIUM, AND INDIUM MIXTURES**

(2.00 mg. of aluminum, 5.00 mg. of gallium, 10.0 mg. of indium)

<table>
<thead>
<tr>
<th>Species Added (mg)</th>
<th>Molar Ratio Diverse Ion</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ga</td>
<td>Al</td>
</tr>
<tr>
<td>Cl-</td>
<td>381</td>
<td>100</td>
</tr>
<tr>
<td>NO3-</td>
<td>666</td>
<td>100</td>
</tr>
<tr>
<td>SO4-2</td>
<td>1052</td>
<td>100</td>
</tr>
<tr>
<td>Acetate</td>
<td>644</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Tartrate</td>
<td>1630</td>
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<tr>
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<td>407</td>
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<tr>
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<td>163</td>
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<tr>
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<td>100</td>
</tr>
<tr>
<td></td>
<td>157</td>
<td>25</td>
</tr>
<tr>
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<td>10</td>
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<tr>
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<td>25</td>
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<tr>
<td></td>
<td>68</td>
<td>10</td>
</tr>
<tr>
<td>Co+2</td>
<td>633</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>158</td>
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<tr>
<td></td>
<td>63</td>
<td>10</td>
</tr>
<tr>
<td>Cr+2</td>
<td>558</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>140</td>
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</tr>
<tr>
<td></td>
<td>56</td>
<td>10</td>
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<td>59</td>
<td>10</td>
</tr>
<tr>
<td>Zn+2</td>
<td>702</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>25</td>
</tr>
</tbody>
</table>

^aVery little extraction occurred.
^bEmulsion formation.
^cPeak unresolved from Ga peak.
The amount of metal listed in Table 17 was always present in 25 ml. of aqueous solution. It would be possible to obtain greater sensitivity if larger ratios of aqueous volume to organic volume were used. Moreover, since only a few microliters of sample is needed for gas chromatographic separation and detection, it is possible that a micro extraction might be made when only a small sample is available.

Aluminum and iron. The extraction curves for iron and aluminum indicated that an extraction of iron from aluminum might be possible. This separation was attempted and found to be quite successful. Both milligram and microgram quantities of iron were separated from aluminum and the iron was determined by either gas chromatography or spectrophotometry. The results of this separation are given in Tables 19 and 20. Since iron interferes in many aluminum determinations, this separation might be quite useful. Such a separation would not be possible using acetylacetone because the extraction curves for these two metals overlap.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Present (mg)</th>
<th>Found (mg)</th>
<th>Absolute Error (mg)</th>
<th>Relative Error (%)</th>
<th>Present (mg)</th>
<th>Found (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.00</td>
<td>5.98</td>
<td>0.02</td>
<td>0.33</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>6.10</td>
<td>6.00</td>
<td>0.10</td>
<td>1.67</td>
<td>3.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>4.00</td>
<td>4.16</td>
<td>0.16</td>
<td>4.00</td>
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<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>8.00</td>
<td>8.10</td>
<td>0.10</td>
<td>1.25</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>4.00</td>
<td>4.16</td>
<td>0.16</td>
<td>4.00</td>
<td>3.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
TABLE 20

SEPARATION OF IRON FROM ALUMINUM
(Iron determined by spectrophotometry)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron Present (p.p.m.)</th>
<th>Iron Found (p.p.m.)</th>
<th>Absolute Error (p.p.m.)</th>
<th>Relative Error (%)</th>
<th>Aluminum Present (mg)</th>
<th>Aluminum Found (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.40</td>
<td>2.44</td>
<td>0.04</td>
<td>1.66</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>1.60</td>
<td>1.58</td>
<td>0.02</td>
<td>1.25</td>
<td>3.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>0.82</td>
<td>0.02</td>
<td>2.50</td>
<td>3.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>2.40</td>
<td>2.43</td>
<td>0.03</td>
<td>1.25</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.39</td>
<td>0.01</td>
<td>2.50</td>
<td>4.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
A spectrophotometric method was developed using the intense red color of the iron chelate. Two peaks, one at 440 μm and one at 375 μm are present. Using the 440 μm peak, the molar absorptivity of the chelate in the organic phase was found to be 3,860 l/mole/cm. This molar absorptivity is somewhat misleading in that a five fold concentration increase is obtained in the extraction. If the molar absorptivity were based on the iron originally in the aqueous phase, it would be 19,300 l/mole/cm. This method was used to determine iron which was extracted with aluminum and also for iron which was separated from aluminum. The results of the former are given in Table 21 and those for the separation are listed in Table 20. The average relative error for both series combined was 1.85%. No separate interference study was made for this spectrophotometric method. However, an interference study, which will be described later was made for iron and aluminum and very few species were found to interfere. Moreover, no other metal included in this study was found to extract at pH 1.5 so this method should be relatively free from interferences.
**TABLE 21**

