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I SPECTROPHOTOMETRIC DETERMINATION OF URANIUM (VI)
WITH 3-THIANAPHTHENOYLTRIFLUOROACETONE
II SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II)
WITH 3-THIANAPHTHENOYLTRIFLUOROACETONE
III SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM (III)
WITH 3-THIANAPHTHENOYLTRIFLUOROACETONE
IV SOLVENT EXTRACTION OF ZIRCONIUM AND HAFNIUM
WITH 3-THIANAPHTHENOYLTRIFLUOROACETONE
V THE KETO-ENOL TAUTOMERISM OF THIANAPHTHENOYLTRIFLUOROACETONE

By

J. R. Johnston

A Dissertation

Submitted to the Faculty of Graduate Studies through the
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Windsor

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1971

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ABSTRACT

PART I

Two visible spectrophotometric methods are described for the determination of uranium (VI) with 3-thianaphthenoyltrifluoroacetone at a pH of 6.0. The effects due to pH, time, solvents, reagent concentration and diverse ions are reported. Beer's law is obeyed in both cases and the molar extinction coefficients at 408 and 446 nm are 1.7×10^4 and 2.3×10^3 respectively.

PART II

Two visible spectrophotometric determinations are described for the determination of copper (II) with 3-thianaphthenoyltrifluoroacetone at a pH of 4.0. The effects due to pH, time, temperature, solvents, reagent concentration, and diverse ions are reported. Beer's law is obeyed in both cases and the molar extinction coefficients at 410 and 430 nm are 9.3×10^2 and 2.9×10^2 respectively.

PART III

A visible spectrophotometric method is described for the determination of chromium (III) with 3-thianaphthenoyltrifluoroacetone at a pH of 4.0 - 4.5. The effects due to pH, time, temperature, solvents, reagent concentration, and diverse ions are reported. Beer's law is obeyed and the molar extinction coefficient at 460 nm is 1.3×10^3 .

PART IV

A method for the solvent extraction of milligram quantities of zirconium (IV) and hafnium (IV) from 3 molar perchloric acid with 3-thianaphthenoyltrifluoroacetone is described. The effects due to acidity, choice of acid, time, temperature, solvents, and reagent concentration are reported.

PART V

The keto-enol tautomerism of the 2- and 3-isomers of thianaphthenoyltrifluoroacetone has been studied and the results explained by considering the relative negativities of the 2 and 3 positions of thianaphthene. The results of the comparison of the keto-enol tautomerism of 3-thianaphthenoyltrifluoroacetone in 80% benzene - 20% ethanol may explain in part the greater sensitivity of the former in trace metal analysis.

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GENERAL INTRODUCTION

The work described in Parts I - IV involves the extraction of a metal chelate from an aqueous phase to an organic phase. In Parts I - III the extracted chelate forms a coloured solution which may be used to estimate the amount of metal present spectrophotometrically. In Part IV, the metals form a colourless complex and the aqueous layer is analyzed spectrophotometrically to determine the amount of metal not extracted. Part V describes an investigation into one of the properties of the reagent.

In order for a species to be extracted from the aqueous phase to the organic phase it must have a low affinity for the aqueous phase.

Factors resulting in such a low affinity are:

- (i) zero or low charge
- (ii) large size
- (iii) low polarity
- (iv) absence of electronegative atoms at the surface
- (v) low water activity and a highly ordered water structure

In general terms a metal M^{n+} is extracted with a chelating agent HA from an aqueous solution into an organic solvent. If the chelating agent has a denticity d and a charge x , and if the coordination number of the metal is N , then ideally $m/x = N/d$. The ratio $N/m = 2$ is very common. Thus when a metal M^{n+} reacts with a bidentate chelate anion A^{2-} , an electrically neutral and coordinatively saturated complex MA_m is

formed which may then be extracted into the organic phase.

The chelating agent HA possesses both acidic and basic properties. The acidic functional group loses a hydrogen ion and the basic group provides a pair of electrons for a covalent bond. The most widely used chelating agents in solvent extraction are the β -diketones. These reagents have the general structure:

Such a compound will enolize to the form:

In the enol form they possess a replaceable hydrogen, and a ketonic oxygen for coordination. The nature and structure of R and R' affect the acidity of the hydrogen. Introduction of a trifluoromethyl group

increases the acidity of the enol form in water by several orders of magnitude (1), enabling the reagent to be used at low aqueous pH.

Among the more common β -diketones are:

(ii) benzoylacetone

(iii) dibenzoylmethane

(iv) thenoyltrifluoroacetone

The latter compound is considered to be the most versatile β -diketone for metal extraction. It possesses the enol form

and in aqueous solution it forms a monohydrate (2)

Using thenoyltrifluoroacetone as a model, an analogue, 3-thianaphthenoyltrifluoroacetone

has been used for the spectrophotometric determination of UO_2^{2+} , Cu^{2+} , and Cr^{3+} , as well as the solvent extraction of Zr^{4+} and Hf^{4+} . An investigation of the keto-enol tautomerism of both 2- and 3-thianaphthenoyltrifluoroacetone is also reported.

In spectrophotometry there are two laws which are fundamental in quantitative analysis. The first, Lambert's law, states that the decrease in intensity of a beam of monochromatic radiation is proportional to the path-length of the absorbing material. The second, Beer's law, states that the intensity of a beam of monochromatic radiation decreases exponentially as the concentration of the absorbing species. Combining

these two laws, the familiar expression

$$A = a b c$$

is obtained, where A is the absorbance, a is the absorptivity, b is the path length in cm, and c is the concentration of the absorbing species. If c is expressed in moles per liter, then a is the molar absorptivity ($1 \text{ mole}^{-1} \text{ cm}^{-1}$).

Two other relationships are useful in spectrophotometry: the optimum concentration range and the Sandell sensitivity.

The optimum concentration range is obtained from a Ringbom plot (3,4). Here I , the percent absorptance ($100 - \% \text{ transmittance}$), is plotted against the logarithm of concentration. If a large enough concentration range has been studied, an S - shaped curve is obtained. If the system obeys Beer's law, the point of inflection, given by

$$\frac{d^2 I}{d \log C^2} = 0$$

occurs at 63.2% absorptance or 36.8% transmittancy. Generally the curve has a considerable portion which is nearly linear. The extent of this straight line indicates the optimum concentration range.

The Sandell sensitivity (5), which is defined as the number of micrograms of element, converted to the coloured product, which in a column of solution having a cross section of 1 cm^2 shows an absorbance of 0.001, indicates the minimum detectable weight of the element.

PART I
SPECTROPHOTOMERIC
DETERMINATION OF URANIUM (IV)
WITH 3-THIANAPHTHENOYLTRIFLUOROACETONE

CHAPTER I

INTRODUCTION

A wide variety of reagents have been used for the solvent extraction of uranium (VI). β -Diketones are quite versatile in that they are not only used as extracting reagents, but the coloured chelate solution may also be used for a spectrophotometric determination of the uranium.

Acetylacetone (6 - 14), benzoylacetone (13 - 15), dibenzoylmethane (13, 16-21), furoyltrifluoroacetone (22), benzoyltrifluoroacetone (23), and thenoyltrifluoroacetone (24 - 31) have been used.

The latter compound has enjoyed the greatest popularity, having been used for the past two decades. More recently, synergistic extraction has been studied with thenoyltrifluoroacetone and tributylphosphate (32 - 36), various sulfoxides (35,37), trioctylphosphine oxide (34,36), and antipyrine (37).

The present work gives two analytical methods for the spectrophotometric determination of uranium (VI) with 3-thianaphthenoyltrifluoroacetone. A number of parameters such as pH, time, temperature, reagent concentration, and diverse ions have been studied. The results are compared to those obtained by Khopkar and De (26,27) using thenoyltrifluoroacetone.

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectral studies and light absorption measurements were made with a Beckman D B spectrophotometer equipped with a Sargent Model-SRL recorder and 1.00 cm silica cells. A Sargent Model - D R pH meter was used for pH measurements.

2) 3-Thianaphthenoyltrifluoroacetone

The synthesis of this reagent is given in Appendix I. A 2% w/v solution of the monohydrate in ethanol was used.

3) Standard Uranium (VI) Solution

A stock solution was prepared by dissolving 2.1 g of uranyl nitrate in 1 liter of water and standardizing gravimetrically with oxine according to the procedure outlined in Vogel (39) to give a solution containing 0.988 mg/ml of uranium (VI).

4) Diverse Cation Solutions

Reagent grade chloride or nitrate salts were used. Osmium, rhenium, and selenium solutions were prepared from the corresponding oxides.

5) Diverse Anion Solutions

These were prepared from reagent grade sodium, potassium, or ammonium salts.

6) Buffer Solution

A 1 molar ammonium acetate solution was adjusted to a pH of 6.0

8.

with acetic acid.

7) Sodium Tartrate, Benzene, and Ethanol

ACS grades were used.

B. PROCEDURES

1) Recommended General Procedure at 408 nm.

An aliquot of sample solution containing 0 - 240 μg of uranium (VI) was taken and placed in a 50 ml beaker. Ten ml of buffer were added and by pipette 2 ml of reagent solution. The mixture was transferred to a separatory funnel and extracted by shaking for 1 minute with 10 ml of a mixture of 80% benzene - 20% ethanol by volume. The aqueous layer was rinsed with 5 ml of the benzene - ethanol solution for 30 seconds. The extracts were transferred to a 25 ml glass stoppered graduated cylinder and were made up to volume with benzene. The solution was filtered through a medium fast filter paper and the absorbance was measured against a reagent blank prepared in a similar manner. The amount of uranium (VI) may be determined from a previously prepared calibration curve.

2) Recommended General Procedure at 446 nm.

An aliquot of sample solution containing 0 - 1600 μg of uranium (VI) was taken and placed in a 50 ml beaker. Two ml of 10% sodium tartrate solution, 10 ml of buffer solution, and 1 ml of reagent solution were added. The solution was mixed, transferred to a separatory funnel, and was extracted with 10 ml of benzene - ethanol for 1 minute. The two phases were separated and 1 ml of the reagent solution was added to the aqueous layer. The extraction was repeated with 10 ml of the benzene - ethanol mixture. The aqueous layer was rinsed with 5 ml of the solvent mixture for 30 seconds. The extracts were transferred to a 25 ml glass stoppered graduated cylinder and were diluted to volume with benzene.

10.

