QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF METAL CHELATES OF ACETYLACETONE AND TRIFLUOROACETYLACETONE USING A THERMAL CONDUCTIVITY DETECTOR

A Thesis

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DEGREE OF DOCTOR OF PHILOSOPHY

by

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The quantitative gas phase chromatography of metal chelates of acetylacetone and trifluoroacetylacetone was investigated. Trifluoroacetylacetone chelates are more volatile and can be eluted at lower column temperatures than the corresponding acetylacetone chelates and were, therefore, more extensively studied. Acetylacetonato complexes of beryllium (II), aluminum (III), zirconium (IV), and thorium (IV), and the trifluoroacetylacetonato complexes of beryllium (II), aluminum (III), chromium (III), iron (III), copper (II), cobalt (III), indium (III), and rhodium (III) were quantitatively determined. The analysis of acetylacetonato complexes of cobalt (II), manganese (III), nickel (II), and zinc (II), and trifluoroacetylacetonato complexes of uranyl, cadmium (II), manganese (III), nickel (II), and zinc (II), and trifluoroacetylacetonato complexes of uranyl, cadmium (II), manganese (III), nickel (II), and zinc (II) were unsuccessfully attempted. Separations of several pairs of chelates were effected and the

chelates quantitatively analyzed. A mixture of the trifluoroacetylacetone complexes of beryllium (II), aluminum (III), and copper (II) was separated and quantitatively determined. In order to demonstrate the practical application of this technique, a beryllium-copper alloy was quantitatively analyzed using gas chromatography.

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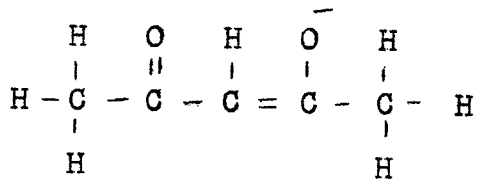
INTRODUCTION

INTRODUCTION

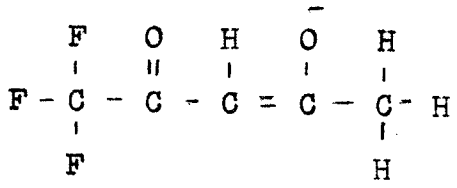
The search for the little "black box" into which a sample may be deposited, and resulting in the complete analysis stamped on a 3" by 5" card, will always be a chemist's dream. Gas chromatography, which has solved many problems for the organic chemist, approaches being the organic chemists' little "black box", for it has enabled the organic chemist to analyze complex mixtures containing over seventy different compounds in one chromatographic determination (1). The use of this technique in inorganic chemistry has developed at a much slower rate, for the applications of gas chromatography in inorganic chemistry have been limited by the difficulty in finding easily volatile compounds. In order to increase the volatility of inorganic compounds, high temperatures would be necessary. Littlewood *et al.* (2) showed that a rise in temperature causes a decrease in the efficiency of separation of a column. High temperature also limits the number of stationary phases that may be used. Under operating conditions the liquid phase should have low volatility and viscosity and a relatively high degree of thermal stability and chemical inertness toward the compounds

to be analyzed. At higher temperatures fewer stationary phases have these properties. High temperatures increase the possibility of thermal decomposition of compounds to be analyzed. Lowering column pressure decreases column efficiency and is avoided whenever possible.

Easily volatile compounds of 1,3 diketone metals (3) and their fluoro derivatives suggested that these could fill the volatility requirements for gas chromatography. Metal chelates containing anions of the following β-diketones were investigated.



2,4 pentanedione (HAA)



1,1,1-trifluoro-2,4 pentanedione (HATA)

This research was aimed at establishing a technique for the quantitative analysis of metal β-diketones via gas chromatography.

GAS CHROMATOGRAPHY

Chromatography was first employed in 1906 by Michael Tswett, a Russian botanist (4), for separating components of plant pigments. Tswett, whose technique is usually referred to as liquid-solid chromatography, found that when a solution of crude chlorophyll was allowed to filter through a column packed with pulverized calcium carbonate, various fractions of the chlorophyll mixture separated distinctively into colored bands. Because he obtained colored bands, he used the term "chromatography"; this term is now misleading when a chromatographic method is applied to colorless materials, but a term which is too well entrenched to be replaced.

In 1941 Martin and Synge (5) introduced liquid-liquid column chromatography, which was further developed by Martin and his co-workers into paper chromatography and proved so rewarding in medical biological research that they were given the Nobel Prize in 1952. Paper chromatography is a useful variation of liquid-solid chromatography where compounds in solution migrate at different rates across and/or down a sheet of porous paper. In their paper, Martin and Synge (5) also

postulated the possibility of gas-liquid chromatography and the advantages of such a technique. In 1952, Martin and James (6) published their classical paper on gas-liquid chromatography and this analytical technique has developed to one which now, by merit of the weight of publication in the field, is worthy of its own journal. More than 1,860 articles and major addresses were published in 1962 and more than 1,800 in 1963. Between 1954 and 1962, the publication rate doubled approximately every two years.

While gas chromatography developed quickly in the field of organic chemistry, the development of this technique in inorganic chemistry was much slower. A review of the application of gas chromatography in inorganic chemistry has been made by Tadmor (7). Tadmor points out that the principles of gas-solid chromatography were applied in inorganic chemistry as early as 1930. The work of Peters and Weil (8) on the separation of inert gases by the adsorption-desorption technique on an activated carbon column can be considered the predecessor of gas-solid chromatography. Van Hook (9) separated ortho and para hydrogen by gas-solid chromatography. The two forms differ slightly in certain physical properties such as thermal conductivity, which provides a method of analysis.

The first experiments using gas-liquid chromatography for the analysis of metal compounds were not reported until 1959, when Wachi (10) used inorganic eutectics and inorganic salts as liquid phases to partially separate the volatile chlorides of tin, antimony and titanium. Keller and Freiser (11) found it possible to separate metals in the form of their volatile halides by a gas-liquid chromatographic technique. They introduced tin (IV) chloride and titanium (IV) chloride as pure liquids and niobium chloride and tantalum chloride in carbon tetrachloride solutions in a chromatographic column packed with Chromosorb (Johns-Manville) carrying a high molecular weight hydrocarbon as liquid phase and column temperature ranged from 100° to 200°C.

The metal halides were not studied in this research because of the high column temperature usually required to elute them and because the reactivity of the compounds presents a problem in sample handling and in choice of materials with which to pack the column. A more serious problem arises from the polymeric, non-volatile, characteristics of many metal halides.

The use of volatile metal β-diketone chelates in gas chromatography was first reported when Duswalt (12)

claimed to have eluted the acetylacetonates of beryllium, scandium and zinc. He dissolved the chelates in benzene and transferred the solution to the column by means of hypodermic syringe. Duswalt stated that all three metal chelates emerged from the column within one minute of injection with a flow of 110 ml per minute of helium at column temperature of 225°C. The chelate peaks were reported as being very broad and, therefore, the peaks that Duswalt observed were probably decomposition peaks for scandium and zinc chelates. Floutz (13) was unable to reproduce Duswalt's work and suggested that "the scandium and zinc chelate peaks observed earlier must have been due to traces of the beryllium chelate which were injected with the scandium and zinc chelates".

In 1960, Biermann and Gesser (14) successfully used gas chromatography for the analysis of the acetylacetonato complexes of beryllium, aluminum and chromium. They suggested that solvent extraction and complex formation combined with gas chromatography would make a useful method of metal analysis. Also, they observed that chromatograms of the complexes were obtained at temperatures well below their boiling points. Bis(2,4-pentanediono)beryllium(II) which has a boiling

point of 270°C and tris(2,4-pentanediono)aluminum(III) which has a boiling point of 314°C gave peaks at 75°C and 120°C respectively. Their paper did not consider the quantitative aspect of the analysis.

Baldwin (15), starting with a copper-beryllium alloy, attempted the quantitative determination of beryllium using gas chromatography. He did not obtain a chromatographic peak for the copper chelate and, therefore, analyzed only the beryllium chelate. If Baldwin would have buffered with solid sodium bicarbonate, he would have been able to determine both beryllium acetylacetonate and copper acetylacetonate, for the chelation is pH dependent.

Sievers and co-workers (16) reported the partial resolution of dl-chromium(III)hexafluoroacetylacetonate by gas-solid chromatography on a dextro quartz column. They (17) also investigated gas liquid chromatography of metal chelates of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone. Sievers and co-workers successfully eluted the trifluoroacetylacetonato complexes of beryllium (II), aluminum (III), indium (III), chromium (III), iron (III), copper (II), rhodium (III), zirconium (IV), and hafnium (IV). They were able to separate multi-component mixtures of these

complexes and also to separate the geometrical isomers of chromium (III) trifluoroacetylacetonate, but there was no mention of any quantitative work being performed.

Hill and Gesser (18) investigated the quantitative gas chromatographic analysis of beryllium, aluminum, and chromium complexes of acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone by using a hydrogen-flame ionization detector. Typical chromatograms of a beryllium, aluminum and chromium acetylacetonate mixture and a beryllium, aluminum and chromium trifluoroacetylacetone mixture were given. Calibration curves for those mixtures were given and the acetylacetonates, the trifluoroacetylacetonates and the hexafluoroacetylacetonates were discussed. The curves were linear, but with the exception of aluminum acetylacetonate, did not pass through the origin. Hill and Gesser explained this as being probably due to the formation of solid metallic oxide particles in the flame.

Ross (19) investigated aluminum and chromium acetylacetonates, trifluoroacetylacetonates, and hexafluoroacetylacetonates to establish conditions for maximum signal-to-noise ratio. An electron

capture detector was used and limits of detection were determined to be 3.3×10^{-11} gram of chromium hexafluoroacetylacetonate and 4.8×10^{-10} gram of aluminum hexafluoroacetylacetonate. Ross and Wheeler (20) reported the determination of chromium hexafluoroacetylacetonate by gas chromatography. An electron capture detector was used to achieve that high sensitivity. There is no quantitative work reported on the aluminum complex even though they had previously reported qualitative work on this complex (19).

Yamakawa and co-workers (21) investigated nineteen kinds of metal acetylacetonates by gas chromatography using columns with various liquid phases. They reported retention volumes for all but the nickel and cobalt (III) acetylacetone complexes. Yamakawa and co-workers arranged the complexes into three catagories, (a) bicoordinate acetylacetonates: barium, beryllium, calcium, cobalt, cadmium, copper, magnesium, manganese, nickel, molybdenum (VI) dioxide, vanadyl and zinc, (b) tricoordinate acetylacetonates: aluminum, cobalt, chromium, iron, and titanium and (c) tetracoordinate acetylacetonates: thorium and zirconium. The only chromatogram given in the paper was for the separation of beryllium, aluminum, and chromium acetylacetonates. Chromatographic peaks for

cobalt(II) and zinc acetylacetonates, for which they reported retention volumes of 275 and 215 respectively at a column temperature of 150°C; were not obtained in the present work. Floutz (13) was also unable to obtain a gas chromatographic analysis for zinc. Floutz reports the following: "Acetylacetonates of the following metals were available for study: aluminum (III), beryllium (II), cerium (III), chromium (III), copper (II), iron (III), manganese (II), scandium (II), thorium (IV), uranium (II), and zinc (II). Of these only aluminum, beryllium and chromium appeared to form chelates of sufficient stability for application of the gas chromatographic method. This study was made over a wide range of operating conditions. The results are in good accordance with reported stabilities of several acetylacetonates. Chelates of the other metals have less definite boiling points and tend to decompose at the temperatures required to carry the sample through the column." He was only able to obtain peaks for three of the eleven acetylacetonates that he tried. Floutz was in disagreement with regard to five compounds with Yamakawa and co-workers: copper (II), iron (III), manganese (II), thorium (IV) and zinc (II) acetylacetonates. Sievers and co-workers (16) report that they were unable to chromatograph the acetylacetonate complexes of

hafnium (IV) and cobalt (III) at column temperatures between 150°C and 230°C. There was no mention of any quantitative work performed in Yamakawa's paper. It is the extension of gas chromatographic technique into the quantitative analysis of metals which constitutes the goal of this thesis.

EXPERIMENTAL

EXPERIMENTAL

Reagents

2,4-Pentanedione (Fischer Reagent Chemical) was found to have turned yellow upon standing: therefore, before being used it was distilled under reduced pressure which produced a water clear product. 1,1,1-Trifluoro-2,4-pentanedione, which had been obtained only a short time before usage, was used as obtained from Columbia Chemicals Co. Inc., and was stored in the refrigerator. Sodium trifluoroacetylacetone was prepared by the condensation of acetone with trifluoroethyl-acetate in the presence of anhydrous sodium ethoxide (22).

$$CF_3COOC_2H_5 + CH_3COCH_3 + NaOC_2H_5 \rightarrow CF_3C(ONa)=CHCOCH_3 + 2C_2H_5OH$$

Chelates

The acetylacetonate complexes of beryllium, aluminum, manganese, nickel, zinc, and cobalt were obtained commercially (MacKenzie Chemical Works, Inc. Central Islip, New York) and were purified by recrystallization from ethanol.

Bis(1,1,1-trifluoro-2,4-pentanedion©)-beryllium(II)

$$BeSO_4 \cdot 4H_2O + 2Na(ATA) \xrightarrow{H_2O} Be(ATA)_2 + Na_2SO_4$$

To a 100 ml of a 5% by weight solution of beryllium sulfate were added 5 g of sodium trifluoroacetylacetone. The mixture was shaken for five minutes, precipitate was collected on a Buchner funnel, washed with water and purified by sublimation at reduced pressure. (See Figure 1, page 14). Melting point was 110° to 111°C, uncorrected. Literature value is 112°C. (25)

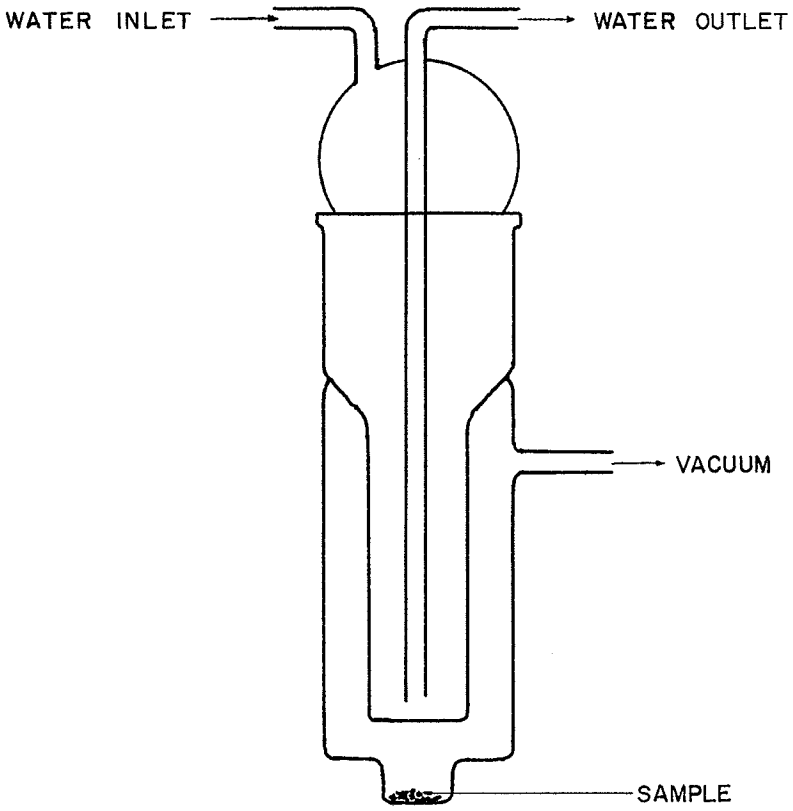
Tris(1,1,1-trifluoro-2,4-pentanediono)aluminum(III)

$$Al(NO_3)_3 \cdot 9H_2O + 3Na(ATA) \longrightarrow Al(ATA)_3 + 3NaNO_3$$

To a 100 ml of a 5% by weight solution of aluminum nitrate were added 5.5 g of sodium trifluoroacetylacetone. The mixture was shaken for five minutes, precipitate was collected on a Buchner funnel, washed with water and purified by sublimation at reduced pressure. (See Figure 1, page 14). Melting point was 119° to 120°C, uncorrected. Literature values are 117°C (25) and 121-122°C (26).