**DETERMINATION OF ALUMINUM BY GAS CHROMATOGRAPHY AND IRON BY SPECTROPHOTOMETRY**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aluminum</th>
<th></th>
<th></th>
<th></th>
<th>Iron</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present</td>
<td>Found</td>
<td>Absolute Error</td>
<td>Relative Error</td>
<td>Present</td>
<td>Found</td>
<td>Absolute Error</td>
<td>Relative Error</td>
</tr>
<tr>
<td></td>
<td>(mg)</td>
<td>(Mg)</td>
<td>(mg)</td>
<td>(%)</td>
<td>(p.p.m.)</td>
<td>(p.p.m.)</td>
<td>(p.p.m.)</td>
<td>(%)</td>
</tr>
<tr>
<td>1</td>
<td>2.00</td>
<td>1.95</td>
<td>0.05</td>
<td>2.50</td>
<td>2.40</td>
<td>2.43</td>
<td>0.03</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>3.00</td>
<td>3.04</td>
<td>0.04</td>
<td>1.33</td>
<td>1.60</td>
<td>1.62</td>
<td>0.02</td>
<td>1.24</td>
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<tr>
<td>3</td>
<td>4.00</td>
<td>3.85</td>
<td>0.15</td>
<td>3.95</td>
<td>1.60</td>
<td>1.61</td>
<td>0.01</td>
<td>0.62</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>1.93</td>
<td>0.07</td>
<td>3.50</td>
<td>1.00</td>
<td>0.97</td>
<td>0.03</td>
<td>3.00</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
<td>2.98</td>
<td>0.02</td>
<td>0.67</td>
<td>0.40</td>
<td>0.39</td>
<td>0.01</td>
<td>2.50</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>3.90</td>
<td>0.10</td>
<td>2.50</td>
<td>0.80</td>
<td>0.82</td>
<td>0.02</td>
<td>2.50</td>
</tr>
</tbody>
</table>
The gas chromatogram for the separation of aluminum and iron chelates was shown in Chapter III. It was thought previously that the iron chelate may decompose slightly in the injection port of the chromatograph. More recently, no evidence for any decomposition was found. In this study no evidence of decomposition of either chelate was found in the glass injection port after a series of samples had been analyzed. Furthermore, the infrared spectrum of the eluent for each metal was identical to that of the pure chelate.

The results for a series of synthetic unknowns which were analyzed by solvent extraction and gas chromatography are given in Table 22. The mean relative error was 2.86% for aluminum and 1.60% for iron.

Table 23 shows the effect of various ions on the method. Many metals present in high concentration were found to interfere. Most of these interferences resulted from emulsion formation. When this emulsion became quite