The solution was filtered through a medium fast filter paper and the absorbance was measured at 446 nm against a reagent blank prepared in a similar manner. The amount of uranium (VI) may be determined from a previously prepared calibration curve.

CHAPTER III

RESULTS

1) Effect of pH

The optimum pH range for complex formation and extraction was 3.0 to 9.0 as is shown in Fig. 1. The pH was varied by the addition of dilute hydrochloric acid and dilute potassium hydroxide to unbuffered solutions containing 10 ml of 1 molar potassium chloride solution. In the presence of tartrate the optimum range was 5.5 to 6.5.

2) Effect of Time and Temperature

The yellow uranyl complex developed almost immediately at room temperature. Heating tended to destroy the complex and should not be employed.

3) Effect of Reagent Concentration

A large excess of reagent was employed. At 408 nm there was no significant change in absorbance when 0.50 or 5.0 ml of reagent solution were used providing measurements were made against a blank containing an identical amount of reagent. Low absorbance readings were obtained when less than 0.5 ml of reagent solution were used. At 446 nm there was no significant difference in absorbance when 1.2 or 5.0 ml of reagent solution were used. Low absorbance readings were obtained for 1.0 ml or less of reagent solution.

4) Stability of the Complex

The benzene - ethanol extracted complex was stable for at least 24 hours in direct light.

Figure 1. Effect of pH on complex formation. Readings were made at 408 nm using 200 μg U(VI).

FIGURE 1

13.

5) Choice of Solvent

Using the recommended procedures in the complex was completely extracted into benzene - ethanol and partially extracted into chloroform, carbon tetrachloride, benzene, and toluene as shown in Table I.

6) Conformity to Beer's Law

At 408 nm a straight line was obtained over the range 0 - 9.5 ppm when absorbance was plotted against concentration as shown in Fig. 2. The optimum concentration range as evaluated by Ringbom's method (3,4) was 3.2 - 6.4 ppm (Fig.3). At 446 nm a straight line was obtained over the range 0 - 63 ppm (Fig. 4) and the optimum range was 24 - 47 ppm (Fig.5).

7) Spectral Characteristics of the Uranium (VI) Complex

The extracted complex exhibited an absorption maximum at 408 nm. At this wavelength the molar extinction coefficient was 1.7×10^4 and the Sandell sensitivity (5) $0.014 \mu\text{g cm}^{-2}$. There was considerable absorption due to the reagent at this wavelength (Fig.6). At 446 nm the spectrum exhibits a slight shoulder analogous to that of the uranyl-thenoyltri-fluoroacetone spectrum at 430 nm. There was a very slight absorption due to the reagent at this wavelength. The molar extinction coefficient at 446 nm was 2.3×10^3 and the Sandell sensitivity, $0.11 \mu\text{g cm}^{-2}$.

8) Effect of Diverse Ions at 408 nm

Five mg of a diverse ion were added to 200 μg of uranium (VI) and the recommended general procedure was followed. An error of 2% in the absorbance reading was considered tolerable. The following ions did

TABLE I.

15.

Extraction of the uranyl-3-thianaphthenoyltrifluoro-
acetone complex* into various solvents

Solvent	Absorbance
80% benzene - 20% ethanol	0.234**
chloroform	0.165
carbon tetrachloride	0.092
toluene	0.113
benzene	0.159

* 600 μ g Uranium (VI) was used in all cases

** complete extraction

16.

Figure 2. Beer's law plot for U(VI) at 408 nm.

FIGURE 2

17

Figure 3. Ringbom plot for U(VI) at 408 nm.

FIGURE 3

Figure 4. Beer's law plot for U(VI) at 446 nm.

FIGURE 4

21

Figure 5. Ringbom plot for U(VI) at 446 nm.

FIGURE 5

Figure 6. Spectra of U(VI) complexes

1. 3-Thianaphthenoyltrifluoroacetone monohydrate (40 mg) extracted into 80% benzene - 20% ethanol according to the procedure at 408 nm against benzene as a blank.
2. Uranium -3-thianaphthenoyltrifluoroacetone (200 μ g U(VI)) extracted into benzene-ethanol according to the procedure at 408 nm.
3. Uranium - thenoyltrifluoroacetone (1 mg U(VI)) extracted into benzene according to the procedure of Khopkar and De (27).

FIGURE 6

25

not interfere: Au^{3+} , Ba^{2+} , Br^- , Cl^- , ClO_3^- , CN^- , Cr^{6+} , I^- , K^+ , Li^+ , Na^+ , NO_3^- , Os^{8+} , Pd^{2+} , Pt^{4+} , SO_3^{2-} , SO_4^{2-} , Se^{4+} , Sr^{2+} , Tl^+ , Zn^{2+} . In the presence of 1 ml of 10% sodium cyanide, 5 mg of the following ions could be tolerated provided that the readings are taken immediately: Hg^{2+} , Ni^{2+} , Rh^{3+} . The following ions at the 5 mg level gave moderate interference (within 10%): Ag^+ , Bi^{3+} , ClO_4^- , Ga^{3+} , NO_2^- , Rh^{3+} , SCN^- . Tartrate interfered at the 50 mg level. The following ions interfered at the 5 mg level: Al^{3+} , As^{3+} , As^{5+} , Be^{2+} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, Ca^{2+} , Ce^{3+} , Ce^{4+} , Co^{2+} , Cr^{3+} , Cu^+ , Cu^{2+} , F^- , Fe^{2+} , Fe^{3+} , Hf^{4+} , In^{3+} , Ir^{3+} , La^{3+} , Mg^{2+} , Mn^{2+} , MnO_4^- , Mo^{6+} , Nb^{5+} , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, Pb^{2+} , Pt^{2+} , Re^{3+} , Re^{7+} , Ru^{3+} , Sb^{3+} , Sb^{5+} , Sn^{2+} , Sn^{4+} , Te^{4+} , Th^{4+} , Ti^{4+} , V^{3+} , VO_3^- , W^{6+} , Zr^{4+} . EDTA, citrate, and NTA interfere severely.

9) Effect of Diverse Ions at 446 nm

Five mg of a diverse ion were added to 600 μg of uranium (VI) and the recommended general procedure at this wavelength was followed. An error of 2% in the absorbance readings was considered tolerable. The following ions did not interfere: Ag^+ , Au^{3+} , Ba^{2+} , Bi^{3+} , Br^- , Ca^{2+} , Cd^{2+} , Cl^- , ClO_4^- , Cr^{6+} , Ga^{3+} , Hg^{2+} , I^- , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , NO_2^- , NO_3^- , Na^+ , Os^{8+} , Pb^{2+} , Pd^{2+} , Pt^{4+} , SCN^- , SO_3^{2-} , SO_4^{2-} , Sb^{3+} , Se^{4+} , Sr^{2+} , Th^{4+} , Tl^+ , W^{6+} , CN^- . A tolerance limits of 2 mg was found for the following ions: La^{3+} , Sb^{5+} , Zn^{2+} . The system could also tolerate 1 mg of the following ions: As^{5+} , In^{3+} , Rh^{3+} , Sn^{2+} . Interferences include: Al^{3+} , As^{3+} , Be^{2+} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, Ce^{3+} , Ce^{4+} , citrate, Co^{2+} , Cu^+ , Cu^{2+} , EDTA, F^- , Fe^{2+} , Fe^{3+} , Hf^{4+} , Ir^{3+} , MnO_4^- , Mo^{6+} , Nb^{5+} , Ni^{2+} , NTA, PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, Pt^{2+} , Re^{3+} , Re^{7+} , Ru^{3+} , Sn^{4+} , Te^{4+} , Ti^{4+} , V^{3+} , VO_3^- , Zr^{4+} .

10) Precision and Accuracy

The precision and accuracy of the methods were studied by analyzing solutions of known amounts of uranium (VI). The results are summarized in Tables II and III.

TABLE II Precision and Accuracy* at 408 nm

Experiment	U (VI) taken		U (VI) found		Relative error %	Standard deviation p.p.m.	Range p.p.m.
	p.p.m.		p.p.m.				
1	3.16		3.06		-3.17	0.05	0.20
2	4.77		4.96		+4.00	0.04	0.16
3	7.90		7.90		0.00	0.04	0.24

TABLE III Precision and Accuracy* at 446 nm

Experiment	U (VI) taken		U (VI) found		Relative error %	Standard deviation p.p.m.	Range p.p.m.
	p.p.m.		p.p.m.				
1	23.7		23.7		0.00	0.10	0.84
2	39.5		39.2		-0.76	0.15	1.60
3	63.2		62.5		-1.11	0.16	2.40

* Each result is the average of 10 separate analyses

CHAPTER IV

DISCUSSION

From the spectrum of the uranyl-3-thianaphthenoyltrifluoroacetone complex (Fig.6) it was clear that the reagent was absorbing strongly in the region of the maximum at 408 nm. For this reason great care had to be taken to see that the blank and the sample solution contained the same amount of reagent. At the shoulder at 446 nm, absorbance due to the reagent is virtually negligible and a procedure was developed at this wavelength as well.

The procedure at 408 nm has limited applicability due to the large numbers of interferences, but it is quite sensitive. Several of the interferences form colourless complexes absorbing in the ultra violet, but with enough overlap to affect the peak at 408 nm. These interferences were often not significant at longer wavelengths.

Tartrate could be used as a masking agent at 446 nm. At 408 nm, tartrate gave a slight interference, but at 446 this was not observed, possibly due to the lower sensitivity at the latter wavelength.

For the above reasons, the procedure at 446 nm would appear to be generally more useful, although it is much less sensitive.

Interference due to tellurium (IV) is to be expected due to the formation of a uranyl-tellurate precipitate (40).

An attempt was made to isolate and analyze the complex. While the results were not reliable due to the difficulty encountered in isolating the pure complex, they indicated that the complex did not have a simple 2:1 ligand: metal complex, but might be a 3:1 ligand: metal complex.

Such complexes have been observed with oxine (39) and with other β -diketones (7,12-15,19) the complex having the general formula $UO_2 \cdot A_2 \cdot HA$.

Such a complex could help explain the lability observed on heating where the complex tended to decompose, and in the case of extraction with carbon tetrachloride following Procedure 2. Here the yellow colour was apparent in the aqueous phase prior to extraction, indicating complex formation. After extraction the aqueous phase was colourless. A further addition of reagent solution again gave a yellow colour in the aqueous layer. This indicated that the solvent was largely stripping the ligand from the uranium.