FIGURE 1

Sublimator


WATER INLET
WATER OUTLET
VACUUM
SAMPLE

Tris-(1,1,1-trifluoro-2,4-pentanediono)-chromium(III)

$$CrCl_3 \cdot 6H_2O + 3NaATA \longrightarrow Cr(ATA)_3 + 3NaCl + 6H_2O$$

Two grams of sodium trifluoroacetylacetone were added to a solution containing 0.5 g of chromium (III) chloride. The solution was neutralized with 6 M hydrochloric acid and was shaken for five minutes. The precipitate was filtered with a Buchner funnel, washed with water, air dried and purified by recrystallization from ethanol. Melting range was 150° to 151°C, uncorrected. Literature reports 112° to 114°C for the cis isomer and 154.5° to 155°C for the trans isomer (26).

Tris-(1,1,1-trifluoro-2,4-pentanediono)iron(III)

$$Fe(NO_3)_3 \cdot 9H_2O + 3NaATA \rightarrow Fe(ATA)_3 + 3NaNO_3 + 9H_2O$$

Preparation of $Fe(ATA)_3$ was the same as for the beryllium complex but it was purified by recrystallization from ethanol. Melting range of the red crystals was 112° to 114°C, uncorrected. Literature values are 115°C (25) and 114°C (26).

Bis-(1,1,1-trifluoro 2,4-pentanediono)-copper(II)

$$Cu(NO_3)_2 \cdot 3H_2O + 2H(ATA) \xrightarrow{NaC_2H_3O_2} Cu(ATA)_2 + 2HNO_3 + 3H_2O$$

Two grams of copper (II) nitrate·trihydrate were dissolved in 10 ml of water. This solution was buffered by the addition of 0.5 g of sodium acetate in order to prevent a marked lowering of the pH of the solution as the reaction proceeds, after which 2.4 g of 1,1,1-trifluoro-2,4-pentanedione were added while the solution was being stirred with a magnetic stirrer. In order to ensure complete reaction, it was then stirred for 15 more minutes. The blue precipitate was filtered, washed with water, air dried and recrystallized from benzene. The melting range was 191° to 192°C, uncorrected. Literature values are 200°C (25) and 189°C (27).

Tris-(1,1,1-trifluoro-2,4-pentanediono)-cobalt(III)

The method of preparation has already been reported by Fay and Piper (26). Inasmuch as their procedure was not followed exactly, because Fay and Piper were not interested in obtaining good yields and were interested in separating the optical isomers, our exact method of preparation of this complex will be given.

Sodium tris-carbonatocobaltate(III) trihydrate was prepared according to the method of Bauer and Drinkard (28). A 50 ml solution of 29.1 g of $Co(NO_3)_2 \cdot 6H_2O$(0.10 mole) and 10 ml of 30% hydrogen peroxide was added dropwise to a cold slurry (approximately 0°C) of 42.0 g of sodium bicarbonate (0.50 mole) in 50 ml of H_2O which was being stirred with a magnetic stirrer, the hydrogen peroxide oxidizes cobalt(II) to cobalt(III). The sodium bicarbonate is a buffer that prevents a marked lowering of the pH of the solution as the reaction proceeds. This is necessary because tri-carbonatocobaltate (III) is decomposed by acids. In order to ensure complete reaction the mixture was allowed to stand at 0°C for one hour with continuous stirring. The olive colored product was filtered on a Buchner funnel, washed with three 10 ml portions of cold water, in order to remove excess sodium bicarbonate, then it was washed with three 10 ml portions of absolute alcohol to remove the water, and with three 10 ml portions of dry ether. Yield was 32.3 g. Literature value is 33.2 g. (28) The product decomposed on heating in the range of 89° to 92°C which compares favorably with Bauer and Drinkard value of 93°C decomposition.

1,1,1-Trifluoro-2,4-pentanedione (4.63 g, 0.030 ml) as obtained from Columbia Organic Chemicals Co. Inc., was dissolved in 50 ml of aqueous alcohol (40% ethanol). Sodium tris-carbonatocobaltate (III) trihydrate (3.63 g, 0.010 mole) and 5 ml of 6N HNO_3 were added, and the mixture was allowed to reflux for 0.5 hr. The green precipitate was filtered on a Buchner funnel, washed with three 10 ml portions of water and air dried. Yield was 4.89 g; Fay and Piper report 1.45 g; the difference in yield could be attributed to the fact that Fay and Piper purified the complex by alumina chromatography, which was not found necessary in this research.

Tris-(1,1,1-trifluoro-2,4-pentanediono)-indium(III)

$$\tfrac{1}{2}In_2(SO_4)_3 + 3HATA \xrightarrow{NH_4OH} In(ATA)_3 + 3/2H_2SO_4$$

Indium sulfate (1.75 g) was dissolved in 25 ml of water. Twenty-five ml of an aqueous solution containing 3.12 grams of 1,1,1-trifluoro-2,4-pentanedione and concentrated ammonium hydroxide were added to this solution dropwise while stirring with a magnetic stirrer. The white precipitate was filtered on a Buchner funnel, washed with water and dried overnight.

The indium (III) complex was extracted with benzene, filtered to remove insoluble matter, and the benzene was vacuum distilled at 75 mm mercury. Yield was 0.8 g whereas Fay and Piper obtained 1.2 g. Melting range was 116° to 119°C, uncorrected. Literature value is 118° to 120°C (26).

Tetrakis-(2,4-pentanediono)zirconium(IV)

The compound obtained from MacKenzie Chemical Works, Inc., Central Islip, New York was crystallized from 95% ethanol after which it gave a melting range of 169° to 170°C, uncorrected. Literature value is 171° to 173°C (29).

Bis-(1,1,1-trifluoro-2,4-pentanediono)-nickel(II)

$$Ni(NO_3)_2 \cdot 6H_2O + 2HATA \xrightarrow{NaC_2H_3O_2} Ni(ATA)_2$$

Fifty ml of a nickel nitrate hexahydrate (11.4 g, 0.039 moles) solution were buffered by adding 2.5 g of sodium acetate. 1,1,1-Trifluoro-2,4-pentanedione (6.16 g, 0.4 mole) was added dropwise while this solution was being stirred with a magnetic stirrer. In order to ensure complete reaction, the mixture was stirred for fifteen more minutes. The green precipitate was filtered on a Buchner funnel, washed three times with

10 ml water and air dried. The yield was 7.3 g, that is, equal to the theoretical yield. It did not melt up to 300°C but turned from a light green to a dark green once heated beyond 250°C indicating decomposition. The literature (25) reported no melting point or decomposition temperature. This decomposition was not checked further inasmuch as the nickel chelate failed to give any satisfactory results with the gas chromatograph.

Tris-(1,1,1-trifluoro-2,4-pentanediono)-rhodium(III)

This compound was prepared by the method of Fay and Piper (26, 30).

$$RhCl_3 \cdot 3H_2O + 3NaOH \longrightarrow Rh(OH)_3$$

$$Rh(OH)_3 + 3HNO_3 \longrightarrow Rh(NO_3)_3$$

$$Rh(NO_3)_3 + 3HATA \longrightarrow Rh(ATA)_3$$

Rhodium (III) chloride trihydrate (1.00 g) was dissolved in 30 ml of water and heated on a steam bath. In order to precipitate rhodium hydroxide, 2 M sodium hydroxide was added until pH 11, measured with pH paper. Rhodium hydroxide was digested for ten minutes more on a steam bath. The precipitate

was collected on a Buchner funnel, washed with 1% ammonium nitrate solution and redissolved in 3 N nitric acid. The procedure was repeated in order to free the rhodium from all traces of chloride. The resulting rhodium nitrate solution was treated with solid sodium bicarbonate until pH 4 was attained. 1,1,1-Trifluoro-2,4-pentanedione (5.0 g) as obtained from Columbia Organic Chemicals Co. Inc., was slowly added to the solution while it was stirred; the mixture was then refluxed for thirty minutes. The pH was again adjusted to 4 with sodium bicarbonate and refluxing was continued for fifteen minutes longer. To ensure that all rhodium capable of reacting had done so, another 1.00 g of 1,1,1-trifluoro-2,4-pentanedione was added, and the mixture was refluxed for thirty minutes longer. The product was filtered on a Buchner funnel, dissolved in hexane-benzene mixture and was purified by being passed through an activated alumina chromatography column. The solvent was evaporated off, the product dried, and dissolved in chloroform. Microliter aliquots of the solution were injected into the gas chromatograph.

Tetrakis(2,4-pentanediono)thorium(IV)

$Th(AA)_4$ obtained from MacKenzie Chemical Works was crystallized from methanol after which it gave a melting range of 163° to 164°C, uncorrected. Literature value is 171°C (31).

Bis-(1,1,1-trifluoro-2,4-pentanediono)cadmium(II)

$$Cd(NO_3)_2 \cdot 4H_2O + 2HATA \xrightarrow{NH_4OH} Cd(ATA)_2 + 2HNO_3 + 4H_2O$$

Six molar NH_4OH was added to 15.4 g trifluoroacetylacetone in 25 ml water until it completely dissolved. This solution was added to a water solution of cadmium nitrate (15.4 g per 25 ml water). The white precipitate was filtered on a Buchner funnel, washed with water and air dried. Melting point was 162° to 163°C, uncorrected.

Bis-(1,1,1-trifluoro-2,4-pentanediono)dioxouranium(VI)

$$UO_2(C_2H_3O_2)_2 \cdot 2H_2O + 2NaATA \rightarrow UO_2(ATA)_2 + 2NaC_2H_3O_2 + 2H_2O$$

To a 100 ml of a 6% by weight solution of uranyl acetate was added 5 g of sodium trifluoroacetylacetone. The mixture was shaken for five minutes, precipitate was collected on a Buchner funnel, washed with water and purified by crystallization from ethanol. Melting point was 186° to 190°C, uncorrected.

Bis-(1,1,1-trifluoro-2,4-pentanediono)zinc(II)

$$Zn(NO_3)_2 \cdot 6H_2O + 2NaATA \rightarrow Zn(ATA)_2 + 2NaNO_3 + 6H_2O$$

To a 100 ml of a 5% by weight solution of zinc nitrate was added 5 g of sodium trifluoroacetylacetone. The mixture was shaken for five minutes, precipitate was collected on a Buchner funnel, washed with water and purified by sublimation. Melting point was 155° to 156°C, uncorrected.

Equipment

Measurements were made either with a Burrell model K3 Kromo-Tog Gas Chromatograph equipped only for isothermal runs or with the Burrell model KD Kromo-Tog Gas Chromatograph which could be operated isothermally or temperature programmed.

The samples ranged from 1-5 wt% concentration. Peak areas were measured with an "Ott" compensating polar planimeter. Each peak area was measured twice and several runs were taken at each calibration point. Any doubtful observation was subjected to the Q test of Dean and Dixon (32), which allows rejection of an observation with a 90% confidence limit. (See Section entitled Measurements and Calculations, page 35)

The model KD detector which was a later model was capable of obtaining higher sensitivity than the K3, but inasmuch as maximum sensitivity was not required to detect the quantity of metal chelate in the sample, maximum detector sensitivity was never of primary concern. This does not mean that greater sensitivity could not extend the lower limit of detecton.

The thermal conductivity detector consists of four tungsten filaments which comprise the four arms

of a Wheatstone bridge. (See Figure 2, page 26). Two of these filaments are mounted in the measuring side and two in the reference side of the detector. Both sides are continuously flushed with carrier gas. A solid state 35 volt D.C. power supply provided the necessary current to heat the filaments. The electrical resistance of the tungsten filaments increase with a rise in temperature. When only the carrier gas was passing over the filaments at a constant flow rate, the filaments were cooled at a constant rate and register a constant resistance. When the sample passed through the detector, the filaments changed in temperature and in electrical resistance. This change was recorded in ink on a strip chart.

The chromatograms were recorded on a 1.25 mv Sargent Recorder, Model SR with 11 inch strip chart paper, at a chart speed of one inch per minute and a balancing speed of one second, full scale.