### TABLE 22

**DETERMINATION OF ALUMINUM AND IRON BY GAS CHROMATOGRAPHY**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aluminum</th>
<th></th>
<th></th>
<th></th>
<th>Iron</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present (mg)</td>
<td>Found (mg)</td>
<td>Absolute Error (mg)</td>
<td>Relative Error (%)</td>
<td>Present (mg)</td>
<td>Found (mg)</td>
<td>Absolute Error (mg)</td>
<td>Relative Error (%)</td>
</tr>
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<td>1</td>
<td>2.00</td>
<td>1.90</td>
<td>0.10</td>
<td>5.00</td>
<td>6.00</td>
<td>5.95</td>
<td>0.05</td>
<td>0.83</td>
</tr>
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<td>0.02</td>
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<td>8.20</td>
<td>0.20</td>
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</tr>
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<td>0.03</td>
<td>1.50</td>
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<td>6.10</td>
<td>0.10</td>
<td>1.67</td>
</tr>
<tr>
<td>4</td>
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<td>1.02</td>
<td>0.02</td>
<td>2.00</td>
<td>8.00</td>
<td>8.20</td>
<td>0.20</td>
<td>2.50</td>
</tr>
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<td>3.00</td>
<td>2.90</td>
<td>0.10</td>
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<td>4.05</td>
<td>0.05</td>
<td>1.25</td>
</tr>
<tr>
<td>6</td>
<td>3.00</td>
<td>2.90</td>
<td>0.10</td>
<td>3.33</td>
<td>4.00</td>
<td>4.03</td>
<td>0.03</td>
<td>0.75</td>
</tr>
<tr>
<td>Species</td>
<td>Added (mg)</td>
<td>Molar Ratio</td>
<td>Diverse Ion</td>
<td>Al Relative Error (%)</td>
<td>Fe Relative Error (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
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<td>100</td>
<td>Fe</td>
<td>2.67</td>
<td>3.05</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
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<td>100</td>
<td>Fe</td>
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<td></td>
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</tr>
<tr>
<td>SO₄²⁻</td>
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<tr>
<td>C₂O₄²⁻H₃⁻</td>
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<td>Fe</td>
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<td>3.20</td>
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<td></td>
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</tr>
<tr>
<td>Ni²⁺</td>
<td>630</td>
<td>100</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>25</td>
<td>Fe</td>
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<td>4.00</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>Fe</td>
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<td>1.00</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>100</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>25</td>
<td>Fe</td>
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<td>c</td>
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<td></td>
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<tr>
<td></td>
<td>170</td>
<td>25</td>
<td>Fe</td>
<td>1.25</td>
<td>2.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>633</td>
<td>100</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>158</td>
<td>25</td>
<td>Fe</td>
<td>3.50</td>
<td>12.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Fe</td>
<td>1.50</td>
<td>4.40</td>
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<td></td>
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</tr>
<tr>
<td>Cr³⁺</td>
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<td>100</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>140</td>
<td>25</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mn²⁺</td>
<td>590</td>
<td>100</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>147</td>
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<td>Fe</td>
<td>a</td>
<td>⋯</td>
<td></td>
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<td>10</td>
<td>Fe</td>
<td>2.50</td>
<td>6.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.9</td>
<td>1</td>
<td>Fe</td>
<td>2.10</td>
<td>3.60</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Zn²⁺</td>
<td>702</td>
<td>100</td>
<td>Fe</td>
<td>a</td>
<td>⋯</td>
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<tr>
<td></td>
<td>175</td>
<td>25</td>
<td>Fe</td>
<td>2.50</td>
<td>1.70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aIntense emulsion formation, no injection made.
bPicolinic acid added.
cIron and copper peaks unresolved.
noticeable, the organic phase was not sampled with a syringe for fear of plugging up the needle or contaminating the chromatographic column. When large amounts of nickel were present, iron and aluminum were not completely extracted. Some precipitate formed when nickel was present and the infrared spectrum of the precipitate was obtained. The spectrum showed similarities to that of nickel hydroxide and the tri-fluoroacetylacetone-nickel chelate. Copper was extracted with the other two species and was not resolved from the iron peak using the chromatographic conditions listed. Both copper and nickel picolinates are rather stable in this pH range; the logarithms of the conditional stability constants at pH 5.0 are 12.0 and 12.7 for copper and nickel respectively.\(^7\) In addition, picolinic acid is an effective buffer in this region (\(pK_a = 5.23\)).\(^8\) This reagent also seems to form complexes with iron and aluminum and prevent these metals from precipitating as the hydroxide or hydrated oxide. This is quite


advantageous because complete extraction of aluminum and iron is attained in fifteen minutes when picolinic acid is used.

Iron and aluminum were determined in a nickel-copper alloy, National Bureau of Standards 162 A, which contained 64.00% nickel and 30.60% copper and minor amounts of other elements. The results of the analysis of the alloy are given in Table 24. Very good agreement with the average value listed by the National Bureau of Standards was obtained. Again picolinic acid served as both a buffer for the pH region needed, and as an effective masking agent for copper and nickel.

**Aluminum and chromium.** These two metals form trifluoroacetylacetonates which can be separated readily by gas chromatography. The chromatogram showing this separation was given in Chapter III. A series of eight samples containing from three to ten mg. of chromium and one to three mg. of aluminum. The mean relative error was 3.16% and 2.85% for aluminum and chromium respectively. The fact that the relative error for aluminum increased may seem inconsistent with previous work. However, pyridine is present so that chromium
### TABLE 24