The reagent, 3-thianaphthenoyltrifluoroacetone, has the following advantages over thenoyltrifluoroacetone:

1. The sensitivity is greater, $0.014 \mu\text{g} \cdot \text{cm}^{-2}$ at 408 nm and $0.11 \mu\text{g} \cdot \text{cm}^{-2}$ at 446 nm as compared to $0.12 \mu\text{g} \cdot \text{cm}^{-2}$ for thenoyltrifluoroacetone at 430 nm.
2. Following the recommended procedure, tartrate does not interfere at 446 nm and may be used as a masking agent. With thenoyltrifluoroacetone tartrate interferes severely (27).
3. The time of extraction is less, two 1 minute extractions as compared to a single 10 minute extraction.
4. Less reagent is required, 2 ml of a 0.07 molar solution in ethanol as compared to 10 ml of a 0.15 molar solution of thenoyltrifluoroacetone in benzene.

CHAPTER V

SUMMARY AND CONCLUSIONS

A method has been developed for the solvent extraction of UO_2^{2+} from aqueous solutions at a pH of 5.5 to 6.5 with 3-thianaphthenoyl-trifluoroacetone. A large excess of reagent was used. Two procedures were developed for the spectrophotometric determination of uranium (VI). At 408 nm the sensitivity is great but there are many interferences. At 446 nm the sensitivity is much less but there are fewer interferences.

Various parameters were investigated. The complex is formed instantaneously at room temperature over a pH range of 3.0 - 9.0, and in the presence of tartrate at a pH of 5.5 - 6.5. The extracted complex was stable for at least 24 hours in direct light. Beer's law was obeyed over wide concentration ranges. Both methods were precise and reasonably accurate, and are superior to that developed with thenoyltrifluoroacetone (27).

A condensed version of this work has been accepted for publication (41).

PART II
SPECTROPHOTOMETRIC
DETERMINATION OF COPPER (II)
WITH 3-THIANAPHTHENOYLTRIFLUOROACETONE

CHAPTER I

INTRODUCTION

A wide variety of β -diketones have been used for the solvent extraction of copper (II): acetylacetone (8,10,13,14,45 - 48), benzoylacetone (13,47), dibenzoylmethane (13,47), thenoyltrifluoroacetone (47,49 - 53), trifluoroacetylacetone (45,54 - 56), furoyltrifluoroacetone (22, 57), and miscellaneous β -diketones (14,45,47,48,56,58 - 60). Acetylacetone (61) and thenoyltrifluoroacetone (62,63) have also been used in synergistic extractions with tributylphosphate.

The present work gives two analytical procedures for the spectrophotometric determination of copper (II) with 3-thianaphthenoyltrifluoroacetone. A number of parameters such as pH, time, temperature, reagent concentration, solvents, and diverse ions have been studied. The results are compared to those obtained by Khopkar and De (50) using thenoyltrifluoroacetone.

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectral studies and light absorption measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model-SRL recorder and 1.00 cm silica cells. A Sargent Model-DR pH meter was used for pH measurements.

2) 3-Thianaphthenoyltrifluoroacetone

The synthesis of the reagent is given in Appendix I. A 2% w/v solution of the monohydrate in ethanol was used at 410 nm. and a 10% w/v solution at 430 nm.

3) Standard Copper (II) Solution

A stock solution was prepared by dissolving 1.00 g of pure copper wire in nitric acid, boiling to remove oxides of nitrogen, and diluting to 1 liter with distilled water to give a solution containing 1.00 mg/ml.

4) Diverse Cation Solutions

Reagent grade chloride or nitrate salts were used. Osmium, rhenium, and selenium solutions were prepared from the corresponding oxides.

5) Diverse Anion Solutions

These were prepared from reagent grade sodium, potassium, or ammonium salts.

6) Buffer Solution

A 0.5 molar sodium acetate solution was adjusted to pH 4.0 with acetic acid.

7) Sodium Fluoride

A saturated solution of A. C. S. grade sodium fluoride was used.

8) Chloroform

Fisher A. C. S. spectroanalyzed grade was used.

B. PROCEDURES

1) Recommended General Procedure at 410 nm

An aliquot of sample solution containing 0-800 μg of copper (II) was taken and placed in a 50 ml beaker. Ten ml of buffer solution were added and by pipette 2 ml of reagent solution. The mixture was heated on a steam bath for 15 minutes, cooled to room temperature, and transferred to a separatory funnel. The copper chelate was extracted by shaking 1 minute with 10 ml of chloroform. The aqueous layer was rinsed for 30 seconds with 5 ml of chloroform and the extracts were transferred to a 25 ml glass stoppered graduated cylinder. Approximately 3 g of anhydrous sodium sulfate were added. The solution was shaken and the absorbance was measured against a reagent blank prepared in a similar manner. The amount of copper (II) may be determined from a previously prepared calibration curve.

2) Recommended General Procedure at 430 nm

An aliquot of sample solution containing 0 - 5 mg of copper (II) was taken and placed in a 50 ml beaker. Two ml of sodium fluoride solution, 10 ml of buffer, and 3 ml of reagent solution were added. The mixture was transferred to a separatory funnel and was extracted with 10 ml of chloroform for 1 minute. The aqueous layer was rinsed for 30 seconds with 5 ml of chloroform. The extracts were transferred to a 25 ml glass stoppered graduated cylinder and were diluted to volume with chloroform. Approximately 3 g of anhydrous sodium sulfate were added. After shaking the absorbance was measured against a reagent blank prepared in a similar manner. The amount of copper (II) may be

determined from a previously prepared calibration curve.

CHAPTER III

RESULTS

1) Effect of pH

The optimum pH range for complex formation was 2.5 to 6.0, as shown in Fig. 7. The study was made by adding 10 ml of 1 molar potassium chloride solution to an unbuffered solution of copper (II) and adjusting the pH with dilute hydrochloric acid and dilute potassium hydroxide solution.

2) Effect of Time and Heating

The green copper complex develops almost immediately at room temperature. Heating gave an increase in absorbance of about 10% at 410 nm, but had no appreciable effect at 430 nm.

3) Effect of Reagent Concentration

A large excess of reagent was required for satisfactory results. At 410 nm 2 ml of 2% w/v reagent solution were sufficient. At 430 nm 3 ml of 10% w/v reagent solution were required.

4) Stability of the Complex

The chloroform extracted complex was stable for at least 24 hours in direct light.

5) Choice of Solvent

The complex was completely extracted into benzene, 80% benzene - 20% ethanol, toluene, xylene, chloroform, and carbon tetrachloride. Chloroform was chosen since it formed the bottom layer.

Figure 7. Effect of pH on complex formation. Readings were made at 410 nm. using 500 μ g Cu(II).

FIGURE 7

40

6) Conformity to Beer's Law

At 410 nm a straight line was obtained over the range 0 - 32 ppm when absorbance was plotted against concentration (Fig. 8). The optimum concentration range evaluated by Ringbom's method (3,4) was found to be 12 - 24 ppm (Fig. 9). At 430 nm a straight line was obtained over the concentration range 0 - 200 ppm (Fig. 10) with an optimum range of 60 - 180 ppm (Fig. 11).

7) Spectral Characteristics of the Copper (II) Complex

The extracted complex exhibited an absorption maximum at 410 nm when read against a reagent blank. At this wavelength the molar extinction coefficient was 9.3×10^2 and the Sandell sensitivity (5), $0.069 \mu\text{g cm}^{-2}$. There was considerable absorption due to the reagent at this wavelength (Fig. 12). At 430 nm the reagent shows very little absorption, the molar extinction coefficient at 430 nm was 2.9×10^{-2} and the Sandell sensitivity was $0.22 \mu\text{g cm}^{-2}$.

8) Effect of Diverse Ions at 410 nm

Five mg of a diverse ion were added to 500 μg of copper (II) and the recommended procedure was followed. An error of 2% in the absorbance readings was considered tolerable. The following ions did not interfere: Ag^+ , As^{3+} , Ba^{2+} , Bi^{3+} , Br^- , Cl^- , ClO_3^- , ClO_4^- , CO_3^{2-} , F^- , Hg^{2+} , I^- , K^+ , Li^+ , Mn^{2+} , Na^+ , Nb^{5+} , NH_4^+ , NO_3^- , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, Re^{3+} , Re^{7+} , Sb^{3+} , Se^{4+} , SO_3^{2-} , SO_4^{2-} , Sr^{2+} , Tl^+ , W^{6+} . A tolerance limit of 2.5 mg was found for the following ions: Ca^{2+} , Cd^{2+} , In^{3+} , La^{3+} , Mg^{2+} , Sb^{5+} , SCN^- , Te^{4+} , Zn^{2+} . The following ions interfered: Al^{3+} , As^{5+} , Au^{3+} , Be^{2+} , Ce^{3+} .

FIGURE 8

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Figure 9. Ringbom plot for Cu(II) at 410 nm.

FIGURE 9

45

Figure 10. Beer's law plot for Cu(II) at 430 nm.

FIGURE 10

47

Figure 11. Ringbom plot for Cu(II) at 430 nm.

FIGURE 11

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Figure 12. Spectrum of the Cu(II) complex.

1. 3-Thianaphthenoyltrifluoroacetone monohydrate (40 mg) extracted into chloroform according to the procedure at 410 nm against chloroform as a blank.
2. Copper -3-thianaphthenoyltrifluoroacetone (500 μ g Cu(II)) extracted into chloroform according to the procedure at 410 nm.

FIGURE 12

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Ce^{4+} , CN^- , Co^{2+} , $\text{C}_2\text{O}_4^{2-}$, Cr^{3+} , Cr^{6+} , Fe^{2+} , Fe^{3+} , Ga^{3+} , Hf^{4+} , Ir^{3+} , MnO_4^- , Mo^{6+} , Ni^{2+} , NO_2^- , Os^{8+} , Pb^{2+} , Pd^{2+} , Pt^{2+} , Pt^{4+} , Rh^{3+} , Ru^{3+} , Sn^{2+} , Sn^{4+} , Th^{4+} , Ti^{4+} , U^{6+} , V^{3+} , VO_3^- , Zr^{4+} . At the 50 mg level the following commonly used masking agents interfered severely: ascorbic acid, N,N-di(2-hydroxy ethyl)glycine, ethylenediaminetetraacetic acid, and nitrilotriacetic acid. At the 50 mg level citrate interfered slightly. At the 100 mg level tartrate interfered severely.