When the KD model was used, the flow was arranged so that the carrier gas went through the reference side of the detector, through the flash vaporizer, where it picked up the sample, through the column, (See Figure 3, page 27) then through the measuring

FIGURE 2

Thermal Conductivity Detector

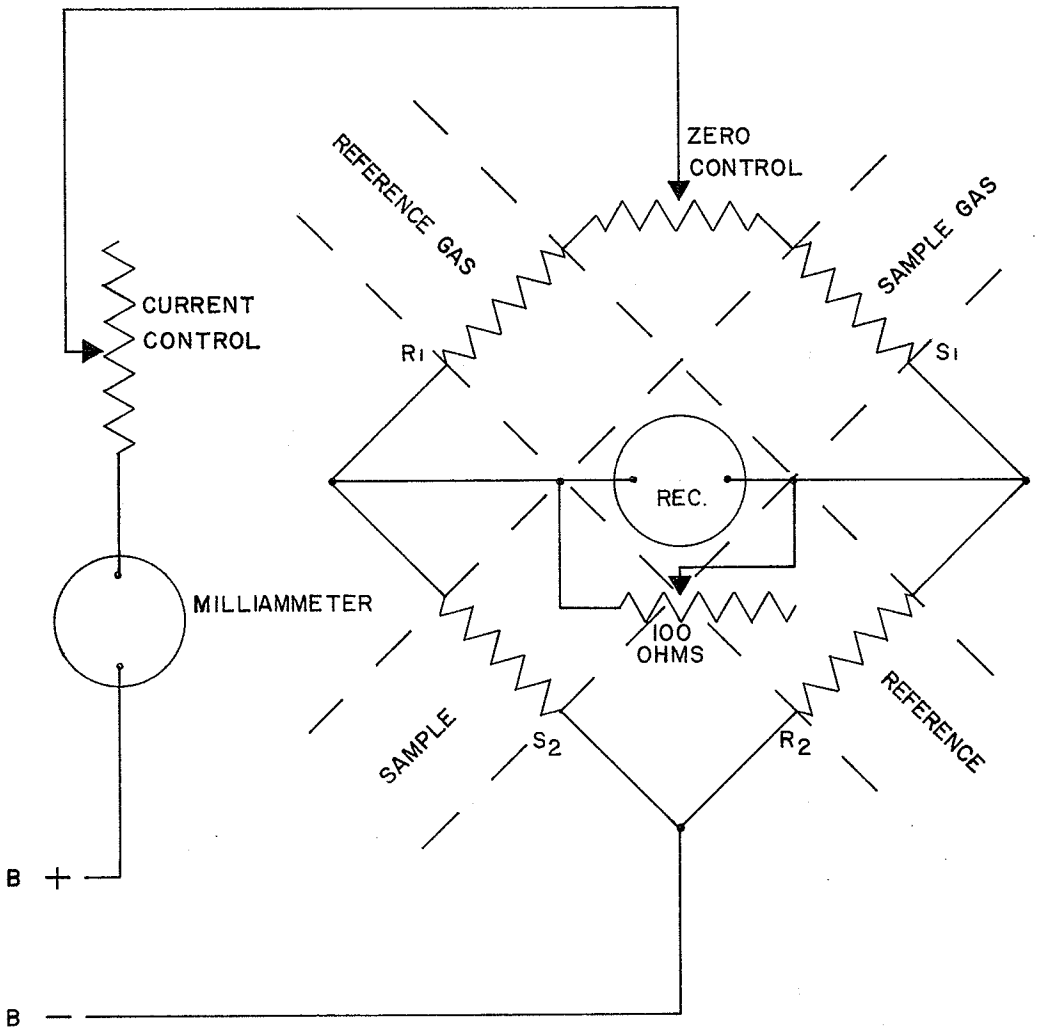
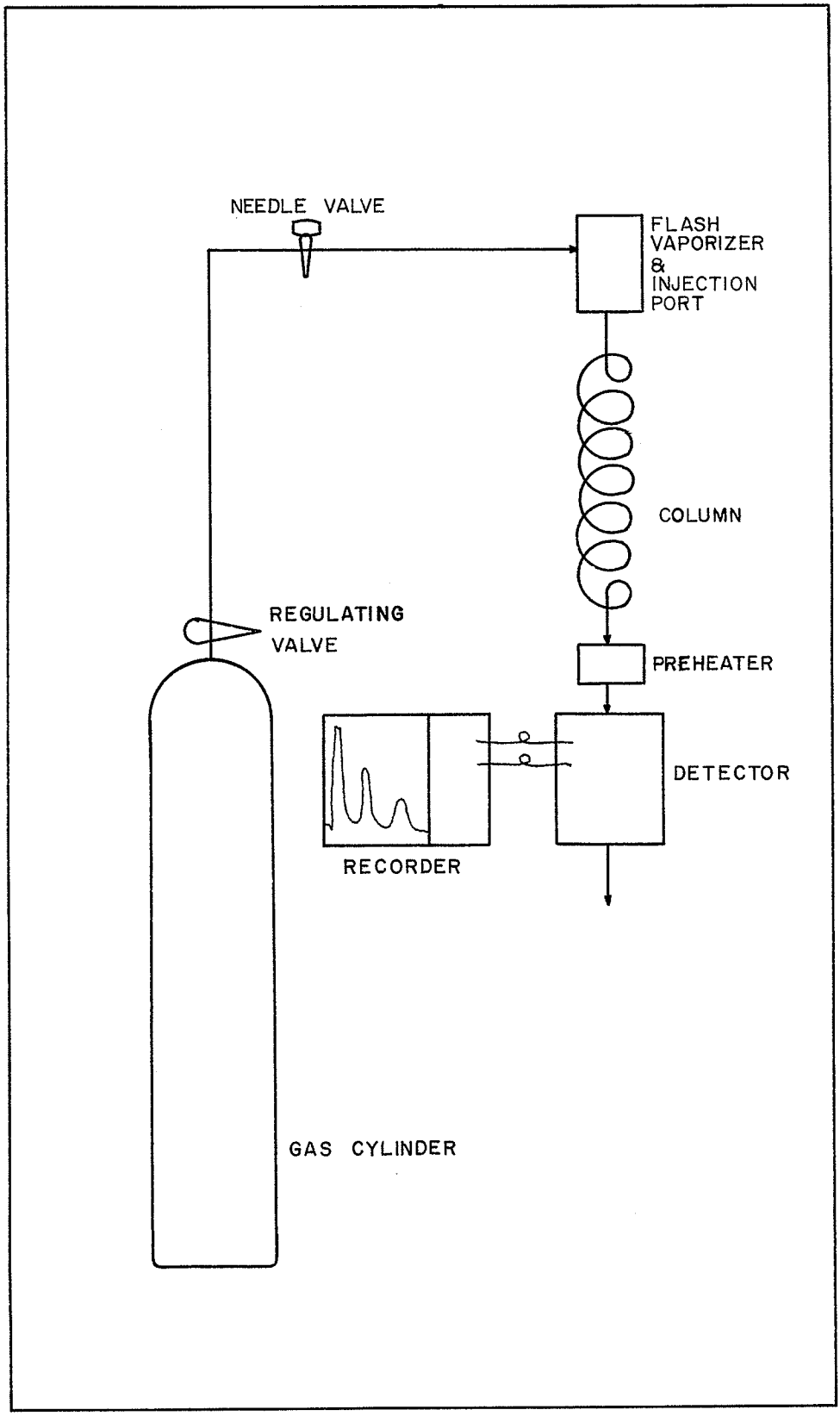

ZERO
CONTROL
REFERENCE GAS
SAMPLE GAS
CURRENT
CONTROL
R1
S1
REC.
MILLIAMMETER
100
OHMS
SAMPLE
S2
R2
REFERENCE
B +
B —

FIGURE 3

Schematic Diagram of Gas Chromatograph


NEEDLE VALVE
FLASH VAPORIZER & INJECTION PORT
COLUMN
REGULATING VALVE
PREHEATER
DETECTOR
RECORDER
GAS CYLINDER

side of the detector; hence the reference flow was identical with the flow rate and, therefore, not recorded in the "Table of Conditions". (See Table 2, page 32).

The solid support was coated with the liquid partitioning agent by dissolving a weighed quantity of the liquid phase in a minimum amount of ether, adding this solution and the solid support to an evaporating dish and heating slowly while stirring. Once all the ether had evaporated, the evaporating dish and its contents were left overnight in an oven at 100°C. Subsequently, the coated solid support material was slowly introduced into the column. Column packing is a process which if improperly done, will cause a great deal of trouble. If the column material is too loosely packed, empty pockets are likely to be formed, reducing the separating ability of the column. A column packed too tightly, on the other hand, will cause a large pressure drop through the column and may even cause clogging. A magnetically driven hammer removed from an electric bell was used to facilitate uniformity in packing. After the column was packed, the vibrating was continued for several hours to ensure uniformity in packing. A

small plug of glass wool was inserted in both ends of the column to hold the column packing in place.

The columns were conditioned overnight at 25°C above the operating temperature for the column while helium was passing through the column at a flow of 10 ml per minute. The detector current was shut off while the column was being conditioned.

The copper tubing for columns #1 through #6 was washed with a soap solution and pipe cleaners; then it was rinsed with tap water, distilled water, acetone and ether respectively, and air dried. Potassium cyanide solution appeared to be a more efficient cleaner; consequently it was used in the place of a soap solution for columns #7 through #10. The stainless steel tubing for column #11 was washed with 2 M hydrochloric acid and dried as above. Column #12 was obtained from Wilkens Instrument and Research Inc. Walnut Creek, California.

The glass beads, which were of two varieties, standard and waterproof, were obtained from Microbead, Inc. Jackson, Mississippi. The latter were waterproofed by application of a "molecular" film of silicone material.

The chelates were dissolved in benzene, carbon tetrachloride, chloroform or a mixture of benzene and carbon tetrachloride. Accurately weighed amounts

TABLE 1

GAS CHROMATOGRAPHIC COLUMNS
used in this research

Number	Dimension and material	Discription of Stationary Phase
1	¼"O.D. by 4'Cu	50 mesh waterproof glass beads
2	¼"O.D. by 6'Cu	60 mesh waterproof glass beads
3	¼"O.D. by 4'Cu	0.5% apiezon L on 50 mesh glass beads
4	¼"O.D. by 4'Cu	0.5% apiezon L on 60 mesh glass beads
5	¼"O.D. by 6'Cu	0.5% apiezon L on 50 mesh glass beads
6 & 7	¼"O.D. by 6'Cu	0.5% apiezon L on 100 mesh glass beads
8	¼"O.D. by 4'Cu	0.5% apiezon L on 100 mesh glass beads
9	¼"O.D. by 4'Cu	0.5% apiezon L on 50 mesh glass beads
10	¼"O.D. by 40"Cu	7.5% SE 30 on 20/40 mesh fire brick
11	1/8"O.D. by 8'ss	7.5% SE 30 on 20/40 mesh fire brick
12	1/8"O.D. by 4'ss	7.5% SE 30 on 42/60 mesh fire brick acid washed

were made up to an exact volume with a volumetric flask. Solutions were introduced into the gas stream through a silicone rubber seal by means of a 10.0 µl or a 50.0 µl Hamilton microsyringe.

Column temperatures varied from 103° to 175°C, depending on the column being used and the metal chelates being chromatographed. With the exception of tetrakis(2,4-pentanediono)zirconium(IV), the flash vaporizer temperature was 13° to 57°C higher than the column temperature. So that the less stable complexes do not undergo thermal decomposition, the high flash vaporizer temperatures (ie over 200°C) were usually avoided. The chelate molecules, because they are in solution, are already dispersed and are further dispersed by the helium when injected into the flash vaporizer. Therefore, much lower flash vaporizer temperatures are necessary for volatilization than would be necessary if the chelates were injected into the gas chromatographs as solids.

Flow rates of the carrier gas, helium, ranged from 11 to 66 ml min^{-1} depending on the metal chelate being chromatographed and the column being used. The flow scheme for the K3 model has already been described. A purifier was used with the model KD gas chromatograph. The purifier, which is simply a glass tube filled with

TABLE 2 - CONDITIONS

Conditions:	$Be(ATA)_2$	$Be(AA)_2$	$Al(ATA)_3$	$Al(AA)_3$	$Cu(AT)_2$	$Cr(ATA)_3$	$Fe(TA)_3$	$Co(ATA)_3$	$In(ATA)_3$	$Th(AA)_4$	$Rh(ATA)_3$	$Zr(AA)_4$
Column	#3	#3	#3	#3	#11	#11	#11	#12	#12	#12	#12	#12
Column Temperature °C.	112°	146°	107°	153°	150°	150°	150°	175°	175°	140°	150°	103°
Flash Vaporizer Temperature C.	140°	205°	120°	190°	170°	170°	170°	205°	198°	190°	207°	227°
Sample Size µl	5-20	10-50	5-20	5-15	1-5	1-10	2-10	4.0	2.0-8.0	1.0-6.0	3.0-10.0	2.0-7.0
Flow Rate ml min^{-1}	45	50	44	55	55	44	64	51	32	41	66	11
Reference Flow Rate	-	-	-	-	11	18	40	10	9.6	9	11	12
Predetector Temperature C.	-	-	-	-	176°	176°	175°	210°	200°	220°	189°	206°
Detector Temperature C.	200°	200°	200°	200°	188°	188°	187°	232°	220°	238°	203°	237°
Detector Current (milliamperes)	145	145	145	195	200	200	200	200	200	200	200	200
Attenuator Setting	2	5	2	1	1	1	1	2	1	2	1	4
Gas Chromatograph Model	K3	K3	K3	K3	KD	KD	KD	KD	KD	KD	KD	KD
Solvent	C_6H_6	CCl_4	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6	$CHCl_3$	$CHCl_3$	$CHCl_3$	$CHCl_3$	$CHCl_3$

13X molecular sieve, removed water and other contaminants from the helium. After each tank of helium gas had been used, the purifier was reactivated by heating to 300°C for several hours while a flow of 5 ml min^{-1} of helium was passing through it. New seals were used and the activated tube was protected from contact with air by placing pins in both seals until installation was made. The helium came from a high pressure cylinder, passed through a reducing valve, after which the flow split into two branches, one going to the reference side of the detector and the other to the measuring side of the detector. The helium which went to the reference side of the detector passed through a needle valve, then into the reference side of the detector and through a flow meter. The other branch of helium flowed through a needle valve, (in each case the needle valve was necessary to maintain a constant flow) then through the purifier, into the flash vaporizer where the sample entered the flow stream, through the preheater which kept the temperature differential between column and detector at a minimum, through the flow meter and out into the atmosphere. The flow meter was constructed from a 30 ml burette without the stopcock. Helium came through a side arm and upon passing through a soap solution caused a

bubble to ascend to the top of the burette. The time of the ascension from zero to the 30 ml mark was measured with a stop watch. This measurement was converted to ml per min. helium. The apparatus is referred to as a bubble-type flow meter.

MEASUREMENTS AND CALCULATIONS

Measurement of Peaks

Once a separation had been effected and a chromatogram obtained, then the chelate peak had to be measured. Chromatographic peaks are usually measured by one of the following methods:

a) Peak height

b) Cutting out the trace and weighing the paper

c) Triangulation

d) Counting squares

e) Automatic integrators

f) Planimeter

Peak heights may be used for the estimation of the amounts of the individual components shown on a chromatogram and this method was rapid and convenient. The establishment of a base line and the measurement of the height of a peak were not difficult, but peak height changed with column temperature and was not an accurate measurement for unsymmetrical peaks. The best quantitative results were obtained when peak area was used rather than peak height.

Cutting out the chart paper enclosed by the chromatographic trace and then weighing the paper on an analytical balance, had two main disadvantages. First, error was introduced because of nonuniformity of chart paper, and, secondly, the method destroyed the chromatogram.

Triangulation methods depend on the assumption that the peak area is proportional to the product of the peak height and the peak width at any specified distance from the base-line or the distance between the intersections of the tangents to the points of inflexion with the base-line. Scott and Grant (33) made a comparison of the triangulation methods and the planimeter method of measuring peak areas. Their results indicated that for symmetrical peaks the triangulation method was more precise, but for unsymmetrical peaks, the planimeter was more precise.