**ANALYSIS OF NATIONAL BUREAU OF STANDARDS ALLOY 162 A**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight of Al Found (mg)</th>
<th>Al Found (%)</th>
<th>N.B.S. Value (%)</th>
<th>Weight of Fe Found (mg)</th>
<th>Fe Found (%)</th>
<th>N.B.S. Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A</td>
<td>1.75</td>
<td>0.500</td>
<td>0.50</td>
<td>7.40</td>
<td>2.12</td>
<td>2.19</td>
</tr>
<tr>
<td>2 A</td>
<td>1.70</td>
<td>0.485</td>
<td></td>
<td>7.60</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>3 A</td>
<td>1.71</td>
<td>0.488</td>
<td></td>
<td>7.41</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>4 A</td>
<td>1.75</td>
<td>0.500</td>
<td></td>
<td>7.59</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>1 B</td>
<td>1.78</td>
<td>0.508</td>
<td></td>
<td>7.85</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>2 B</td>
<td>1.79</td>
<td>0.511</td>
<td></td>
<td>7.85</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>3 B</td>
<td>1.79</td>
<td>0.511</td>
<td></td>
<td>7.87</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>4 B</td>
<td>1.78</td>
<td>0.508</td>
<td></td>
<td>7.87</td>
<td>2.25</td>
<td></td>
</tr>
</tbody>
</table>
may be extracted in a reasonable length of time and it
tails into the aluminum peak. Thus, the area measure­
ment of the aluminum peak is more uncertain.

This method was also checked for possible
interfering ions and the results are given in Table 25.
The presence of pyridine increases the number of inter-
fering ions. This is especially true of some divalent
metals which usually do not extract. However, when an
amine is present, such as pyridine, many divalent metals
are extracted into the organic phase; probably as amine
adducts of the metal chelate. This of course uses some
of the reagent that would otherwise be used to extract
aluminum or chromium.

Aluminum and chromium were then determined in a
chromium, molybdenum, aluminum steel sample (NBS 106A).
This steel sample contained 1.15% chromium, 1.08%
aluminum, 0.203% molybdenum, 0.546% manganese, 0.277%
nickel and minor amounts of other elements. The results
of the determination of aluminum and chromium in this
alloy are given in Table 26. Accurate results for both
of these metals were obtained although the error for
aluminum increased because pyridine was present.
TABLE 25

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF CHROMIUM
(6.00 Mg of Chromium added)

<table>
<thead>
<tr>
<th>Species Added (Mg)</th>
<th>Molar Ratio Fe Diverse Ion</th>
<th>Cr Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1- 381</td>
<td>100</td>
<td>3.16</td>
</tr>
<tr>
<td>NO3- 666</td>
<td>100</td>
<td>2.42</td>
</tr>
<tr>
<td>SO4^-2 1052</td>
<td>100</td>
<td>3.30</td>
</tr>
<tr>
<td>Acetate 644</td>
<td>100</td>
<td>6.05</td>
</tr>
<tr>
<td>Ni^+2 630</td>
<td>100</td>
<td>a</td>
</tr>
<tr>
<td>157</td>
<td>25</td>
<td>8.25</td>
</tr>
<tr>
<td>157</td>
<td>...</td>
<td>4.10</td>
</tr>
<tr>
<td>Cu^+2 682</td>
<td>100</td>
<td>a</td>
</tr>
<tr>
<td>170</td>
<td>25</td>
<td>b</td>
</tr>
<tr>
<td>170</td>
<td>...</td>
<td>b</td>
</tr>
<tr>
<td>Co^+2 633</td>
<td>100</td>
<td>a</td>
</tr>
<tr>
<td>158</td>
<td>25</td>
<td>7.31</td>
</tr>
<tr>
<td>63</td>
<td>...</td>
<td>2.67</td>
</tr>
<tr>
<td>Mo^+3 248</td>
<td>25</td>
<td>10.2</td>
</tr>
<tr>
<td>97</td>
<td>10</td>
<td>4.21</td>
</tr>
<tr>
<td>Mn^+2 590</td>
<td>100</td>
<td>a</td>
</tr>
<tr>
<td>147</td>
<td>25</td>
<td>11.12</td>
</tr>
<tr>
<td>59</td>
<td>10</td>
<td>5.20</td>
</tr>
<tr>
<td>5.9</td>
<td>1</td>
<td>2.60</td>
</tr>
</tbody>
</table>

^a Emulsion formation, no injection made.  
^b Copper and chromium peaks unresolved.
TABLE 26