9) Effect of Diverse Ions at 430 nm

Ten mg of a diverse ion were added to 2 mg of copper (II) and the recommended general procedure was followed. An error of 2% in the absorbance readings was considered tolerable. The following ions did not interfere: Ag^+ , Al^{3+} , As^{3+} , As^{5+} , Ba^{2+} , Be^{2+} , Bi^{3+} , Br^- , Ca^{2+} , Cd^{2+} , Ce^{3+} , Cl^- , ClO_3^- , ClO_4^- , CO_3^{2-} , Cr^{6+} , Ga^{3+} , Hf^{4+} , I^- , In^{3+} , Ir^{3+} , K^+ , La^{3+} , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Nb^{5+} , NH_4^+ , NO_3^- , Pb^{2+} , Pt^{2+} , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, Re^{3+} , Re^{7+} , Sb^{3+} , Sb^{5+} , SCN^- , Se^{4+} , Sn^{2+} , Sn^{4+} , SO_3^{2-} , SO_4^{2-} , Sr^{2+} , Te^{4+} , Th^{4+} , Tl^+ , U^{6+} , W^{6+} , Zn^{2+} , Zr^{4+} . A tolerance limit of 5 mg was found for the following ions in the presence of 50 mg citrate: Mo^{6+} and Ti^{4+} . The following ions interfered: Au^{3+} , CN^- , $\text{C}_2\text{O}_4^{2-}$, Ce^{4+} , Cr^{3+} , Fe^{2+} , Fe^{3+} , MnO_4^- , NO_2^- , Ni^{2+} , Os^{8+} , Pd^{2+} , Pt^{4+} , Rh^{3+} , Ru^{3+} , V^{3+} , VO_3^- . The masking agents N,N-di(2-hydroxyethyl)glycine, nitrilotriacetic acid, and ethylenediaminetetraacetic acid interfered.

10) Precision and Accuracy

The precision and accuracy of the methods were studied by analyzing solutions containing known amounts of copper (II). The results are

summarized in Tables IV and V.

11) Formula of the Complex

A green coloured solid (m.p. $294 - 296^{\circ}\text{C}$) was isolated from ethanol solution. Elemental analysis indicated a 2:1 ligand to metal complex.

Analysis calculated for $\text{Cu}(\text{C}_{12}\text{H}_6\text{F}_3\text{O}_2\text{S})_2$: Cu, 10.48 %; C, 47.52 %; H, 2.00 %. Found: Cu, 10.49 %; C, 47.25 %; H 2.15 %. The copper was determined with α benzoin oxime according to the procedure outlined in Vogel (64). The carbon and hydrogen analyses were done by Midwest Microlab, Inc., Indianapolis, Ind.

The complex was dissolved in chloroform and gave a spectrum identical to that obtained by extracting the copper with the reagent from aqueous solution.

TABLE IV Precision and Accuracy* at 410 nm

Experiment	Cu(II) taken p.p.m.	Cu(II) found p.p.m.	Relative error %	Standard deviation p.p.m.	Range p.p.m.
1	8.0	7.94	-0.75	0.046	0.66
2	20.0	20.0	0.00	0.12 ^a	0.60
3	28.0	28.2	+0.71 _e	0.18	1.9

TABLE V Precision and Accuracy* at 430 nm

Experiment	Cu(II) taken p.p.m.	Cu(II) found p.p.m.	Relative error %	Standard deviation p.p.m.	Range p.p.m.
1	40.0	39.6	-1.0	0.24	2.0
2	80.0	81.7	+2.1	0.25	2.7
3	160	160	0.00	0.30	4.4

* Each result is the average of 10 separate analyses.

CHAPTER IV

DISCUSSION

Since the reagent absorbs strongly at 410 nm (Fig. 12), it was decided to develop a second procedure at 430 nm, even though this meant working on a slope. Khopkar and De (50) using thenoyltrifluoroacetone also worked on a slope. It must be pointed out that when working on a slope, care must be taken in adjusting the wavelength setting, and a good instrument must be used.

Both procedures are fairly selective and the precision and accuracy (Tables IV and V) shows them to be reliable. The use of fluoride as a masking agent in Procedure 2 greatly increases the selectivity.

The reagent 3-thianaphthenoyltrifluoroacetone has the following advantages over thenoyltrifluoroacetone in the determination of copper (II):

1. The sensitivity is greater, $0.069 \mu\text{g cm}^{-2}$ at 410 nm and $0.22 \mu\text{g cm}^{-2}$ at 430 nm as compared to $0.29 \mu\text{g cm}^{-2}$ for thenoyltrifluoroacetone at 430 nm.
2. Following the recommended procedure at 430 nm, fluoride does not interfere and may be used as a masking agent. No masking agent was reported with thenoyltrifluoroacetone (50).
3. The time of extraction is less, 1 minute, as compared to 10 minutes.

CHAPTER V

SUMMARY AND CONCLUSIONS

Two procedures have been developed for the spectrophotometric determination of copper (II). The copper-3-thianaphthenoyltrifluoroacetone complex is formed at a pH of 4.0 and develops almost instantaneously at room temperature. Heating enhances the maximum at 410 nm slightly but has no effect at 430 nm.

The complex may be extracted into a variety of solvents. In chloroform, the complex is stable for at least 24 hours in direct light.

Beer's law is obeyed at both wavelengths. The methods are selective and accurate, and are superior to that developed with thenoyltrifluoroacetone (50).

A condensed version of this work has been accepted for publication (65).

PART III
SPECTROPHOTOMETRIC
DETERMINATION OF CHROMIUM (III)
WITH 3- THIANAPHTHENOYLTRIFLUOROACETONE

CHAPTER I

INTRODUCTION

Most methods for the spectrophotometric determination of chromium involve oxidation to chromium (VI); very few have used chromium (III). Di-Na 1,2-diaminocyclohexane-N,N,N',N'-tetraacetate (66,67), xylenol orange (68 - 70), eriochrome cyanine R (68,71), thorin (68), isochinchomeronic (72), and miscellaneous dyes (69) have been used.

β -Diketones such as acetylacetone (13, 73, 74), benzoylacetone (13,75), dibenzoylmethane (75), and thenoyltrifluoroacetone (75 - 77) have been applied to the solvent extraction and determination of chromium (III).

Gas chromatographic analysis of the chromium (III) chelates of hexafluoroacetylacetone (78) and trifluoroacetyl-pivaloylmethane (79) have not proved popular.

This work presents a spectrophotometric method using 3-thianaphthenoyltrifluoroacetone. Various parameters such as pH, time, temperature, reagent concentration, and diverse ions have been studied. The results are compared to those obtained by Majumdar and De (76) using thenoyltrifluoroacetone.

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectral studies and light absorption measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model-SRL recorder and 1.00 cm silica cells. A Sargent Model -DR pH meter was used for pH measurements.

2) 3-Thianaphthenoyltrifluoroacetone

The synthesis of the reagent is described in Appendix I. A 5% w/v solution of the monohydrate in ethanol was used.

3) Standard Chromium (III) Solution

A stock solution was prepared by dissolving 3.85g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water, 1 ml of nitric acid was added and the solution was diluted to 500 ml with distilled water. The solution was standardized gravimetrically by precipitating the chromium as the hydroxide with NH_4OH and igniting to Cr_2O_3 to give a solution containing 1.019 mg/ml.

4) Diverse Cation Solutions

Reagent grade chloride or nitrate salts were used. Osmium, rhenium, and selenium solutions were prepared from the corresponding oxides.

5) Diverse Anion Solutions

These were prepared from reagent grade sodium, potassium, or ammonium salts.

6) Potassium Chloride Solution

A 1 molar solution of A.C.S. grade potassium chloride was used.

7) Xylene

A.C.S. grade was used.

B. PROCEDURE

An aliquot of sample solution containing 0 - 1 mg of chromium (III) was taken and placed in a 50 ml beaker. Ten ml of potassium chloride solution were added. The pH was adjusted to 4.0 - 4.5 with dilute potassium hydroxide and hydrochloric acid. The solution was transferred to a large test tube and 2 ml of reagent solution were added. The mixture was heated in a boiling water bath for at least 30 minutes. The mixture was then cooled to room temperature, transferred to a separatory funnel, and extracted for 1 minute with 10 ml of xylene. The aqueous layer was washed once or twice for 30 seconds with 5 ml of xylene. The extracts were transferred to a 25 ml glass stoppered graduated cylinder and were diluted to volume with xylene. Approximately 3 g of anhydrous sodium sulfate were added. The solution was shaken and the absorbance was measured at 460 nm against a reagent blank prepared in a similar manner. The amount of chromium (III) may be determined from a previously prepared calibration curve.

CHAPTER III

RESULTS

1) Effect of pH

The optimum pH range for complex formation was 4.0 to 4.5 as shown in Fig. 13. Attempts to buffer the solution with acetate, tartrate, citrate, succinate, phthalate, and phosphate were unsuccessful, probably due to some complex formation with chromium (III).

2) Effect of Time and Heating

The orange chromium complex develops slowly and must be heated at at least 90°C for at least 30 minutes for complete complex formation.

3) Effect of Reagent Concentration

At least a six-fold excess of reagent was required. Over the concentration range 0 - 1 mg of chromium (III) 2 ml of 5% w/v reagent solution were sufficient.

4) Stability of the Complex

The xylene extracted complex was stable for at least 24 hours in direct light.

5) Choice of Solvent

The complex was completely extracted into 80% benzene - 20% ethanol and xylene. It was partially extracted into benzene, toluene, hexane, carbon tetrachloride, chloroform, methylene dichloride, and 20% amyl alcohol - 80% methylene dichloride. Xylene was chosen because it was not a mixed solvent and its vapour pressure was lower.

Figure 13. Effect of pH on complex formation. Readings were made with 50 μg Cr(III) at 410 nm.

FIGURE 13

64

6) Conformity to Beer's Law

A straight line was obtained over the range 0 - 40 ppm when absorbance was plotted against concentration (Fig. 14). The optimum concentration range as evaluated by Ringbom's method (3,4) was 8 - 28 ppm (Fig. 15).

7) Spectral Characteristics of the Chromium (III) Complex

The extracted complex exhibited an absorption maximum at 408 nm when read against a reagent blank. At this wavelength the molar extinction coefficient was approximately 3×10^5 . However it proved extremely difficult to obtain reproducible results at this wavelength. For this reason it was decided to use the first shoulder on the spectrum at a wavelength of 460 nm (Fig. 16). At this wavelength the reagent shows very little absorption. The molar extinction coefficient was 1.3×10^3 and the Sandell sensitivity (5) $0.040 \mu\text{g cm}^{-2}$.