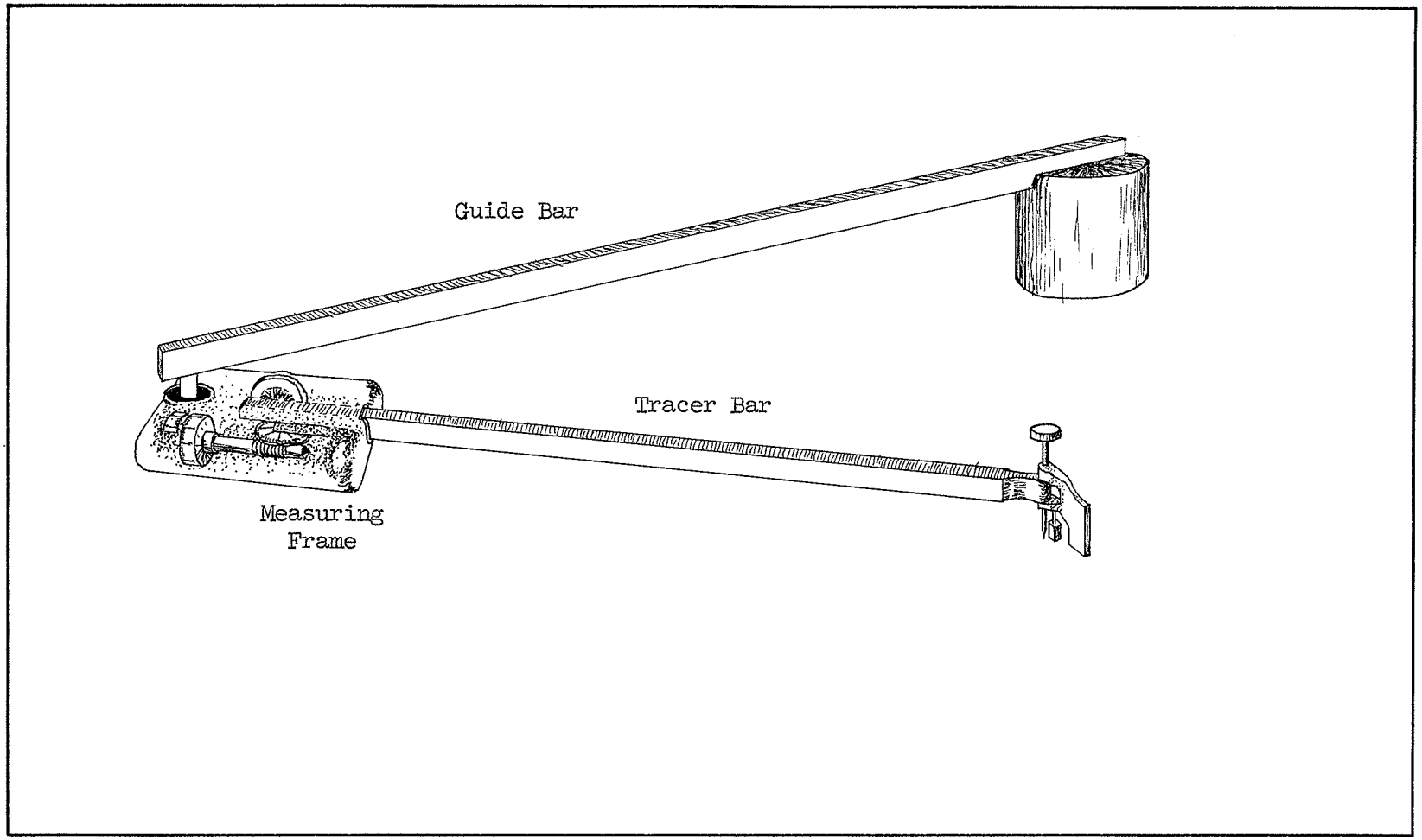
The manual counting of the number of boxes of cross-sectioned (chart) paper contained within the peak's area was not found satisfactory because of limited accuracy, the length of time necessary to accomplish a measurement and the tedious nature of the technique.

Obviously, the use of fully automatic integration methods would have been most convenient for obtaining peak areas, but none were available in this research.

The Ott compensating polar planimeter (See Figure 4, page 38) is a device which consists of three main parts: the measuring frame, the tracer bar and the guide bar(34). The tracer arm was firmly connected to the measuring frame at one end and at the other end of the tracer arm was the tracing point which was used to follow the curve. The peak area was mechanically determined by tracing the peak area with the planimeter. Manipulation of the polar planimeter was as follows: the base line was drawn and the beginning and the end of the peak marked with a pencil. The measuring frame which was coupled to the guide bar by inserting the ball pivot of the guide bar into the reception socket of the measuring frame was placed over the chromatographic peak. The tracing point was set in the center of the chromatographic peak and the measuring frame was adjusted so that it was above and to the left of the peak while the guide bar and tracer bar formed an approximate right angle. The tracing point was then placed on the pencil mark at the front part of the

FIGURE 4

Ott Compensating Polar Planimeter


Guide Bar
Tracer Bar
Measuring
Frame

chromatographic peak. A reading was taken from the measuring frame, resulting in a four digit number "abcd"; "a" from the counting disk, "bc" from the measuring wheel and "d" from the vernier. The tracing point was guided by means of the small handle, with the thumb and middle finger. The peak area was traced by going to the apex, then to the end of the peak and finally returning to the starting point by way of the base-line. A second reading was taken from the measuring frame, then the peak area was traced a second time and a third reading was taken. The difference between consecutive readings were calculated and the average of the two measurements was recorded in which rounding off, whenever necessary, was always made to an even number. Area of a peak could be measured within 0.1 cm^2 with the planimeter.

Determing the Peak to be Measured

An advantage of the planimeter method over the triangular method was that the peak did not have to be symmetrical to be measured. The planimeter method was always used in this research because symmetrical peaks, especially in multicomponent samples, could not always be obtained. As long as the peak overlap

and peak tailing were not excessive, the measuring of the peak area was a simple matter as previously described.

Whenever peaks overlapped, the best solution to this problem whenever possible, was to separate the peaks by adjusting column conditions. Lowering column temperature and decreasing flow rate increased separation, but on the other hand also increased retention time, tailing, time of analysis, adsorption and, therefore, usually decreased accuracy. Increasing column length, which appeared as an obvious method of improving the separation, was tried and usually met with very little success because, as Karger and Cooke (35) had shown, short columns can give better resolution in a shorter time and at lower temperatures than very long columns. So after it had been discovered that, for certain components, it was more efficient to work with slightly overlapping peaks than attempting to completely separate them, the problem of defining the boundaries of the individual peak areas had to be solved and the following procedure was employed to define the individual peak boundaries. First, the same complexes which overlapped in the mixture were put separately through the gas chromatograph in approximately the same quantity they were in the mixture.

Then each chromatogram was studied, particular notice being made to retention time, and characteristic shape of chromatogram. Each of these characteristics helped to define the boundaries of the peak areas in a mixture. Then the mixture was chromatographed, the base-line drawn and finally a line, dividing the peaks, was drawn. This line was usually straight, exactly divided the two peaks and perpendicular to the base-line. The calculations for all the standardization curves and the mixtures were accomplished by one standard technique.

This technique shall be demonstrated by following the calculations and preparations of the Tables for $Be(ATA)_2$, $Al(ATA)_3$ and $Cu(ATA)_2$ mixture. First, a standard solution was prepared by weighing a 2 ml volumetric flask, adding $Be(ATA)_2$, weighing, adding $Al(ATA)_3$, weighing, adding $Cu(ATA)_2$ and weighing. This mixture was then dissolved in benzene. Columns 2, 4 and 6 of Table 2, page 32 were studied and the conditions at which a possible analysis could be accomplished were determined by using the information in Table 2 in the following manner. Column #12 was chosen as a compromise between column #3 and #11 (See Table 1, page 30). The choice of column temperature

was from 107° to 150°C, and in order to avoid extensive tailing, the highest temperature of 150°C was used. The flash vaporizer temperatures were 140°C, 120°C, 170°C, for $Be(ATA)_2$, $Al(ATA)_3$ and $Cu(ATA)_2$ respectively. A higher temperature than any of these was used in order to compensate for the low flow rate which was necessary. Sample size was maintained within the range described in Table 2 which was 1 to 10 microliters. In order to obtain a separation, the flow rate was lowered for the mixture than for any of the individual components. The predetector temperature was 216°C; that is between the column temperature of 150°C and the detector temperature of 246°C. Detector current was 200 milliamperes and the solvent was benzene; that is the solvent which was used for the individual chelates.

Once conditions had been established, three runs of $Be(ATA)_2$ in benzene, three runs of $Al(ATA)_3$ in benzene, and three runs of $Cu(ATA)_2$ in benzene were made to determine the retention time of each complex. It was then decided that five runs of each of six different sample sizes (2.0 µl to 7.0 µl) would suffice for the standardization curves. After the runs were finished and the areas measured, the results were formulated into Tables. (See Table 3, page 44).

When all the data were in tabulated form, it was seen that the results were reproducible. Then any area that appeared to be outside of experimental error was marked with a question mark (?). Those areas were subjected to the Q-test of Dean and Dixon (32). The Q-test is a rapid statistical method which is applicable to a small number of observations (ten or less). This method which gives a 90% confidence limit was used because it is simple and takes a short time to apply. Application of the Q-test for sample size 2.0 ul (See Table 3, page 44) was as follows:

Run #1 for $Be(ATA)_2$ area

(1) Calculate the difference between a doubtful observation and the observation numerically closest to the doubtful observation.

$$2.1 - 1.5 = 0.6 \text{ cm}^2$$

(2) Determine Q by dividing this difference 0.6 cm^2 by the range 0.9 cm^2 which equals 6/9 or 2/3 or 0.67 = Q

(3) If Q calculated was larger than Q tabulated (0.64) (See Table 4, page 46), the questionable observation was rejected with 90% confidence and marked with an asterisk (*).

TABLE 3

AREAS (in cm^2) OBTAINED FOR THE $Be(ATA)_2$, $Al(ATA)_3$, AND $Cu(ATA)_2$ MIXTURE

Sample Size 2.0 µl

Run	$Be(ATA)_2$	$Al(ATA)_3$	$Cu(ATA)_2$
1	?1.5*	?3.2*	**
2	2.2	4.7	**
3	2.1	4.6	**
4	2.4	4.6	**
5	2.3	4.6	**
Average	2.2	4.6	**

Sample Size 3.0 µl

1	3.2	7.0	3.5
2	3.4	7.0	3.4
3	3.3	6.9	3.9
4	3.4	7.4	4.6
5	3.6	7.0	4.8
Average	3.4	7.1	4.0

Sample Size 4.0 µl

1	4.4	9.6	6.6
2	4.4	9.6	7.6
3	4.4	10.0	7.1
4	4.3	9.8	7.4
5	4.4	9.6	8.0
Average	4.4	9.7	7.3

** areas too small to measure

TABLE 3 (continued)

Run	$Be(ATA)_2$	$Al(ATA)_3$	$Cu(ATA)_2$
		Sample Size 5.0 µl	
1	5.3	12.2	11.9
2	5.8	12.7	12.4
3	5.4	12.2	11.6
4	5.7	12.4	12.8
5	5.7	12.6	11.7
Average	5.6	12.5	12.1
		Sample Size 6.0 µl	
1	6.4	15.3	?12.6*
2	6.8	15.0	14.8
3	6.7	14.9	15.0
4	6.5	15.3	14.4
5	6.8	14.9	14.3
Average	6.6	15.1	14.6
		Sample Size 7.0 µl	
1	7.6	17.4	18.0
2	8.8	17.8	18.4
3	7.8	18.4	18.2
4	7.7	17.8	18.1
5	8.5	18.2	18.6
Average	8.1	17.9	18.3

? = questionable

* rejected by Q test

TABLE 4

Rejection Quotients*

Number of Observations	Rejected Quotient
2	-
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

*reference (32), page 637

The observation 1.5 cm^2 was rejected because Q calculated 0.67 cm^2 was larger than Q tabulated 0.64 cm^2 This procedure was followed for any other questionable results and only when Q calculated was larger than Q tabulated, was the value rejected.

After all questionable results had been checked the arithmetic averages and ranges were calculated. These are given in Table form in the section "Results and Conclusions" of this thesis. (Table 26, page 130). The standard points were then plotted and a straight line was drawn to best fit the points. (Figure 38, page 123) The "Method of Averages" (36) was then applied to the calculation of a straight line. When the standardization curve passed through the origin, then y-intercept was 0 and the method of calculation was simplified as for $Be(ATA)_2$ in the data on page 48.

Method of Averages for $Be(ATA)_2$

Putting the data into equations of a straight line:

$y = ax+b$ where y = area, a = slope of curve, x = sample size and b = y-intercept which was equal to zero in this case.

Mg of $Be(ATA)_2$	$\overline{\text{Area}}$ (cm^2)
8.1×10^{-3}	2.2
12.1×10^{-3}	3.4
16.2×10^{-3}	4.4
20.2×10^{-3}	5.6
24.3×10^{-3}	6.6
28.4×10^{-3}	8.1
Total = 109.3×10^{-3}	30.3

30.3 cm^2 divided by 109.3×10^{-3}mg = 277 $cm^2\ mg^{-1}$ = a

The calculated areas for $Be(ATA)_2$ were obtained by multiplying the slope by mg of $Be(ATA)_2$ in the sample which was then compared to the average areas. It was seen that average empirical areas for $Be(ATA)_2$ were within experimental error of the calculated areas

for $Be(ATA)_2$ at every point. Within experimental error the empirical area of $Be(ATA)_2$ was, therefore, a linear function of the quantity of $Be(ATA)_2$ added.

Method of Averages for $Al(ATA)_3$

Putting the data into equations of a straight line:

$y = ax+b$ where y = area, a = slope of curve, x = sample size and b = y- intercept

cm^2		mg	y-intercept
4.6	=	$23.2 \times 10^{-3}a$	+ b
7.1	=	$34.8 \times 10^{-3}a$	+ b
9.7	=	$46.4 \times 10^{-3}a$	+ b
21.4	=	$104.4 \times 10^{-3}a$	+ 3b (equation 1)
12.5	=	$58.0 \times 10^{-3}a$	+ b
15.1	=	$69.6 \times 10^{-3}a$	+ b
17.9	=	$81.2 \times 10^{-3}a$	+ b
45.5	=	$208.8 \times 10^{-3}a$	+ 3b (equation 2)

equation (2) minus equation (1)

$24.1 = 104.4 \times 10^{-3}a$

$a = 231\ cm^2\ mg^{-1}$

Equation 1 plus equation 2

$$66.9\ cm^2 = (313.2 \times 10^{-3}\ mg)a + 6b$$

Substituting the value of a

$$66.9\ cm^2 = (313.2 \times 10^{-3}\ mg)\ 231\ cm^2\ mg^{-1} + 6b$$

$$(66.9 - 72.0)cm^2 = 6b$$

$$b = -0.85\ cm^2$$

Therefore, in order to calculate the expected area for the aluminum complex, we substituted the quantity of $Al(ATA)_3$ present into the equation:

$$\text{Area} = (\text{mg of } Al(ATA)_3)\ 231\ cm^2\ mg^{-1} - 0.85\ cm^2$$

The remainder of the procedure was identical with that followed for $Be(ATA)_2$.

When the "Method of Averages" was applied to $Cu(ATA)_2$ the result was:

$$\text{Area} = (\text{mg of } Cu(ATA)_2)\ 243\ cm^2\ mg^{-1} - 5.9\ cm^2$$

This section demonstrates the procedure used in compiling the Tables contained in the following section of this thesis entitled "Results and Conclusions".