DETERMINATION OF ALUMINUM AND CHROMIUM IN CHROMIUM-MOLYBDENUM-
ALUMINUM STEEL NATIONAL BUREAU OF STANDARDS SAMPLE, 106A

<table>
<thead>
<tr>
<th>Sample Wgt Grams</th>
<th>Wgt Al Present (mg)</th>
<th>Wgt Cr Present (mg)</th>
<th>Wgt Al Found (mg)</th>
<th>Wgt Cr Found (mg)</th>
<th>Percent Al Found</th>
<th>Percent Cr Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3330</td>
<td>3.59</td>
<td>3.83</td>
<td>3.33</td>
<td>3.80</td>
<td>1.00</td>
<td>1.14</td>
</tr>
<tr>
<td>0.3355</td>
<td>3.62</td>
<td>3.86</td>
<td>3.48</td>
<td>4.00</td>
<td>1.04</td>
<td>1.19</td>
</tr>
<tr>
<td>0.3360</td>
<td>3.63</td>
<td>3.86</td>
<td>3.56</td>
<td>4.00</td>
<td>1.06</td>
<td>1.19</td>
</tr>
<tr>
<td>0.3350</td>
<td>3.62</td>
<td>3.85</td>
<td>3.42</td>
<td>3.90</td>
<td>1.02</td>
<td>1.16</td>
</tr>
</tbody>
</table>

NBS Values -- 1.08 % Al, 1.15 % Cr
Summary

The extraction of aluminum (III), gallium (III), indium (III), thallium (III), thallium (I), chromium (III), manganese (III), manganese (II), and iron (III) by solutions of trifluoroacetylacetone in benzene has been studied. Distribution ratios and percent extraction values at various pH increments are given for each metal.

Using the distribution ratio, pH, distribution coefficient, acidity constant of trifluoroacetylacetone, and other values, stability constants were calculated for several metal chelates. The logarithm of the overall stability constant was found to be 12.06, 14.93, 13.21, and 18.34 for the trifluoroacetylacetonato complexes of aluminum, gallium, indium, and iron respectively.

Gas chromatographic conditions were found so that several separations of metal-trifluoroacetylacetates were obtained.

The infrared spectra of the acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone complexes of aluminum, gallium, and indium were studied. Attempts were made to relate the frequency of the band in the 400-500 cm\(^{-1}\) region to the stability of the chelate.
Several analytical methods which combine solvent extraction and gas chromatography for the simultaneous determination of several metals were developed. The metals were extracted into benzene with trifluoroacetylacetone and a portion of the benzene layer was injected into a gas chromatograph. The chelates gave well resolved symmetrical peaks. Aluminum, gallium, and indium were determined with a relative mean error of 2.32, 2.34, and 5.20% respectively. Iron and aluminum were determined in a National Bureau of Standards Alloy 162A and aluminum and chromium were determined in a steel alloy, 106A.
# APPENDIX I

Rate Data on the Extraction of Chromium (III)

**Extraction of Chromium (III) With Trifluoroacetylacetone at pH 5.5**

<table>
<thead>
<tr>
<th>Time, Hours</th>
<th>Percent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>11.1</td>
</tr>
<tr>
<td>12.0</td>
<td>30.6</td>
</tr>
<tr>
<td>24.0</td>
<td>47.5</td>
</tr>
<tr>
<td>48.0</td>
<td>69.3</td>
</tr>
</tbody>
</table>

**Extraction of Chromium (III) With Trifluoroacetylacetone and Pyridine at pH 6.0**

<table>
<thead>
<tr>
<th>Time, Minutes</th>
<th>Percent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>9.6</td>
</tr>
<tr>
<td>15.0</td>
<td>40.5</td>
</tr>
<tr>
<td>30.0</td>
<td>73.2</td>
</tr>
<tr>
<td>60.0</td>
<td>97.4</td>
</tr>
<tr>
<td>120.0</td>
<td>99.4</td>
</tr>
</tbody>
</table>

**Extraction of Chromium (III) With Pyridine at pH 6.0**

<table>
<thead>
<tr>
<th>Time, Minutes</th>
<th>Percent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>3.5</td>
</tr>
<tr>
<td>15.0</td>
<td>30.0</td>
</tr>
<tr>
<td>30.0</td>
<td>39.8</td>
</tr>
<tr>
<td>60.0</td>
<td>51.0</td>
</tr>
</tbody>
</table>

**Replacement of Pyridine With Trifluoroacetylacetone in Benzene**

<table>
<thead>
<tr>
<th>Time, Minutes</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>3.0</td>
<td>0.315</td>
</tr>
<tr>
<td>5.5</td>
<td>0.590</td>
</tr>
<tr>
<td>9.0</td>
<td>0.685</td>
</tr>
<tr>
<td>12.0</td>
<td>0.702</td>
</tr>
<tr>
<td>15.0</td>
<td>0.700</td>
</tr>
</tbody>
</table>
SELECTED BIBLIOGRAPHY