8) Effect of Diverse Ions at 460 nm

Five mg of a diverse ion were added to 500 μg of chromium (III) and the recommended procedure followed. An error of 2% in the absorbance readings was considered tolerable. The following ions did not interfere: Ag^+ , Ba^{2+} , Br^- , CN^- , CO_3^{2-} , Ca^{2+} , Cd^{2+} , ClO_3^- , ClO_4^- , Co^{2+} , Ga^{3+} , Hg^{2+} , I^- , La^{3+} , Li^+ , Mg^{2+} , Mn^{2+} , NH_4^+ , NO_2^- , NO_3^- , Na^+ , Ni^{2+} , Pb^{2+} , Pt^{4+} , Re^{3+} , Re^{7+} , SCN^- , SO_3^{2-} , SO_4^{2-} , Sr^{2+} , Tl^+ , Zn^{2+} , acetate. In the presence of 100 mg of N,N-di(2-hydroxyethyl)glycine a tolerance level of 5 mg was found for Bi^{3+} , Ce^{4+} , Ir^{3+} , and Pt^{2+} ; a tolerance level of 4 mg was found for Au^{3+} , of 2.5 mg for Y^{3+} , and 1 mg for Os^{8+} .

It was found that the chromium (III) complex, when formed, is quite

66.

Figure 14. Beer's law plot for Cr(III) at 460 nm.

FIGURE 14

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Figure 15. Ringbom plot for Cr(III) at 460 nm.

FIGURE 15

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Figure 16. Spectrum of Cr(III).

1. 3-Thianaphthenoyltrifluoroacetone monhydrate (100 mg) extracted into xylene according to the recommended procedure against xylene as a blank.
2. Chromium -3-thianaphthenoyltrifluoroacetone (500 μ g Cr(III)) extracted into xylene according to the recommended procedure.

FIGURE 16

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resistant to attack by both acid and base. In the presence of 100 mg of N,N-di(2-hydroxyethyl)glycine, the following ions could be tolerated at the 5 mg level when 3 ml of concentrated hydrochloric acid were added to the separatory funnel just prior to extraction with xylene: Ce^{3+} , Cu^{1+} , UO_2^{2+} . A tolerance level of 2 mg was found for Cu^{2+} under these conditions.

The following ions interfered: Al^{3+} , As^{3+} , As^{5+} , Be^{2+} , $\text{C}_2\text{O}_4^{2-}$, CrO_4^{2-} , F^- , Fe^{2+} , Fe^{3+} , Hf^{4+} , In^{3+} , MnO_4^- , Mo^{6+} , Nb^{5+} , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, Pd^{2+} , Rh^{3+} , Ru^{3+} , S^{2-} , Sb^{3+} , Sb^{5+} , Sn^{2+} , Sn^{4+} , Te^{4+} , Ti^{4+} , V^{3+} , VO_3^- , W^{6+} , Zr^{4+} . At the 50 mg level the following commonly used masking agents interfered severely: ascorbic acid, citrate, ethylenediaminetetraacetic acid, nitrilotriacetic acid, and tartrate.

9) Precision and Accuracy

The precision and accuracy of the method was studied by analyzing solutions containing known amounts of chromium (III). The results are summarized in Table VI.

10) Formula of the Complex

A brown coloured solid (m.p. 242 - 243°C) was isolated from ethanol solution. Elemental analysis indicated a ligand to metal ratio of 3:1.

Analysis calculated for $\text{Cr}(\text{C}_{12}\text{H}_6\text{F}_3\text{O}_2\text{S})_3$: Cr, 6.01%; C, 50.0%; H, 2.05%. Found: Cr, 5.85%; C, 50.17%; H, 2.24%. The carbon and hydrogen analyses were done by Midwest Microlab, Inc., Indianapolis, Ind.

The complex was dissolved in xylene and gave a spectrum identical to that obtained by extracting chromium (III) with the reagent from aqueous solution.

TABLE VI Precision and Accuracy* of chromium (III)

Experiment	Cr (III) — taken p.p.m.	Cr (III) found p.p.m.	Relative error %	Standard deviation p.p.m.	Range p.p.m.
1	8.0	8.15	+1.9	0.04	0.47
2	20.0	20.0	0.0	0.16	0.80
3	28.0	27.7	-1.1	0.14	0.50

* Each result is the average of 10 separate analyses.

CHAPTER IV

DISCUSSION

Similar to the spectra of the uranyl-3-thianaphthenoyltrifluoroacetone (Part I) and copper (II)-3-thianaphthenoyltrifluoroacetone (Part II) complexes, the spectrum of the chromium (III)-3-thianaphthenoyltrifluoroacetone complex exhibited an absorption maximum at 408 nm. The molar absorptivity was approximately 3×10^5 . It was found that extreme care had to be taken to achieve results approaching reproducibility, particularly in the presence of foreign ions. It was therefore concluded that this maximum was unsuitable for quantitative work. At best it might be useful for semi-quantitative analysis or for detection purposes.

The narrow pH range (0.5 pH units) for optimum complex formation indicated that a buffered system was desirable. However, all the buffer systems tried resulted in lower absorbance readings than were obtained by simply adjusting the pH with dilute hydrochloric acid and potassium hydroxide solutions. Majumdar and De (76) used an acetate buffer and reported some difficulties. They investigated and found that a chromium (III)-acetate complex was being formed. A similar explanation could account for the results obtained in this work with buffered solutions.

Once the complex was formed, however, it proved to be very resistant to attack by both acid and base, a fact that was used to increase the selectivity of the procedure.

The fact that the solution had to be heated is not surprising.

Most of the reagents mentioned in Chapter I require heat, frequently boiling for several minutes.

The molar absorptivity of the chromium (III)-3-thianaphthenoyltrifluoroacetone was found to be 1.3×10^3 . While this is not as good as the molar absorptivity with xylenol orange (10^4 at 560 nm), or eriochrome cyanine R ($\approx 2 \times 10^4$ at 520 nm), it is definitely superior to di-Na 1, 2-diaminocyclohexane-N,N,N',N'-tetraacetate (2.4×10^2 at 550 nm), isochinchomeronic (6.9×10 at 520 nm), acetylacetone (6.7×10 at 560 nm), and thenoyltrifluoroacetone (4.2×10^2 at 430 nm).

The precision and accuracy study (Table VI) shows that the method is reliable, and the diverse ion study indicates that it is fairly selective.

The reagent, 3-thianaphthenoyltrifluoroacetone has the following advantages over thenoyltrifluoroacetone:

1. Readings are made on a shoulder and not on a slope (the spectrum of the thenoyltrifluoroacetone complex shows no shoulders (76)).
2. The sensitivity is greater, $0.04 \mu\text{g cm}^{-2}$ at 460 nm as compared to $0.12 \mu\text{g cm}^{-2}$ for thenoyltrifluoroacetone at 430 nm.
3. Following the recommended procedure all of the chromium (III) is extracted compared to at least 80% with thenoyltrifluoroacetone.

CHAPTER V

SUMMARY AND CONCLUSIONS

A method has been developed for the solvent extraction and spectrophotometric determination of chromium (III) with 3-thianaphthenoyltrifluoroacetone. The complex forms slowly at at least 90°C at a pH of 4.0 - 4.5 and is then extracted into xylene.

Beer's law is obeyed over the range 0 - 40 ppm. and the optimum concentration range was found to be 8 - 28 ppm. The molar extinction coefficient was 1.3×10^3 , and the Sandell sensitivity was $0.040 \mu\text{g cm}^{-2}$. The xylene extracted complex was stable for at least 24 hours in direct light. The method was found to be superior to that developed with thenoyltrifluoroacetone (76).

A condensed version of this work has been accepted for publication (80).

PART IV
SOLVENT EXTRACTION OF
ZIRCONIUM AND HAFNIUM WITH
3-THIANAPHTHENOYLTRIFLUOROACETONE

CHAPTER I

INTRODUCTION

Zirconium and hafnium occur in the titanium triad. They are extremely similar chemically, so much so that most monographs discuss zirconium only and close by making a statement to the effect that hafnium reacts identically.

A wide variety of β -diketones have been used to extract the two metals. Acetylacetone for hafnium (10, 81 - 83) and zirconium (10, 13, 83 - 86); benzoylacetone for hafnium (87) and zirconium (13, 88, 89), dibenzoylmethane for zirconium (13); furoyltrifluoroacetone for hafnium (83, 90) and zirconium (83, 90); trifluoroacetylacetone for hafnium (83, 90, 91) and zirconium (86, 91-95); benzoyltrifluoroacetone for hafnium (96, 97) and zirconium (89, 93 - 97); furoylacetone for hafnium (83, 90) and zirconium (83, 90); thenoylacetone for hafnium (83, 90) and zirconium (83, 90); pyrrolyltrifluoroacetone for hafnium (83, 89) and zirconium (83, 89); heptafluoropropionyltrifluoroacetone for hafnium (98) and zirconium (98); isovaleryltrifluoroacetone for hafnium (96) and zirconium (94, 95); methyltrifluoroacetylacetone for zirconium (95); methylpropionyltrifluoroacetone for zirconium (95); trifluoropropionylacetone (95) for zirconium; 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone for hafnium (99) and zirconium (99, 100); and selenoyltrifluoroacetone for hafnium (101) and zirconium (101) have been used.

The most widely used β -diketone, however, is thenoyltrifluoroacetone, described by De (102) as being the most selective extractant for zirconium.

This reagent has been used for both hafnium (83, 90, 96, 103 -107) and zirconium (83, 89, 90, 103, 108 - 118). Synergism with alkyl phosphates has been studied with hafnium (119, 120) and zirconium (121), and with amines for both metals (122).

Since the thenoyltrifluoroacetone chelate is colourless in an organic solvent, the direct determination of zirconium or hafnium has not found favour. Rather, the metal is back-extracted into a sulfuric acid solution and is determined spectrophotometrically with another reagent, e.g. pyrocatechol violet (118).

Gas chromatographic (91) and mass spectrographic (97) analyses of the β -diketone chelates have been of limited use.

In this work, the reagent 3-thianaphthenoyltrifluoroacetone was used to extract milligram amounts of zirconium and hafnium. Various parameters such as acid concentration, type of acid, effect of time and temperature, reagent concentration, and choice of solvent were studied. The amount of metal not extracted was directly determined spectrophotometrically in the aqueous phase with alazarine red S.