The Quantitative Gas Chromatographic Analysis of a Beryllium-Copper Alloy

The final part of this research was concerned with studies of the applicability of gas-liquid chromatography to the analysis of metal alloys, of which beryllium-copper alloy is an example.

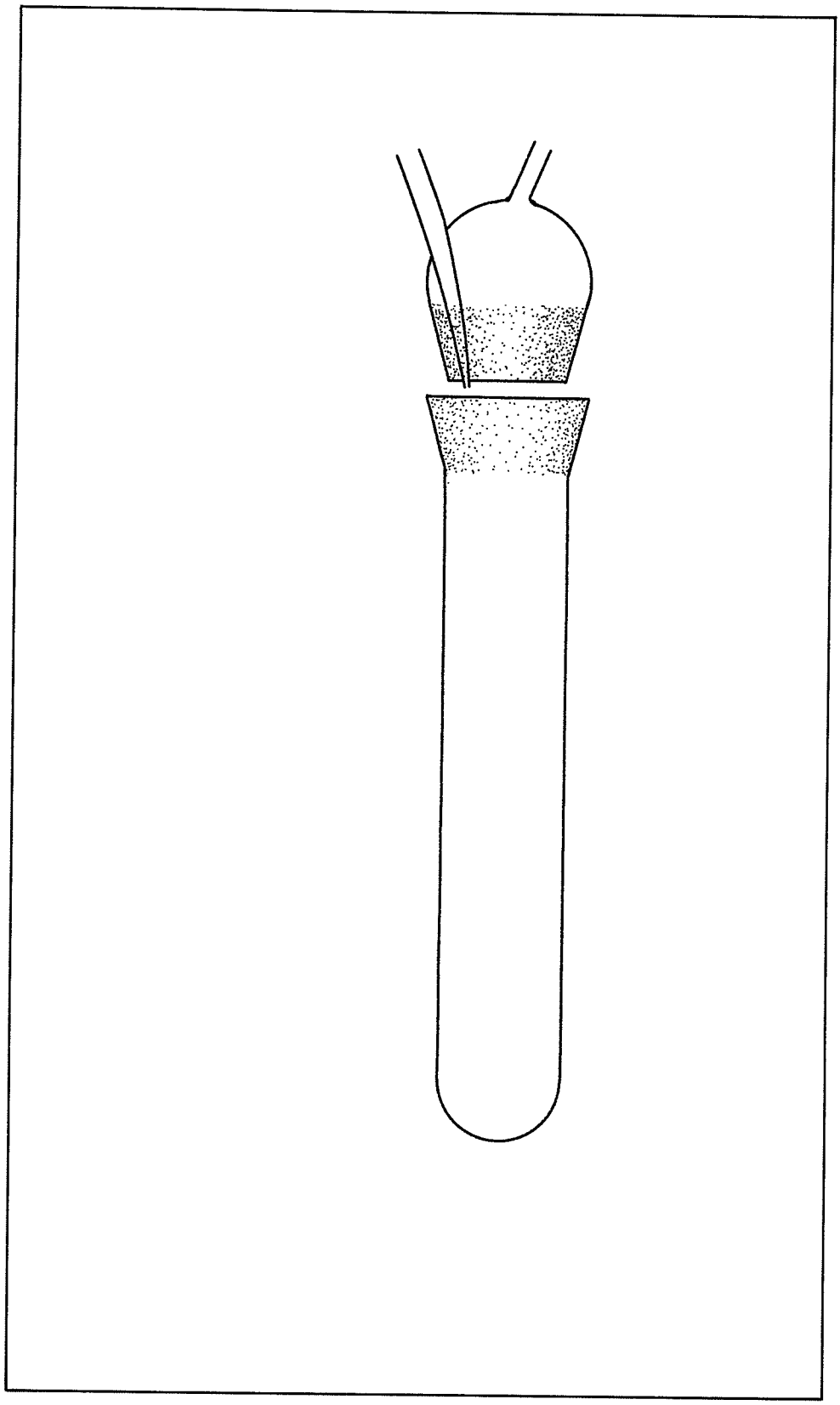
A weighed portion of the alloy was dissolved in concentrated nitric acid, and then evaporated to dryness under reduced pressure in a pyrex reaction tube. (See Figure 5, page 53) Fifteen milliliters of trifluoroacetylacetone were added, and the mixture was allowed to stand overnight. The mixture was made up to a 100 ml in benzene.

This solution of mixed chelates in benzene gave a peak only for beryllium trifluoroacetylacetone and not for the copper chelate. (See Figure 40, page 129).

When this procedure was repeated, with the addition of one gram of solid sodium bicarbonate, which was added in order to buffer the solution of metal chelates for chelation is pH dependent (24), both beryllium trifluoroacetylacetone and copper trifluoroacetylacetone peaks were obtained. (See Figure 41, page 131).

FIGURE 5

Pyrex Reaction Flask



In order to measure the percentage of beryllium and copper in the alloy, the following procedure was used. First, the column was conditioned to the copper complex by passing three 5.0 ul samples of copper trifluoroacetylacetone in benzene solution through the gas chromatograph. Then five runs of a standard beryllium trifluoroacetylacetone solution were used as the standard for beryllium. Following this, five runs of a standard copper trifluoroacetylacetone solution were run, also to be used as the comparative standard and finally five runs of the alloy solution were run. The solvent in each case was benzene.

By comparing the peak areas obtained from alloy samples to those of the standard solutions, (See Table 26, page 130), the weight of each component was determined and then their percentages. This was done and shown to agree with the known analysis of this alloy (15). (See Table 28, page 133).

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Reagents

The acetylacetone complexes of beryllium, aluminum, zinc, manganese, nickel, cobalt, thorium, and zirconium were obtained commercially.

The trifluoroacetylacetone complexes of beryllium, aluminum, chromium, iron, copper, cobalt, indium, nickel, rhodium, cadmium, uranyl, and zinc were prepared as described in the "Experimental" section of this thesis.

Sodium trifluoroacetylacetone was used in the preparations of some metal chelates because it was found widely applicable and usually gave a good yield of product.

Apparatus

The column is the heart of the gas chromatograph because it is there that the separation takes place. It was in determining the best column for the separation and analysis of the metal chelates that much time was spent in this research. In the gas chromatography of metal chelates, the column should possess certain characteristics. Some of these are obvious, it must have high thermal stability and a low vapor pressure at the temperature of use. Apizon L is stable up to 250°C and SE 30 up to 300°C,

so these two liquids have high thermal stability. The chelates must not undergo reaction with the liquid phase or with the solid which supports this phase. The liquid phase should have good solvent properties for differentiating the solvent and the different chelates examined. The columns which were tried in this research are described in Table 1, page 30.

When glass beads are used as a stationary support in gas chromatography, they are lightly loaded, and it was hoped that the waterproofing material could behave as the stationary liquid in this research. It was shown that the waterproofing material was a very poor stationary phase for metal chelates. This may have been due to the fact that there was too low a percentage of stationary phase, and, therefore, an efficient separation could not be achieved.

Column #3 proved to be very effective in separating beryllium chelate from the solvent and in separating aluminum chelate from the solvent, but very poor in separating the beryllium complex from the aluminum complex. There was too small a difference in the retention times of these two compounds, which was noticed by extensive overlapping of their peaks.

Column #4 was tried as it had a smaller bead size, therefore, it would give a larger surface area and consequently an improved separation. The increase in separation power was not appreciable. A longer column, #5 was tried next. Increasing the column length had a much greater effect on increasing the time of the analysis and on increasing the tailing of the components than it had on increasing the peak separation. Karger and Cooke (35) have reported on the effect of column length on resolution under normalized time conditions and their paper agrees with our findings.

Columns #6 and #7 used a much smaller bead size and larger column length with the net result that the pressure drop across the column was too large to make the columns useful. Reducing the column length (column #8), did not reduce the pressure drop enough so that the large bead size was again tried (column #9). SE 30 appeared to be better suited for this work (37), so column #10 was tried. This work was continued with the Model KD. Columns #11 and #12 functioned well, as will be seen from the results which follow.

Gas Chromatographic Analysis of Single Complexes

A series of experiments were undertaken to quantitatively analyze twenty-one β-diketone

chelates with varying sample sizes and/or solutions of different concentrations and the same sample size. For purpose of simplicity, they are discussed in two groups. Group I contains those chelates which failed to give reproducible results under conditions studied. (See Table 5, page 59). Group II which is the larger group, contains only those chelates which gave reproducible quantitative results. (See Table 6, page 67).

GROUP I

After four hours in the gas chromatograph, uranyl trifluoroacetylacetone gave no peak and there was no chelate in the collector at the exit of the gas chromatograph. Thus the vapor pressure of uranyl trifluoroacetylacetone at the temperature of the column was too low to allow the complex to pass through the gas chromatograph or else could not be eluted because it was held too strongly by the stationary phase. If it had decomposed, peaks for the decomposition products would have been detected.

Cadmium trifluoroacetylacetone decomposed giving two shoulders in front of the main peak. (See Figure 5, page 60). It is possible that if this decomposition occurred to the same extent each time when the conditions were held constant, than

TABLE 5 GROUP I

Common Name	IUPAC Nomenclature	Abbreviation
Uranyl trifluoroacetylacetone	Bis-(1,1,1-trifluoro-2,4-pentanediono)dioxouranium(VI)	$UO_2(ATA)_2$
Cadmium trifluoroacetylacetone	Bis-(1,1,1-trifluoro-2,4-pentanediono)cadmium(II)	$Cd(ATA)_2$
Manganese trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)manganese(III)	$Mn(ATA)_3$
Nickel trifluoroacetylacetone	Bis-(1,1,1-trifluoro-2,4-pentanediono)nickel(II)	$Ni(ATA)_2$
Zinc trifluoroacetylacetone	Bis-(1,1,1-trifluoro-2,4-pentanediono)zinc(II)	$Zn(ATA)_2$
Cobaltic acetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)cobalt(III)	$Co(AA)_3$
Cobaltous acetylacetone	Bis-(2,4-pentanediono) cobalt(II)	$Co(AA)_2$
Manganese acetylacetone	Tris-(2,4-pentanediono) manganese(III)	$Mn(AA)_3$
Nickel acetylacetone	Bis-(2,4-pentanediono) nickel(II)	$Ni(AA)_2$
Zinc acetylacetone	Bis-(2,4-pentanediono) zinc(II)	$Zn(AA)_2$

FIGURE 5b

A Typical Chromatogram of Cadmium Trifluoroacetylacetone in Benzene

Conditions:

Column - #12 ie.½" O.D. by 4'ss, 7.5% SE 30 on 42/60 mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 175°C

Sample Size - 4.0 µl

Flow Rate - 40 ml min^{-1}

Detector Temperature - 215°C

Predetector Temperature - 200°C

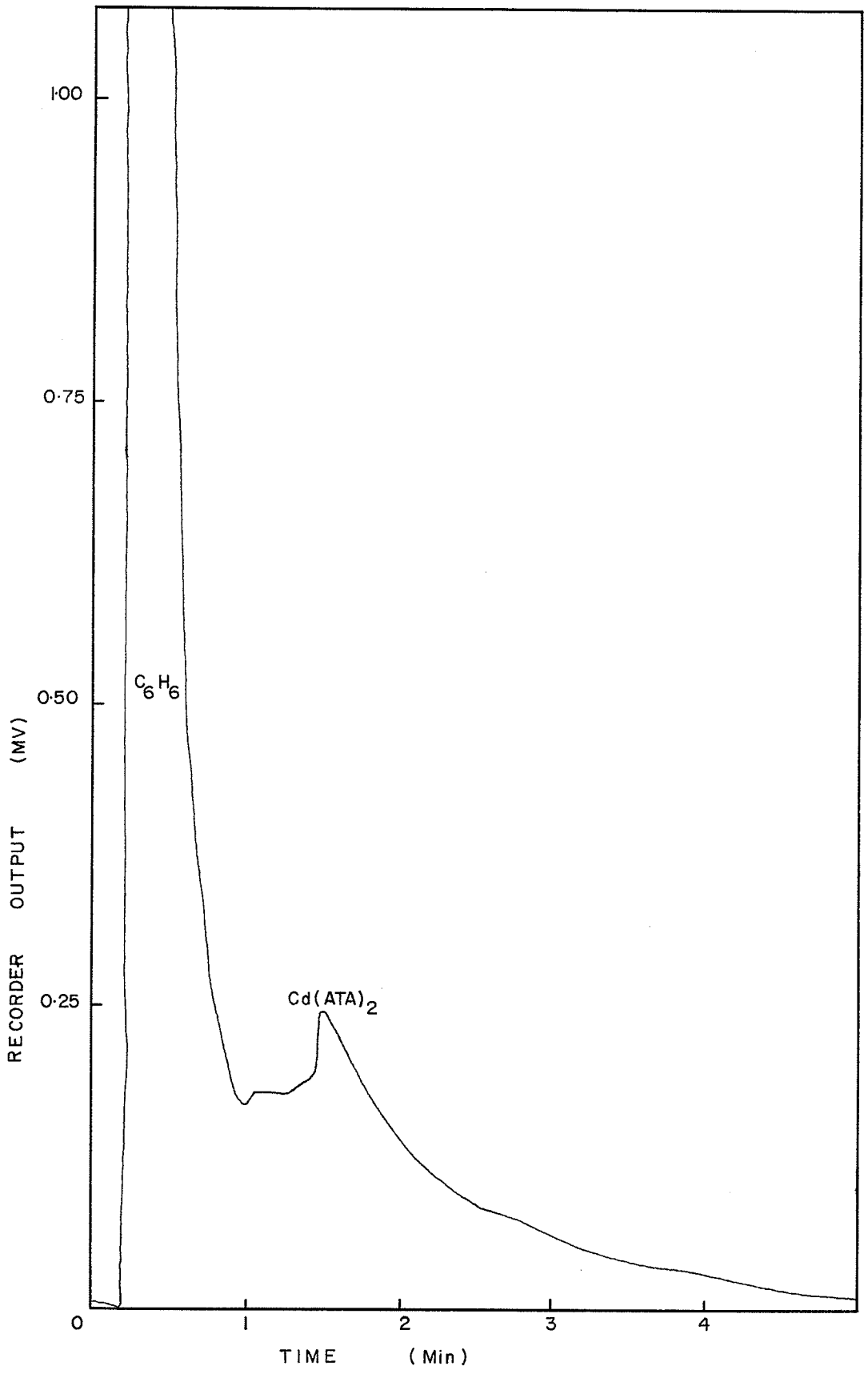
Detector Current - 200 milliamperes

Attenuator Setting - 2

Solvent - benzene

Concentration - saturated solution

Gas Chromatograph Model - KD


1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
Cd(ATA)2
1
2
3
4
TIME (Min)

some quantitative information could be obtained. This was tried, but with very poor results; two runs of the same sample under identical conditions gave peak areas which varied by as much as 50%, so no quantitative results were obtained for the cadmium complex.