CHAPTER II

EXPERIMENTAL

A. APPARTUS AND MATERIALS

1) Instruments

Light absorption measurements were made with a Beckman DB spectrophotometer and 1.00 cm silica cells. A Sargent Model-DR pH meter was used for pH measurements.

2) 3-Thianaphthenoyltrifluoroacetone

1.50 g of the monohydrate was dissolved in about 5 ml of hot ethanol and was added directly to the zirconium or hafnium solution.

3) Standard Zirconium (IV) Solution

A stock solution was prepared by dissolving 10.4057 g of pure zirconium metal in hydrofluoric acid, oxidizing by boiling with nitric acid, removing the hydrofluoroic acid by fuming with perchloric acid, and diluting to 1 liter with distilled water to give a solution containing 10.406 mg/ml. Working solutions of 1.041 mg/ml and 0.520 mg/ml were freshly prepared by evaporating aliquots of the stock solution to a low volume, boiling with concentrated acid to decompose polymeric species, adding the desired amount of acid, and diluting to volume with distilled water.

4) Standard Hafnium (IV) Solution

A stock solution was prepared by treating 10.9701 g of pure hafnium metal according to the procedure for zirconium given above to give a solution containing 10.970 mg/ml. Working solutions of 1.097 mg/ml and

0.549 mg/ml were prepared in a similar manner to the zirconium working solutions.

8) Acids

Reagent grade sulfuric, phosphoric, hydrochloric, nitric, and perchloric acids were used.

9) Xylene

A.C.S. grade was used.

B. PROCEDURE

An aliquot containing 10 mg of zirconium (IV) or hafnium (IV) was taken and placed in a 100 ml beaker. The volume was adjusted to about 20 ml and the acidity to 3M perchloric acid. 1.50 g of 3-thianaphthenoyl-trifluoroacetone dissolved in about 5 ml of hot ethanol were added. The mixture was heated on a steam bath for 15 minutes, then cooled to room temperature and transferred to a separatory funnel. The chelate was extracted into 10 ml of xylene by shaking for 1 minute. The aqueous layer was rinsed for 30 seconds with 5 ml of xylene. The amount of zirconium or hafnium not extracted was determined directly in the aqueous layer spectrophotometrically with alizarine red S according to the procedure given in Elwell and Wood (123).

CHAPTER III

RESULTS

1) Choice of Acid

Preliminary investigations showed that sulfuric and phosphoric acids were unsuitable. At the 10 mg level, zirconium is at best 96% extracted from hydrochloric acid as shown in Table (VII) and completely extracted from at least 1 molar nitric and perchloric acid solutions.

2) Effect of Acid Concentration

The optimum range was from 1 molar to at least 6 molar. Concentrations greater than 6 molar were not investigated. Acid concentrations in the optimum range were determined by titrating an aliquot of the aqueous layer with sodium hydroxide after adding sufficient sodium fluoride to complex any zirconium or hafnium present. Other acid concentrations were obtained by adjusting the pH with potassium hydroxide solution and dilute acid solution. The results for nitric acid are shown in Fig. 17, and for perchloric acid in Fig. 18.

3) Effect of Time and Heating

The complex is completely formed by heating for 15 minutes on a steam bath as is shown in Table VIII.

4) Effect of Reagent Concentration

A large excess of reagent was required. For 10 mg of zirconium, 1.5 g of reagent was sufficient as is shown in Table IX.

TABLE VII
Extraction of zirconium (IV)* from hydrochloric acid

Acid Concentration	$\mu\text{g Zr (IV)}$ Found (aqueous)	% Extraction
2M	625	94
4M	405	96
6M	480	95

* 10.41 mg Zr (IV) in each case.

Figure 17. Effect of HNO_3 concentration on the complex formation of 10.41 mg of Zr(IV) .

FIGURE 17

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Figure 18. Effect of HClO_4 concentration on the complex formation of 10.41 mg of Zr(IV) .

FIGURE 18

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TABLE VIII

Effect of time of heating on the extraction of Zr(IV)*

Time (min)	$\mu\text{g Zr(IV)}$ Found (aqueous)	% Extraction
0	770	92
5	200	98
10	0	100
15	10	100
20	5	100
30	0	100
45	5	100

* 10.41 mg Zr(IV), 2 molar HNO_3 , and 2.0 g of reagent were used in each case. The solvent was 80% benzene - 20% ethanol.

TABLE IX

Effect of reagent concentration on Zr(IV)* extraction.

Amount of Reagent (mg)	$\mu\text{g Zr (IV)}$ Found (aqueous)	% Extraction
100	9700	7.0
205	3070	70.5
402	1430	86.3
612	1250	88.0
804	310	97.0
1002	270	97.4
1200	0	100
1398	0	100
1606	0	100
1802	15	99.9
2004	10	99.9

* 10.41 mg Zr (IV), 2 molar HNO_3 , and 15 minutes heating were used in each case. The solvent was 80% benzene - 20% ethanol.

5) Choice of Solvent

The zirconium complex was completely extracted into 80% benzene-20% ethanol and xylene. It was incompletely extracted into benzene, toluene, chloroform, and carbon tetrachloride as shown in Table X. Xylene was chosen since it was not a mixed solvent and its vapour pressure was lower.

6) Precision

The precision of the method was studied by extracting known amounts of zirconium (IV) and hafnium (IV) and analyzing the aqueous layers spectrophotometrically with alizarine red S (123). The results are summarized in Table XI.

7) Extraction of a Mixture of Zirconium and Hafnium

A mixture of 5.20 mg zirconium and 5.49 mg of hafnium was found to be quantitatively extracted if the procedure was followed.

8) Extraction of an Equimolar Amount of Hafnium

An aliquot containing 20.37 mg of hafnium (IV), equimolar to 10.41 mg zirconium (IV) was treated according to the procedure. The hafnium was found to be quantitatively extracted.

9) Formulae of the Complexes

The xylene - extracted complexes were treated as follows: xylene was evaporated under a stream of air. Excess reagent was removed by stirring in ethanol. Elemental analyses indicated a 4:1 ligand to metal complex in each case.

TABLE X
Extraction of Zr (IV)* into various solvents

Solvent	$\mu\text{g Zr (IV)}$ Found (aqueous)	% Extraction
Chloroform	525	95.0
Carbon tetrachloride	180	98.1
Toluene	160	98.5
Benzene	148	98.6
80% benzene - 20% ethanol	5	100
Xylene	0	100

* 10.41 $\mu\text{g Zr (IV)}$, 2 molar HNO_3 , 1.50 g reagent, and 15 minutes heating were used.

TABLE XI

Precision for the extraction of Zr(IV)* and Hf(IV)**

$\mu\text{g Zr(IV)}$ Found (aqueous)	%Extraction	$\mu\text{g Hf(IV)}$ Found (aqueous)	% Extraction
10	99.90	3	99.97
15	99.85	7	99.93
7	99.93	4	99.96
5	99.95	1	99.99
8	99.92	3	99.97
6	99.94	1	99.99
6	99.94	0	100.00
7	99.93	3	99.97
5	99.95	1	99.99
5	99.95	2	99.98

* 10.41 mg Zr (IV)

** 10.97 mg Hf (IV)

Analysis calculated from $\text{Zr}(\text{C}_{12}\text{H}_6\text{F}_3\text{O}_2\text{S})_4$: Zr, 7.75%; C, 49.1%; H, 2.04%. Found: Zr, 8.00%; C, 49.32%; H, 2.29%. Analysis calculated for $\text{Hf}(\text{C}_{12}\text{H}_6\text{F}_3\text{O}_2\text{S})_4$: Hf, 14.1%; C, 45.6%; H, 1.90%. Found: Hf, 13.8%; C, 45.79%; H, 2.04%.

Carbon and hydrogen analyses were done by Midwest Microlab, Inc., Indianapolis, Ind.

The zirconium complex melted at $245 - 247^\circ\text{C}$, the hafnium complex at $250 - 252^\circ\text{C}$. Both complexes were pale yellow in colour.

CHAPTER IV

DISCUSSION

During the preliminary investigation a number of acid media were studied. It appeared that good results could be obtained from hydrochloric, nitric, and perchloric acids, and more detailed work was done with them. Sulfuric and phosphoric acids gave poor results. This was not surprising since sulfate and phosphate were also found to interfere with the thenoyltrifluoroacetone extraction of zirconium and hafnium (109) due to the formation of stable complexes. A more detailed investigation of hydrochloric acid (Table VII) indicated that this medium was not ideal. Complete extraction was obtained from both nitric and perchloric acids. The optimum, or near optimum range of acid concentration was greater for perchloric acid, and all further work was done in this medium.

When working with aqueous solutions of zirconium and hafnium, the problem of polymerization of the metals arises. Connick and Reas (110) pointed out that the small size and high charge of the Zr^{4+} ion tends to favour hydrolysis in aqueous solution. Their results indicated the presence of dimers and trimers of the general formula $(Zr(OH)_3 \cdot x H_2O)_n^{n+}$. Zielen and Connick (112) working in 1 and 2 molar perchloric acid solutions found evidence for trimers and tetramers. Other workers (124, 125) found that hafnium (IV) forms trimers and tetramers in 1 molar perchloric acid and in 1 molar hydrochloric acid. Continuous polymerization did not occur, the species formed appeared to be stable. They also found (125) that the higher the acid concentration, the less was the amount of polymerization. For these reasons, 3 molar perchloric acid was chosen as the working medium.

The extraction was quantitative for both zirconium and hafnium after shaking for 1 minute. The thenoyltrifluoroacetone extraction of milligram amounts zirconium and hafnium (103) showed that both metals could be extracted with that reagent. Detailed work using radioactive tracers indicated that zirconium was preferentially chelated. Such a study was considered beyond the scope of the present work. Moore (111) working with zirconium, had to extract into xylene for 10 minutes to achieve a quantitative separation. This indicates that the reagent 3-thianaphthenoyltrifluoroacetone may be superior to thepoyltrifluoroacetone for the extraction of zirconium.

CHAPTER V

SUMMARY AND CONCLUSIONS

A method has been developed for the solvent extraction of zirconium (IV) and hafnium (IV) using 3-thianaphthenoyltrifluoroacetone and extracting the complex into xylene. The extraction may be carried out in nitric or perchloric acid solutions. The amount of metal not extracted was determined spectrophotometrically in the aqueous layer with alizarine red S. The results indicate that quantitative extraction was obtained from solutions having an acid concentration of at least 1 molar. To decrease adverse effects due to polymerization of the metals in the aqueous layer, it was recommended that the aqueous layer be at least 3 molar acid.