The preparation of manganese(III) trifluoroacetylacetone was attempted by the method of Fay and Piper (26). Three attempts in the preparation failed with no apparent reason for these failures. A sample was then obtained from Dr. Fay and a sample was obtained from Dr. Sievers. Dr. Sievers (38) was able to get a chromatographic peak for $Mn(ATA)_3$ but noticed evidence of decomposition in the injection port. Portions of each of these samples were dissolved in benzene and different aliquots of each of these samples were dissolved in chloroform; under a wide range of conditions the only peak which was obtained was a decomposition peak.

Nickel trifluoroacetylacetone decomposes below the temperature which is needed to obtain a vapor pressure high enough to pass through the column in a reasonable length of time. Trumper (39) showed that nickel trifluoroacetylacetone begins to

decompose above 70°C, where its vapor pressure is only 0.25mm. Therefore, it would not be anticipated that nickel trifluoroacetylacetone could be analyzed with a gas chromatograph because "the vapor pressure of a component should exceed, say 1mm Hg at the temperature of the column, otherwise its rate of transport through the column will be too slow for practical purposes" (40). This behavior could be related to the tendency of nickel(II) β-diketone to associate into trimers by sharing oxygen atoms. This trimeric unit, in which each nickel ion is surrounded by a distorted octahedron of oxygen atoms, probably exists in benzene solution and in a chloroform solution because such a unit has been shown to exist in these solvents for the analogous acetylacetone compound (41). (See Figure 6, page 63)

Zinc trifluoroacetylacetone could only be obtained as a shoulder on the solvent peak (benzene). (See Figure 7, page 64). It appeared that maybe a longer column or a different solvent would give a quantitative measurement. These were tried but with no measureable improvement. Sievers (38) was able to obtain a characteristic and reproducible retention time for zinc trifluoroacetylacetone but

FIGURE 6

A Typical Chromatogram of Nickel Trifluoroacetylacetone in Benzene

Conditions:

Column - #11 ie.1/8" O.D. by 8'ss, 7.5% SE 30 on 20/40 mesh fire brick

Column Temperature - 125°C

Flash Vaporizer Temperature - 170°C

Sample Size - 5.0 ul

Flow Rate - 30 ml min^{-1}

Detector Temperature - 187°C

Predetector Temperature - 175°C

Detector Current - 200 milliamperes

Attenuator Setting - 2

Solvent - benzene

Concentration - saturated solution

Gas Chromatograph Model - K3

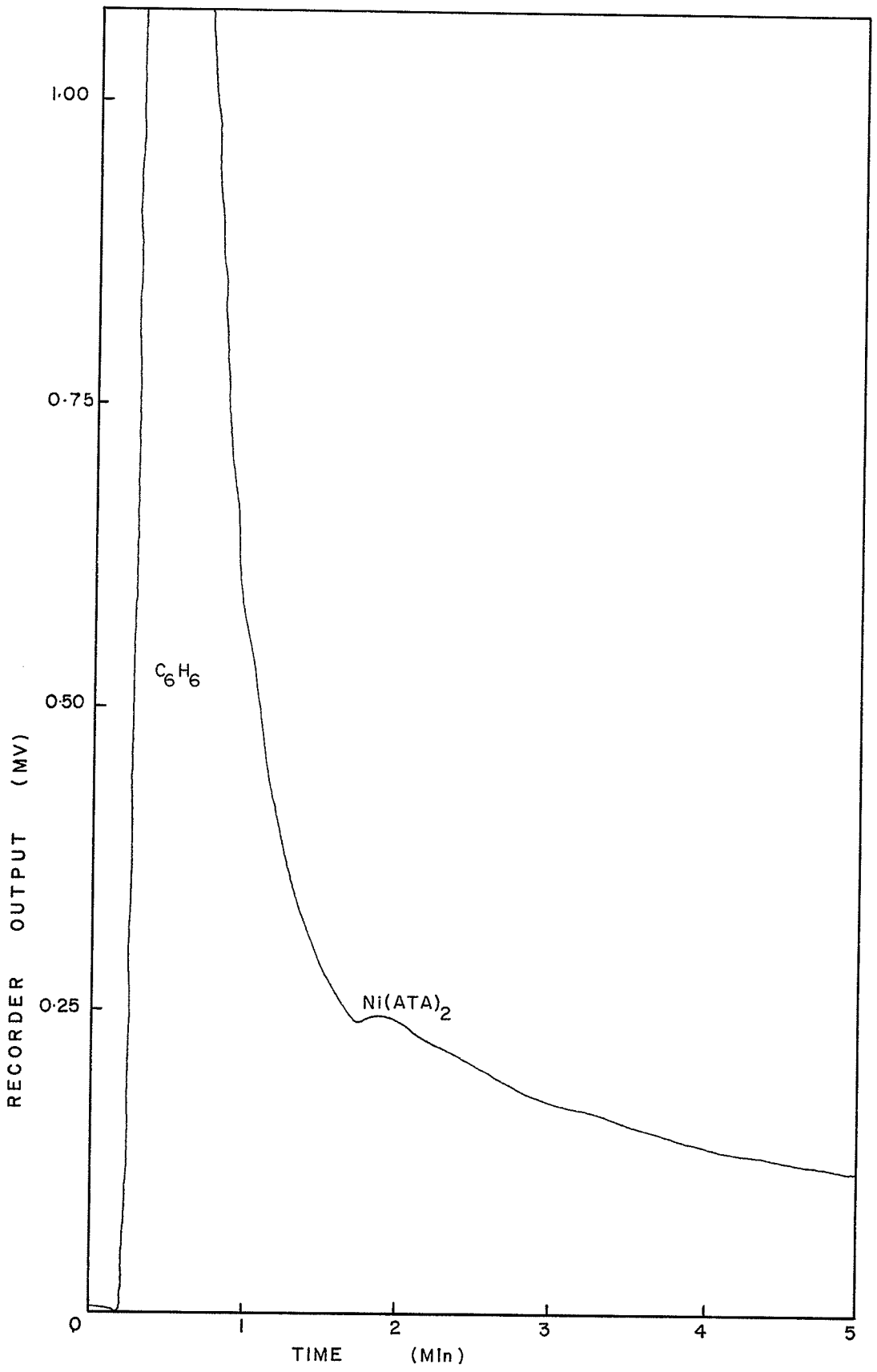

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
Ni(ATA)2
1
2
3
4
5
TIME (MIn)

FIGURE 7

A Typical Chromatogram of Zinc Trifluoroacetylacetone in Benzene

Conditions:

Column - #12 ie.1/8"O.D. by 4'ss, 7.5% SE 30 on 42/60 mesh fire brick

Column Temperature - 80°C

Flash Vaporizer Temperature - 170°C

Sample Size - 3.0 µl

Flow Rate - 26 ml min^{-1}

Reference Flow Rate - 8 ml min^{-1}

Detector Temperature - 225°C

Predetector Temperature - 205°C

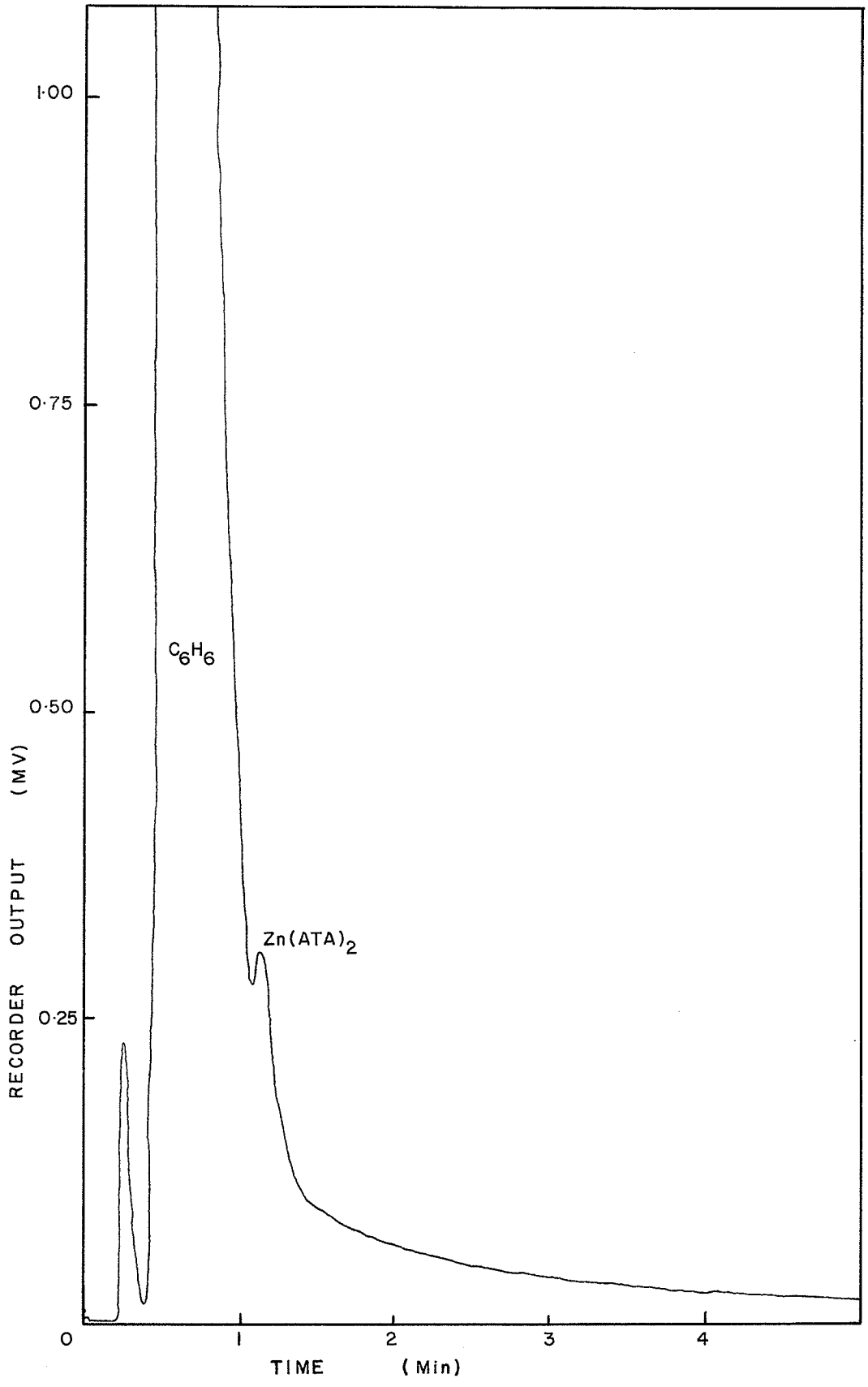
Detector Current - 200 milliamperes

Attenuator Setting - 4

Solvent - benzene

Concentration - saturated solution

Gas Chromatographic Model - KD


1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C_6H_6
$Zn(ATA)_2$
1
2
3
4
TIME (Min)

noticed some evidence of decomposition in the flash vaporizer.

The acetylacetone complex of cobalt (III) decomposed in the gas chromatograph and all attempts to correlate peak areas to sample size relating to this chelate failed. Sievers (17) attempted to chromatograph cobalt acetylacetonate and obtained a sharp, well defined peak, distinct from the solvent peak in the chromatogram, but he discovered that the peak he obtained was the result of a decomposition product of cobalt acetylacetonate.

When the cobalt (II) complex was substituted for the cobalt (III) complex no chromatographic peak was obtained. The acetylacetonato complexes of manganese, nickel, and zinc decomposed giving similar results as the acetylacetonato complexes previously discussed. Therefore, this research had concentrated on the trifluoroacetylacetonato complexes because the fluorine containing chelates are more volatile and can be eluted at lower column temperatures than the corresponding acetylacetonates.

GROUP II

The following tables and graphs summarize the results obtained and show the linearity of response given by a thermal conductivity detector. These results are obtained when using conditions listed in the "Table of Conditions". (See Table 2, page 32). Each of the following Tables consist of four sections. Column one gives sample size, abbreviated SS and given in microliters or reported in the number of milligrams per run. The second column gives the arithmetic average and the fourth column gives the range of the measured peak areas. Peak areas were measured with an "Ott" compensating polar planimeter. Each individual peak area was measured twice. Column three gives the areas calculated by the "Method of Averages" (36). For further details on calculation, see section of this thesis entitled "Measurements and Calculations". A sample of pure solvent was first injected into the gas chromatograph, after which the sample to be analyzed was run. By comparing the two chromatograms, it could be determined which section of the second chromatogram was the result of the metal chelate and which was the result of the solvent.

TABLE 6 - GROUP II

Common Name	IUPAC nomenclature	Abbreviation
Beryllium trifluoroacetylacetone	Bis-(1,1,1-trifluoro-2,4-pentanediono)beryllium(II)	$Be(ATA)_2$
Beryllium acetylacetone	Bis-(2,4-pentanediono) beryllium(II)	$Be(AA)_2$
Aluminum trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)aluminum(III)	$Al(ATA)_3$
Aluminum acetylacetone	Tris-(2,4-pentanediono) aluminum(III)	$Al(AA)_3$
Copper trifluoroacetylacetone	Bis-(1,1,1-trifluoro-2,4-pentanediono)copper(II)	$Cu(ATA)_2$
Chromium trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)chromium(III)	$Cr(ATA)_3$
Iron trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)iron(III)	$Fe(ATA)_3$
Cobalt trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)cobalt(III)	$Co(ATA)_3$
Indium trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)indium(III)	$In(ATA)_3$
Thorium acetylacetone	Tetrakis-(2,4-pentanediono) thorium(IV)	$Th(AA)_4$
Rhodium trifluoroacetylacetone	Tris-(1,1,1-trifluoro-2,4-pentanediono)rhodium(III)	$Rh(ATA)_3$
Zirconium acetylacetone	Tetrakis-(2,4-pentanediono) zirconium(IV)	$Zr(AA)_4$

By examining the calibration curves, it was noticed that not all curves pass through the origin; chromium trifluoroacetylacetonate (Figure 17, page 86) has a positive y-intercept and cobalt trifluoro-acetylacetone (Figure 21, page 92), has a negative y-intercept. Ideally, all standardization curves should pass through the origin for when zero amount of chelate is added to the gas chromatograph, the response is naturally zero. A satisfactory explanation to non-origin intercept was not found in the literature, even though this had been noticed by other workers. Hill and Gesser (18) said that it was probably due to the formation of solid metallic oxide particles in the flame, for their quantitative work was done with a hydrogen-flame ionization detector. A thermal conductivity detector was used in this research; thus whenever the calibration curves did not pass through the origin, Hill and Gesser's explanation to the problem could not be the answer. The research described in this thesis was concerned with the quantitative measurement of sixteen different metals, and included some of the metal chelates in Hill and Gesser's paper. It appears from their paper, that either of the three acetylacetonates would work equally

well in studying metal analysis; but this research showed that the trifluoroacetylacetone chelates were more volatile than the corresponding acetylacetone chelates and were, therefore, more easily studied. Ross and Wheeler (20), who used an electron capture detector, had results where the calibration curve went through the origin but had a non-linear curve where a slope change at low concentration enabled the curve to pass through the origin. This phenomenon was never observed in the present work possibly due to the fact that the electron capture detector, which they used, is more sensitive than a thermal conductivity detector. In as much as their quantitative work was done with only one compound it becomes difficult to draw any definite conclusions. One explanation for non-origin intercept can be obtained from the two calibration curves of copper trifluoroacetylacetone obtained in this research. The first (Figure 15, page 83) was obtained for $Cu(ATA)_2$ in benzene and the calibration curve passed through the origin. In the second case, (Figure 38, page 123) copper trifluoroacetylacetone was standardized, in order to determine it in a mixture of beryllium trifluoroacetylacetone, aluminum trifluoroacetylacetone, and copper trifluoroacetylacetone, and it was demonstrated

that under the chromatographic conditions used $Cu(ATA)_2$ had a negative y-intercept. The first calibration for $Cu(ATA)_2$ was done when the complex had a retention time of 3.7 minutes, in the second case, the retention time was 7.2 minutes. In the second calibration, the complex was in the column almost twice as long, which suggests that column conditioning with the component appeared to have a much greater effect on the y-intercept. Column conditioning with the compound is the successive injections of the compound under investigation until maximum and reproducible peak areas are obtained (19). The longer a sample was in the column, the greater was the chance for adsorption to take place. That is, when measuring only one component, conditions were set up so that the component did not have time enough to be substantially adsorbed on the solid substrate and still had a retention time large enough to be separated from the solvent peak. When this was accomplished the calibration curve went through the origin as in the case of the first calibration plot of $Cu(ATA)_2$. It was impossible when dealing with multi-component systems to have the best conditions for each component. If conditions were such that a component, for example $Cu(ATA)_2$, spends a relatively

long time in the column, then, in order to compensate for the adsorption effect, the column was conditioned with the component. Inasmuch as non-origin intercept did not influence the goal of this research, it was not vigorously studied. It would be a very interesting problem to investigate all the parameters of non-origin intercepts.

Tables 7 through 18 and Figures 9 through 30 summarize the results obtained and show the linearity of response given by a thermal conductivity detector. The results are those obtained while using conditions listed in the "Table of Conditions". (See Table 2, page 32).

On pages 72 through 104 there is a chromatogram for each single component studied and quantitatively analyzed, followed by a Table comparing the experimental results with areas calculated from the "Method of Averages". A calibration curve for each of these metal complexes is also reported. It should be noted that the two areas are within experimental error of each other.

For Figure 18, page 87, the cis and trans isomers are speculative for there should be more trans isomers than cis in a benzene solution.

FIGURE 8

A Typical Chromatogram of Beryllium Trifluoroacetylacetone in Benzene

Conditions:

Column - #3 ie, $\frac{1}{4}$"O.D. by 4'Cu, 0.5% apiezon L on 50 mesh glass beads

Column Temperature - 112°C

Flash Vaporizer Temperature - 140°C

Sample Size - 5 - 20 ul

Flow Rate - 45 ml min^{-1}

Detector Temperature - 200°

Predetector Temperature - -

Detector Current - 145 milliamperes

Attenuator Setting - 2

Solvent - benzene

Gas Chromatograph Model - K3

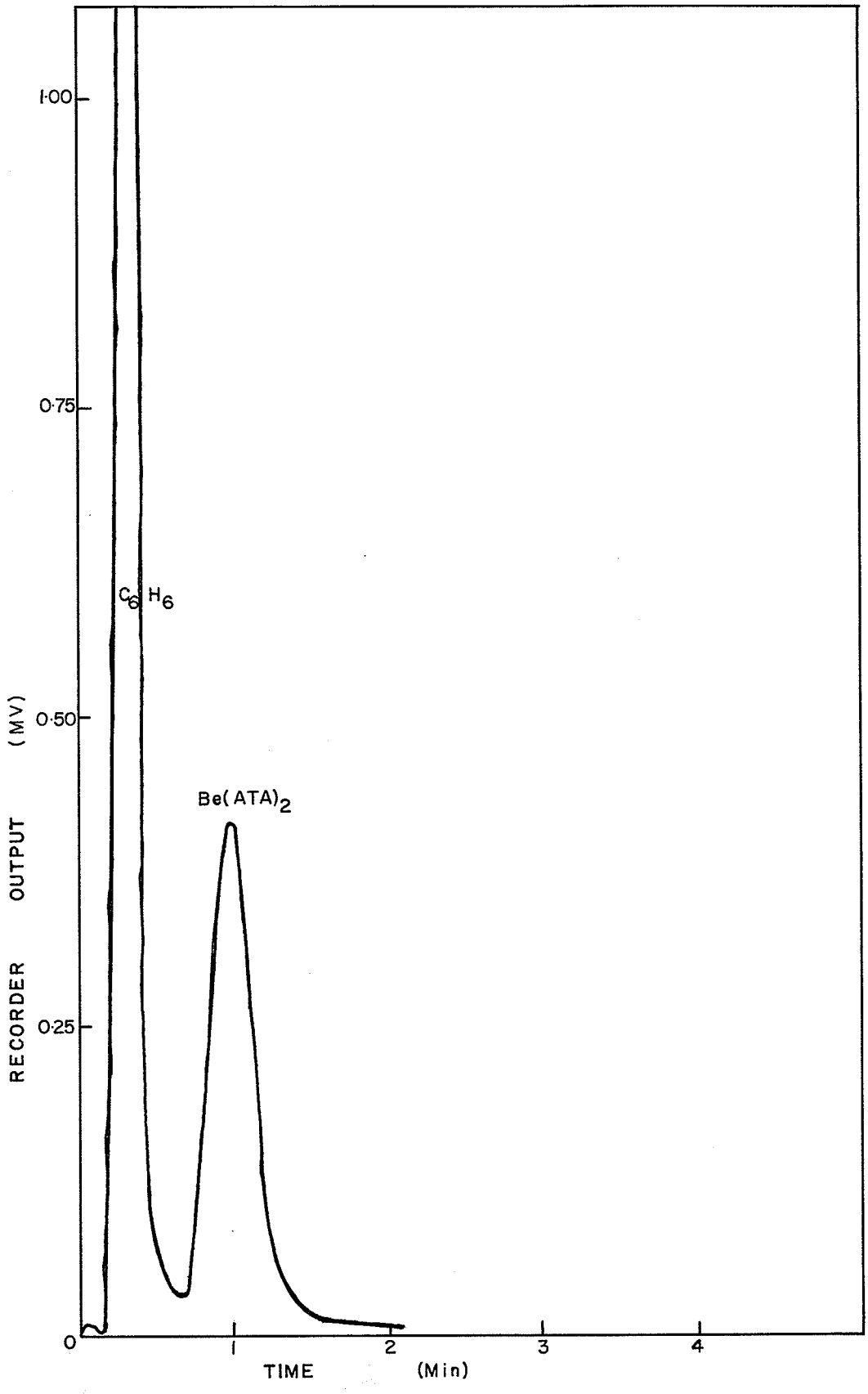

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
Be(ATA)2
1
2
3
4
TIME (Min)

TABLE 7

ANALYSIS OF KNOWN AMOUNTS OF
Bis(1,1,1-trifluoro-2,4-pentanediono)beryllium(II)

Sample Size (mg)	Average area(cm^2)	*Calculated area(cm^2)	Range of areas(cm^2)
0.258	4.9	4.6	4.5 - 5.2
0.516	9.8	10.2	9.0 - 10.6
0.775	15.6	15.8	14.6 - 16.6
1.03	21.9	21.4	21.8 - 22.2

*Calculated from the Method of Averages

FIGURE 9

Calibration Curve for
Beryllium Trifluoroacetylacetone

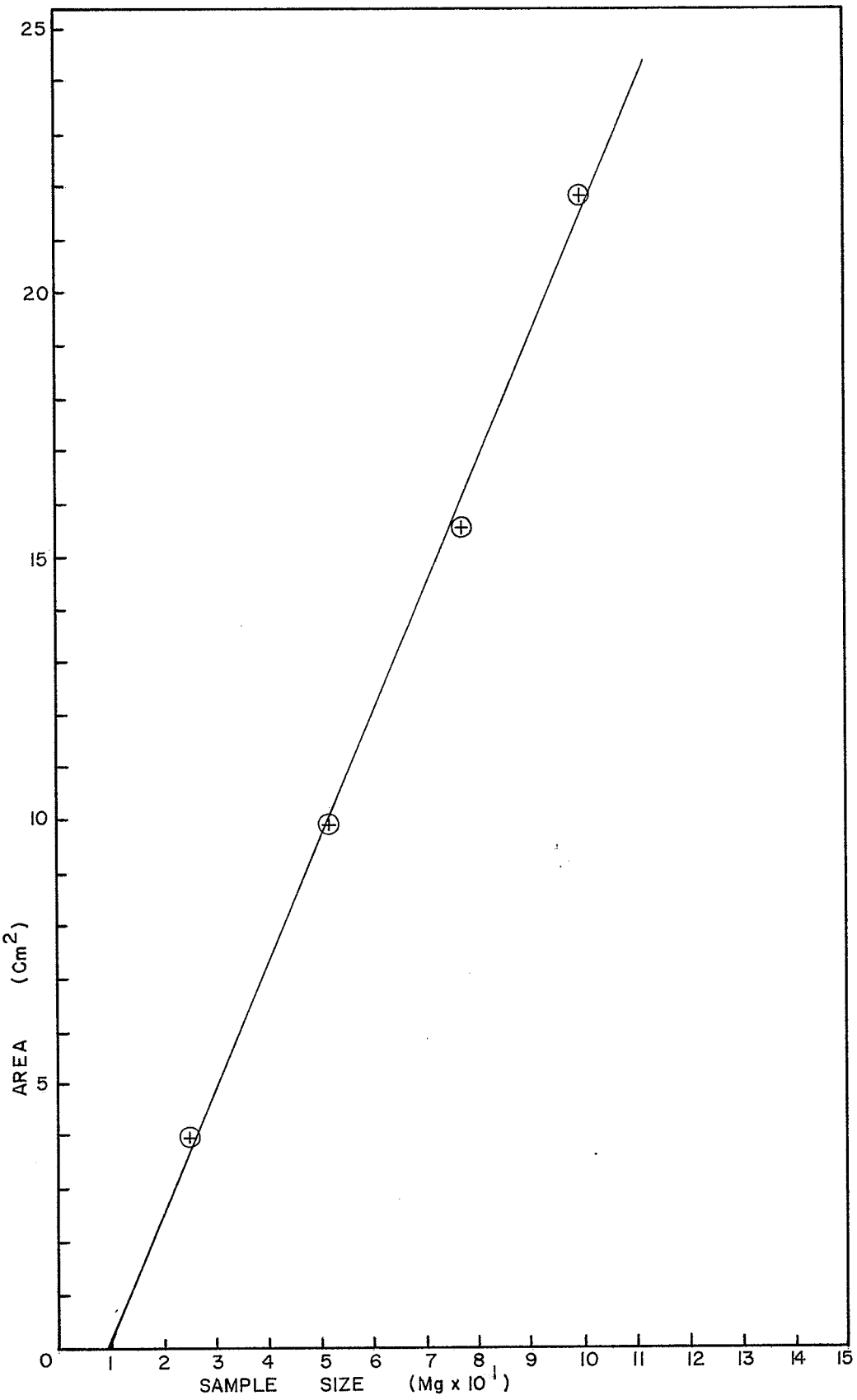

25
20
15
10
5
0
AREA (Cm2)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
SAMPLE SIZE (Mg x 10 1)

FIGURE 10

A Typical Chromatogram of Beryllium Acetylacetone in Benzene

Conditions:

Column - #3 ie.$\frac{1}{4}$"O.D. by 4'Cu, 0.5% apiezon L on 50 mesh glass beads

Column Temperature - 146°C

Flash Vaporizer Temperature - 205°C

Sample Size - 10.0 to 50.0 µl

Flow Rate - 50 ml min^{-1}

Detector Temperature - 200°C

Detector Current - 145 milliamperes

Attenuator Setting - 5

Solvent - Carbon tetrachloride

Gas Chromatograph Model - K3

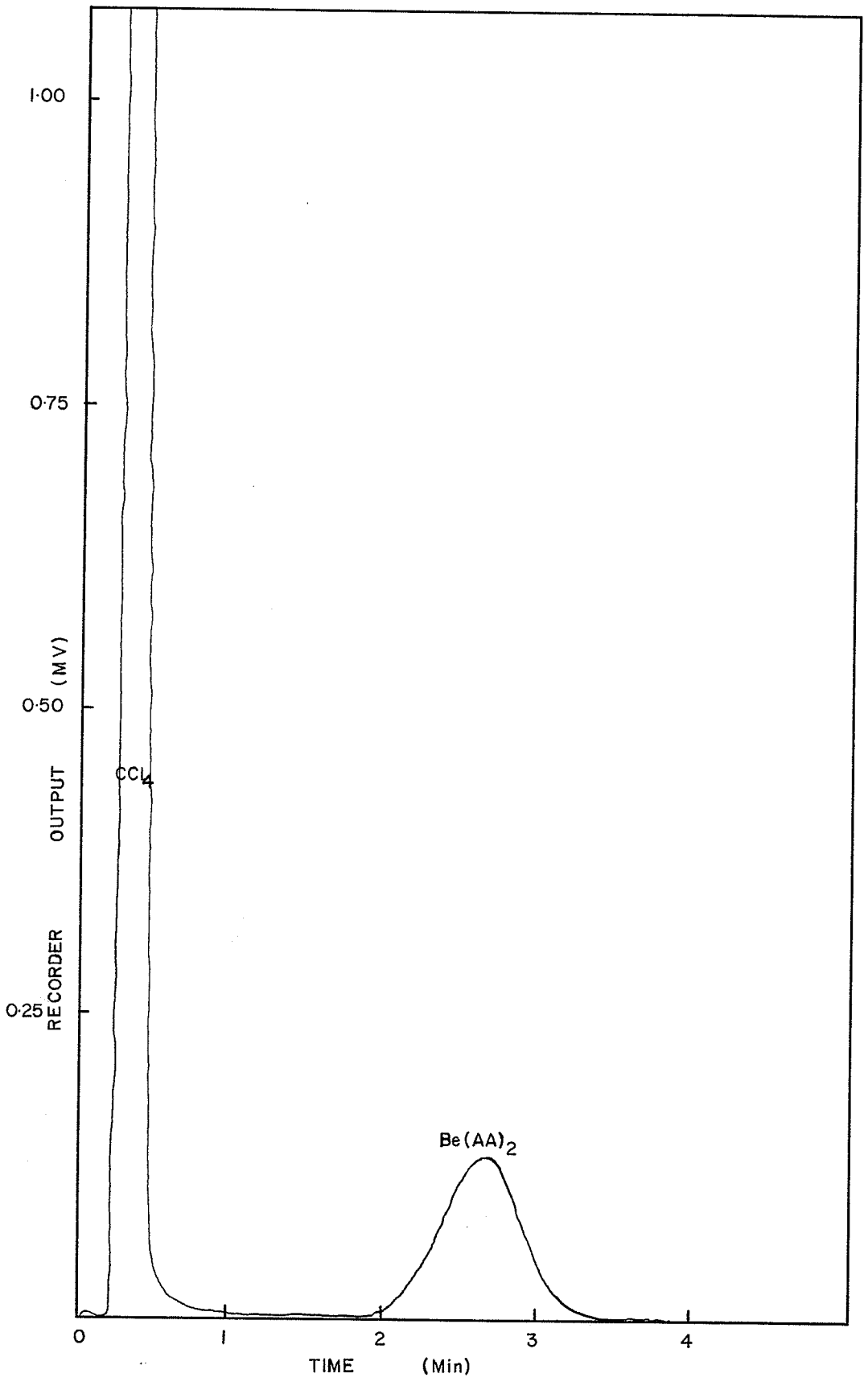

1·00
0·75
0·50
0·25
RECORDER OUTPUT (MV)
CCl4
Be(AA)2
0
1
2
3
4
TIME (Min)