PART V
THE KETO-ENOL TAUTOMERISM
OF THIANAPHTHENOYLTRIFLUOROACETONE

CHAPTER I

INTRODUCTION

The reagent 3-thianaphthenoyltrifluoroacetone has been applied to the spectrophotometric analysis of iron (III) (126) cerium (IV) (127), uranium (VI) (41), copper (II) (65), and chromium (III) (80). In all cases it was found that 3-thianaphthenoyltrifluoroacetone is a more sensitive reagent than the classical reagent thenoyltrifluoroacetone. It was felt that a comparison of the keto-enol tautomerism of 2-thianaphthenoyltrifluoroacetone (I), 3-thianaphthenoyltrifluoroacetone (II), and thenoyltrifluoroacetone (III) might prove useful in explaining the greater sensitivity of (II) over (III).

(I)

(II)

(III)

CHAPTER II.

EXPERIMENTAL

A. MATERIALS

1) 2-Thianaphthenoyltrifluoroacetone

The synthesis of this reagent is described in Appendix I. A 5% w/v solution in 95% ethanol was used for the aqueous-alcohol solution. All other samples were weighed directly into the reaction flask.

2) 3-Thianaphthenoyltrifluoroacetone Monohydrate

The synthesis of this reagent is described in Appendix I. A 5% w/v solution in 95% ethanol was used for the aqueous-ethanol solution. All other samples were weighed directly into the reaction flask.

3) Thenoyltrifluoroacetone

Fisher certified reagent was used. A 5% w/v solution in 95% ethanol was used for the aqueous-ethanol solution. All other samples were weighed directly into the reaction flask.

4) Bromine, Phenol, Benzene, Ethanol, Potassium Iodide and Sodium Thiosulfate

Reagent grades were used.

5) Bromine Solution

A solution of 1 ml of bromine dissolved in 39 ml of ethanol was prepared immediately before use.

6) Phenol Solution

A 10% w/v solution in ethanol was used.

B. PROCEDURES

1) Aqueous and Aqueous-Ethanol Systems

In the case of aqueous systems, 25 ml of water were added to a weighed sample of the reagent. Aqueous-ethanol solutions were prepared by adding 2 ml of a 5% w/v ethanol solution of the appropriate diketone to 23 ml of water giving a final solution containing about 8% ethanol. The flasks were stoppered and placed in a water bath at 25.0°C for at least 3 hours. The flasks were then removed and 2 ml of bromine solution were added. Bromination was allowed to proceed for 5 seconds, 3 ml of the phenol solution were then added followed by the addition of 5 ml of 0.2 molar potassium iodide solution. The flasks were restoppered and let stand for 30 minutes. The liberated iodine was then titrated with 0.05 N thiosulfate solution. A procedure blank was deducted to give the true titer.

2) Benzene and Benzene-Ethanol Systems

Weighed samples of the diketones were dissolved in 25 ml of solvent and the stoppered flasks were equilibrated for at least 48 hours in a water bath at 25.0°C . The flasks were then removed and 3 ml of the bromine solution were added. After 5 seconds, 4 ml of phenol solution were added followed by 10 ml of a saturated solution of potassium iodide in ethanol. The flasks were restoppered and let stand for 1 hour. The liberated iodine was then titrated with 0.05 N thiosulfate solution. A procedure blank was deducted to give the true titer.

RESULTS AND DISCUSSION

$$\begin{array}{c}
 \text{O} & & \text{OH} \\
 || & & | \\
 \text{R} - \text{C} - \text{CH} = \text{C} - \text{CF}_3 & \xrightarrow{\text{Br}_2} & \text{R} - \text{C} - \underset{\text{Br}}{\overset{|}{\text{C}}} - \underset{\text{Br}}{\overset{|}{\text{C}}} - \text{CF}_3 \\
 & & | \quad | \\
 & & \text{H} \quad \text{OH} \\
 & & | \quad | \\
 & & \text{Br} \quad \text{Br}
 \end{array}$$

-HBr

$$\downarrow$$

$$\text{HBr} + \text{I}_2 + \text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{CF}_3 \longleftarrow \text{2HI} \quad \text{R} - \overset{\text{O}}{\parallel} \text{C} - \underset{\text{Br}}{\overset{|}{\text{C}}} - \overset{\text{O}}{\parallel} \text{C} - \text{CF}_3$$
$$\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$$

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TABLE XII

% Enol *

System	2-Thianaphthenoyl- trifluoroacetone	3-Thianaphthenoyl- trifluoroacetone	Thenoyltri- fluoroacetone
Aqueous **	0.8	1.3	8.2
8% Ethanol	39.9	6.2	10.7
80% benzene- 20% ethanol	41.2	24.4	16.6
benzene	72.5	60.4	94.3

* Average of 3 determinations. All solutions were approximately 0.01 molar.

** Incomplete dissolution with all samples.

Figure 19. The percent enol of the three reagents in various solvents.

- 2-Thianaphthenoyltrifluoroacetone
- 3-Thianaphthenoyltrifluoroacetone
- ▲ Thenoyltrifluoroacetone

- 1 Water
- 2 8% ethanol
- 3 80% benzene - 20% ethanol
- 4 Benzene

FIGURE 19

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bromination indicated thenoyltrifluoroacetone to exist in the enol form in water solution to the extent of 5 to 10%. The close agreement between their results and the results shown in Table XI and Fig. 19 with thenoyltrifluoroacetone indicate that the results found for 2- and 3-thianaphthenoyltrifluoroacetone using the same procedure are reliable. While all three diketones were found to be more enolic as the solvent system becomes less polar, it can be seen that 2-thianaphthenoyltrifluoroacetone exists in the enol form to a greater extent than does 3-thianaphthenoyltrifluoroacetone in the same system.

Farrar and Levine (129) attributed the predominance of the 3-isomer over the 2-isomer found in the acetylation of thianaphthene to greater resonance stability. Since the 3- position is the more favoured for electrophilic substitution this position is presumed to be more electronegative than the 2-position. The results of Auwers and Jacobsen (130) indicate that electron donating substituents decrease the amount of enol formed. Therefore it seems reasonable to conclude that such an inductive effect is responsible for 2-thianaphthenoyltrifluoroacetone being more enolic in nature than 3-thianaphthenoyltrifluoroacetone.

The fact that 2-thenoyltrifluoroacetone is the most enolic in water is probably due to its greater solubility. This may also be the reason for it being more enolic in the 8% ethanol-water solution than is 3-thianaphthenoyltrifluoroacetone. (Both isomers of thianaphthenoyltrifluoroacetone gave turbid systems, thenoyltrifluoroacetone dissolved completely). The reason for the dramatic increase in the per cent enol of thenoyltrifluoroacetone in going from benzene-ethanol to benzene as a

solvent is not clear, but is likely due to a solvent effect.

In the case of cerium (IV) (127) and uranium (VI) (41) an 80% benzene - 20% ethanol solvent was used for extraction of the resulting chelates. From Table XII and Fig. 19 it can be seen that 3-thianaphthenoyltrifluoroacetone in this solvent mixture exists to a significantly greater extent in the enol form than does 2-thienoyltrifluoroacetone. This may in part explain the greater sensitivity of (II) over (III).

It is possible of course that the larger molecular size of (II) compared to (III) has a much greater effect on the relative sensitivities. Since 2-thianaphthenoyltrifluoroacetone has a much larger per cent enol content in this solvent mixture than either 3-thianaphthenoyltrifluoroacetone or thenoyltrifluoroacetone, then studies of the reaction of (I) with uranium (VI) and cerium (IV) may determine whether or not the keto-enol tautomerism of these compounds is of significance regarding sensitivity since the molecular size of (I) is identical to that of (II).

CHAPTER IV

SUMMARY AND CONCLUSIONS

The keto-enol tautomerism of the isomers of thianaphthenoyltrifluoroacetone, as well as that of thenoyltrifluoroacetone has been studied in various solvents by the bromination procedure. The results for thenoyltrifluoroacetone in water and in benzene agree with previously published results (128), indicating that the results given in Table XII and Fig. 19 are reliable.

The greater enol content of 2-thianaphthenoyltrifluoroacetone vs. 3-thianaphthenoyltrifluoroacetone is likely due to the greater electronegativity of the 3- position of the thianaphthene ring producing an inductive effect decreasing the amount of enol.

The results indicate that further studies should be made comparing the sensitivities of the reactions between 2-thianaphthenoyltrifluoroacetone and uranium (VI) and cerium (IV) to those obtained using 3-thianaphthenoyltrifluoroacetone to eliminate the possibility that the greater sensitivity of 3-thianaphthenoyltrifluoroacetone over thenoyltrifluoroacetone is due to the difference in molecular size.

GENERAL SUMMARY AND CONCLUSIONS

Spectrophotometric methods of analysis have been developed for uranium (VI), copper (II), and chromium (III) using 3-thianaphthenoyltrifluoroacetone. The results indicate that the methods are more sensitive than those using the classical reagent thenoyltrifluoroacetone.

On the macroscopic scale, a method has been developed for the solvent extraction of milligram quantities of zirconium (IV) and hafnium (IV).

A study of the keto-enol tautomerism of thenoyltrifluoroacetone and the isomers of thianaphthenoyltrifluoroacetone was made in an attempt to see whether or not this property could explain the greater sensitivity of 3-thianaphthenoyltrifluoroacetone over thenoyltrifluoroacetone.

APPENDIX I

SYNTHESIS OF THE REAGENT

A. ACYLATION OF THIANAPHTHENE (129)

Sixty seven g of thianaphthene (0.5 moles) were dissolved in 60 g acetic anhydride in a 500 ml erlenmeyer flask, and the solution was warmed to room temperature. Eight g of anhydrous ferric chloride catalyst were quickly added, the flask was covered, and the mixture was stirred for at least one hour. The reaction is exothermic; no heating or cooling is required at this stage.

The reaction was stopped by adding 200 ml water. The mixture was transferred into a 1 liter separatory funnel with diethyl ether and was extracted with ether until the extracts were almost colourless (about four extractions). The ether extracts were neutralized with a 10% w/w Na_2CO_3 solution in a beaker or flask of at least 800 ml capacity. Neutralization was assumed to be complete when the addition of Na_2CO_3 solution produced no effervescence on stirring. The contents of the vessel were transferred to the liter separatory funnel with ether and the phases were separated. The aqueous layer was rinsed once with ether. The combined ether extracts were dried over anhydrous calcium sulfate (Drierite), and were filtered through a fast filter paper to remove any small particles of drying agent. The filtrate was transferred to a 200 - 300 ml round-bottomed flask having a standard taper mouth. The ether was evaporated overnight under a stream of air. The residue was a black oil.

Unreacted thianaphthene was recovered by distilling the oil at 60-90°C at less than 3 mm Hg pressure into a 50 ml receiving flask. Bumping was

overcome by stirring (using a teflon coated magnet). Heating was best done in an oil bath, although a close fitting heating mantle also gave satisfactory results. The distillation column was wrapped with heating tape. An aircooled condenser was sufficient, and traces of ether were removed in a liquid nitrogen trap.

When the unreacted thianaphthene had been distilled, the vacuum was broken and the small receiving flask was removed and stoppered. About 10 - 15 g of unreacted thianaphthene were recovered and kept for recycling.

A receiving flask of at least 100 ml capacity was substituted. The system was evacuated to at least 3 mm Hg and the monoketones were distilled. The bulk of the distillate came over at 125 - 130°C. Heating was continued until a temperature of about 140°C was reached. The distillate was usually clear and slightly yellow-brown in colour, although it was white on at least two occasions. The oil must be crystallized by seeding before the isomers of the monoketone can be separated. If no monoketone crystals are available for seeding, the flask should be placed in an ice bath and stirred until crystals form. The yield was about 80% based on the thianaphthene consumed.

(The distillation flask, on cooling, is coated with a gummy to hard tar which is best dissolved by soaking with chloroform or xylene overnight.)

B. SEPARATION OF THE MONOKETONES (129)

Ten g of the mixed monoketone crystals were dissolved in a beaker by warming in 100 ml of 95% ethanol. When in solution, 50 ml of water were added. The solution was stirred and placed in an ice-water bath. The solution was stirred occasionally until a considerable amount (about 4 g) of the 3-isomer had formed. A few mls of ethanol were added and the solution was filtered through a Büchner funnel. The crystals were almost white and melted at not less than 60°C (literature value 64-65°C (129)). The yield was usually about 40% of fairly pure 3-isomer on this first cut. If the melting point was low, a second recrystallization from the ethanol-water solution gave high purity.

The 2-isomer was much more difficult to isolate. The ethanolic filtrates from the first 3-isomer cut described above were evaporated to dryness by heating gently in a heating mantle under a stream of air. Five to 10 g of the dry crystals were dissolved in a beaker in about 300 ml of warm petroleum ether (b.p. 65 - 110°C). When dissolved, the solution was placed in an ice-water bath and stirred occasionally until a considerable amount of crystals had formed (about 2 g). A few ml of solvent were added and the solution was filtered. The crystals were almost white and melted at about 40°C. At least one more crystallization was required before pure 2-isomer was obtained (m.p. of at least 82°C, literature value 87-88°C (129)). The yield is about 5% on this and all subsequent petroleum ether cuts.

More 3-isomer may be isolated by evaporating the petroleum ether from the filtrates and recrystallizing the residue from ethanol-water

as described above. The yield is about 10% on this and all subsequent cuts from ethanol-water.

NOTE: Yields may be increased slightly by seeding with pure crystals when the solutions are cooled in the ice-water bath.

Farrar and Levine (129) tried unsuccessfully to separate the monoketones by fractional distillation. In the course of the present study, attempts using thin-layer chromatography, and gas chromatography also proved unsuccessful; details are given below:

1) Thin-Layer Chromatography on Silica Gel

The following solvent systems were tried using pure monoketones and a 1:1 mixture of the monoketones:

chloroform

carbon tetrachloride

benzene

methylethylketone

methanol

diethyl ether

petroleum ether (b.p. 30 - 60°C)

1:1 benzene : petroleum ether (b.p. 60 - 80°C)

1:2 benzene : petroleum ether (60 - 80°C)

3:2 benzene : petroleum ether (60 - 80°C)

2:1 benzene : petroleum ether (60 - 80°C)

3:2.5 benzene : petroleum ether (60 - 80°C)

3.5:2 benzene : petroleum ether (60 - 80°C)

1:1 methanol : petroleum ether (60 - 80°C)

1:1 chloroform : petroleum ether (60 - 80°C)

2:1 chloroform : petroleum ether (60 - 80°C)

3:2 chloroform : petroleum ether. (60 - 80°C)

Of these solvent systems, 3:2 benzene: petroleum ether gave the greatest amount of tailing for the mixture of monoketones.

2) Gas Chromatography

The following columns and conditions were tried using pure monoketones to ascertain retention times and a 1:1 of the monoketones to see how good the method would be in practice:

R column (general purpose) at 120°C

R column at 180°C

Capillary R column at 130°C

Capillary R column at 140°C

Silicone rubber column at 220°C

10% lac column at 175°C

Carbowax column at 205°C

Silicone rubber column at 230°C

The carrier gases used in the above were nitrogen and helium.

At best, two overlapping peaks were observed, too close together to give pure fractions.

C. SYNTHESIS OF THE DIKETONES (131)

The monoketone must be dry before the condensation reaction can be run. Since the 3-isomer is crystallized from an aqueous solution, it must be dried first by drawing air through the crystals in the Büchner funnel for 5 - 10 minutes, and then by storing for at least 24 hours in a dessicator under line vacuum, or in an ordinary dessicator for at least 48 hours. The 2-isomer may be dried simply by drawing air through the crystals while they are in the Büchner funnel.

The reaction is as follows: 4.5 g of sodium methoxide (which has been stored in a dessicator, preferably under vacuum) were suspended in 75 ml anhydrous diethyl ether (preferably from a freshly opened can) in a dry 200 - 300 ml 3-necked flask. A drying tube containing anhydrous calcium sulfate was placed in one neck and a dry addition funnel was placed in another neck. The third neck was stoppered.

While stirring, 15 g of ethyl trifluoroacetate were added via the addition funnel over a 15 minute period. The mixture tends to effervesce slightly during this time. Then 13 g of monoketone dissolved in the minimum amount of warm anhydrous diethyl ether were added via the addition funnel over a 15 minute period. The beaker in which the monoketone was dissolved was rinsed with diethyl ether and the rinsings were added to the reaction flask via the addition funnel. Stirring was continued for at least 2 hours, often overnight. The reaction was allowed to continue for at least 12 hours after the addition of the monoketone.

The reaction was stopped by adding a dilute solution of acetic acid (5 ml of glacial acetic acid dissolved in 25 ml of water). The contents of the reaction flask were transferred to a 500 ml separatory funnel and

were shaken for about 30 seconds. The aqueous layer was drawn off and the ether layer was rinsed with about 50 ml of water to remove traces of sodium acetate. The aqueous layers were combined. They were rinsed 3 times with diethyl ether, rinsing the ether layer with water each time as described above. The aqueous layers were discarded. The ether extracts were combined and filtered through a fast paper to dry them. Then the yellow ether solution was evaporated under a stream of air with occasional stirring until no odour of acetic acid could be detected. The residue was a mustard yellow powder. If it was not a powder but rather a sludge, washing with petroleum ether converted it to a powder by removing any unreacted monoketone. The petroleum ether washings were evaporated and the residue was recycled.

3-Thianaphthenoyltrifluoroacetone was found to be present as a mono-hydrate. Analysis calculated for $C_{12}H_7F_3O_2S \cdot H_2O$: C, 49.66%; H, 3.14%; H_2O , 6.20%. Found: C, 50.12%; H, 3.32%; H_2O 5.9%. After drying at the melting point, analysis calculated for $C_{12}H_7F_3O_2S$: C, 52.94%; H, 2.59%. Found: C, 52.72%; H, 2.69%. The melting point was 58 - 59°C, literature value 58.5 - 59.5°C (131).

2-Thianaphthenoyltrifluoroacetone was recovered in the anhydrous form, m.p. 95 - 97°C (literature value 96 - 96.5°C (131)). Analysis calculated for $C_{12}H_7F_3O_2S$: C, 52.94%; H, 2.59%. Found: C, 53.20%; H, 2.64%.

The reaction was found to be almost quantitative.

D. SEPARATION OF THE DIKETONES

Attempts to separate the diketones by thin-layer chromatography under the same conditions as described for the monoketones gave similar results. Column chromatography on silica gel using benzene, ethanol, acetone, and petroleum ether was unsuccessful. Fractional distillation at 3 mm Hg was also unsuccessful.

It does appear, however, that the 2-thianaphthenoyltrifluoroacetone sodium salt is relatively insoluble in chloroform or carbon tetrachloride. Attempts to utilize this as a method for the separation of the diketones was not nearly as successful in terms of yield as was the separation of the monoketones by fractional crystallization as described above.

APPENDIX II

Data for the reactions of various metal ions with 3-thianaphthenoyltri-fluoroacetone is summarized below:

Rhodium (III)

Rhodium (III) reacted with the reagent at an optimum pH of 4.0 to form a yellow complex, having a molar absorptivity of 10^3 at the absorption maximum at 410 nm. Heat was required.

Titanium (IV)

Titanium (IV) reacted with the reagent in concentrated hydrochloric acid to form a greenish-yellow complex having an absorption maximum at 410 nm with $a = 10^4$. Heating appeared to increase the colour.

Osmium (VIII)

Osmium (VIII) reacted with the reagent over the pH range 3-6 to form a green complex. Heat was required. The spectrum shows an absorption maximum at 410 nm ($a = 5 \times 10^3$), and shoulders at 420 nm ($a = 3 \times 10^3$), 480 nm ($a = 1 \times 10^3$), and 580 nm ($a = 6 \times 10^2$).

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PUBLICATIONS

1. Effect of pH and phosphate ions on the polarographic behaviour of D-glucuronolactone, by R.J.Thibert and J.R.Johnston. Can. J. Chem., 47 265 (1969):
2. Polarographic reduction of D-mannurono - γ - lactone, by J.R.Johnston and R.J.Thibert. Can. J. Chem., 47, 1433 (1969).
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5. 3-Thianaphthenoyltrifluoroacetone: a new reagent for the spectrophotometric determination of chromium (III), by J.R.Johnston and W.J.Holland. Mikrochim. Acta (Wien), in press.

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