TABLE 8

ANALYSIS OF KNOWN AMOUNTS OF
Bis(2,4-pentanediono)beryllium(II)

Sample* Size(μl)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
10.0	7.5	8.4	7.3 - 7.6
20.0	14.6	15.1	14.2 - 15.1
30.0	23.0	21.7	21.2 - 24.1
40.0	28.9	28.3	26.6 - 29.8
50.0	34.3	34.9	33.4 - 35.8

*0.0450 mg per μl

FIGURE 11

Calibration Curve for Beryllium Acetylacetone

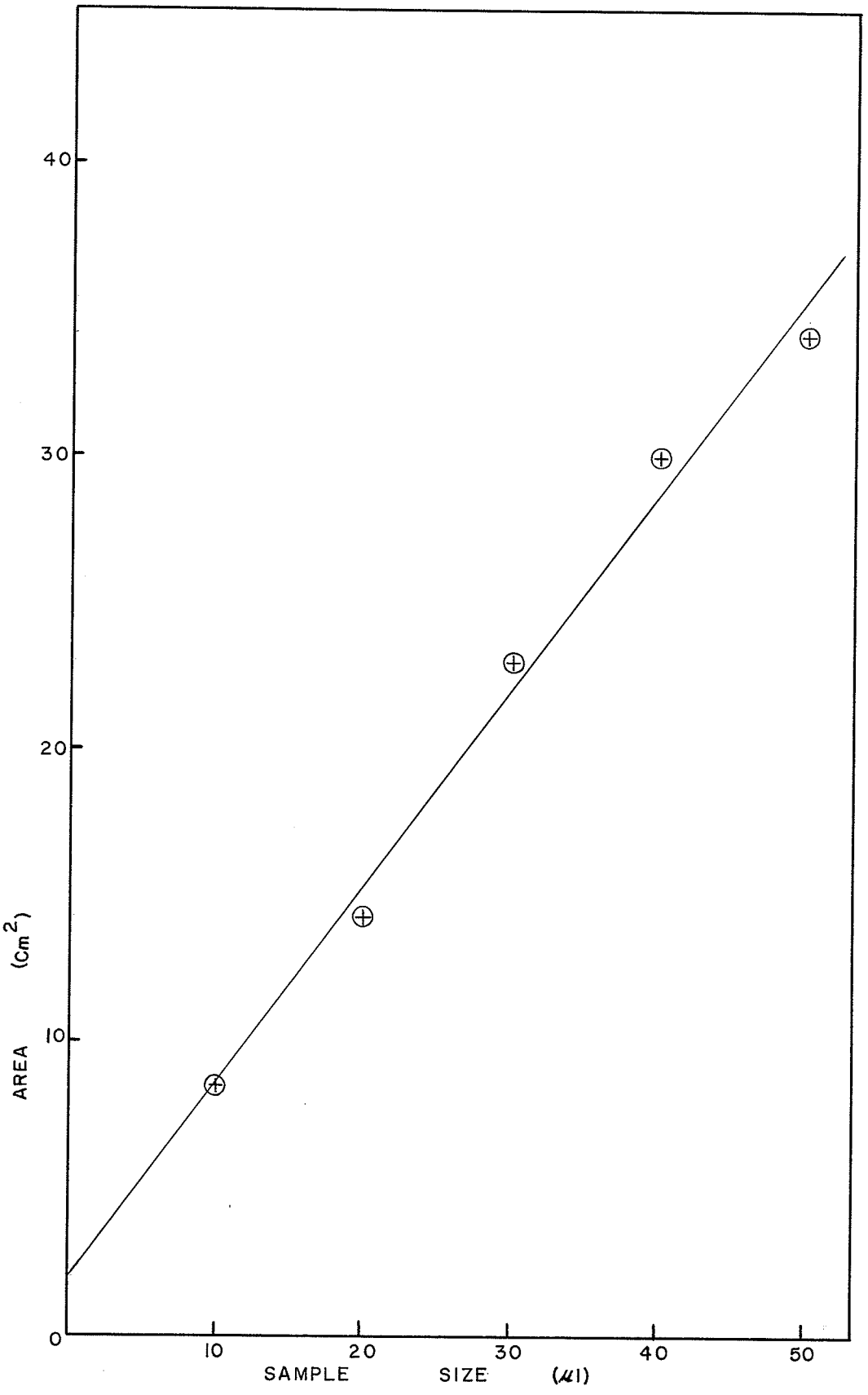

40
30
20
10
0
AREA (Cm²)
10
20
30
40
50
SAMPLE SIZE (µl)

FIGURE 12

A Typical Chromatogram of
Aluminum Trifluoroacetylacetone

Conditions:

Column - #3 ie, ¼"O.D. by 4' Cu. 0.5% apiezon L on 50 mesh glass beads

Column Temperature - 107°C

Flash Vaporizer Temperature - 120°C

Sample Size - 5-20 ul

Flow Rate - 44 ml min^{-1}

Detector Temperature - 200°C

Predetector Temperature - -

Detector Current - 145 milliamperes

Attenuator Setting - 2

Solvent - benzene

Gas Chromatograph Model - K3

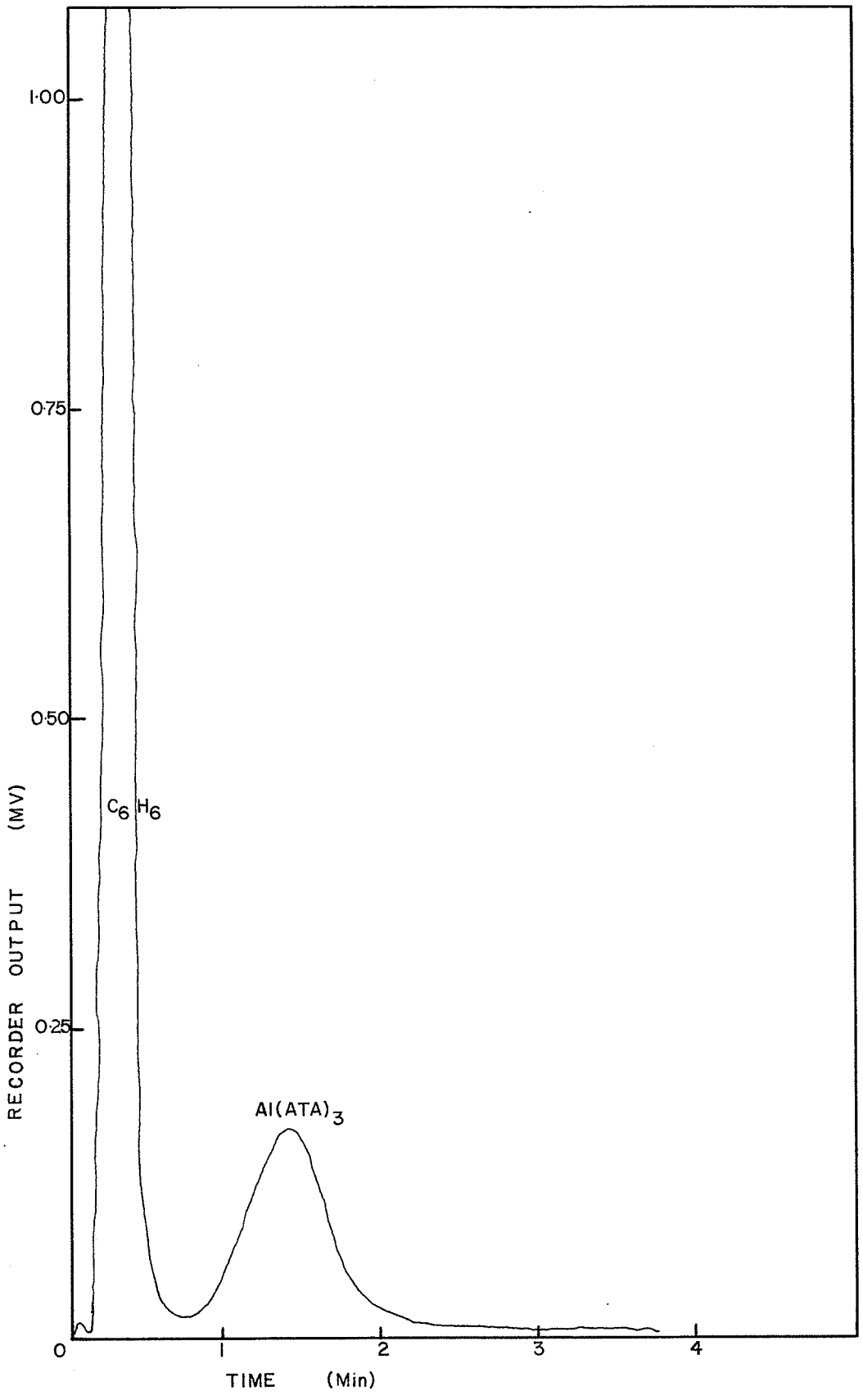

1·00
0·75
0·50
0·25
0
1
2
3
4
RECORDER OUTPUT (MV)
TIME (Min)
C6 H6
Al(ATA)3

TABLE 9

ANALYSIS OF KNOWN AMOUNTS OF
Tris(1,1,1-trifluoro-2,4-pentanediono)aluminum(III)

Sample* Size(µl)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
5.0	4.2	4.2	4.0 - 4.4
10.0	8.2	8.4	7.5 - 8.6
15.0	12.9	12.6	12.2 - 13.4
20.0	16.9	16.8	15.1 - 18.0

*concentration = 0.049 mg per µl

FIGURE 13

Calibration Curve for
Aluminum Trifluoroacetylacetone

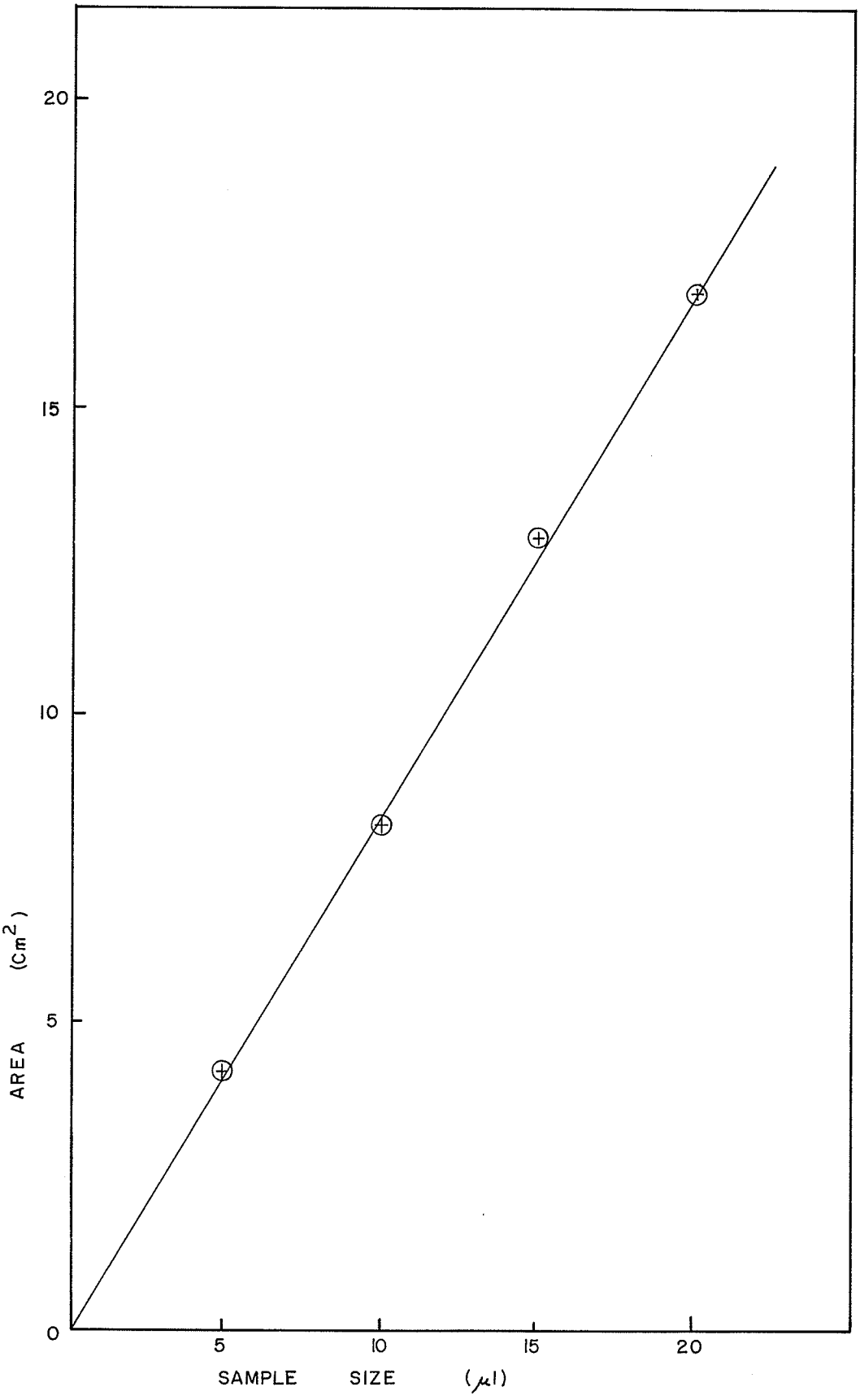

20
15
10
5
0
AREA (Cm²)
5
10
15
20
SAMPLE SIZE (µl)

FIGURE 14

A Typical Chromatogram of
Copper Trifluoroacetylacetone

Conditions:

Column - #11 ie. 1/8" O.D. by 8' ss 7.5% SE 30 on 20/40 mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 170°C

Sample Size - 1-5 ul

Flow Rate - 55 ml min^{-1}

Detector Temperature - 188°C

Predetector Temperature - 176°C

Detector Current - 200 milliamperes

Attenuator Setting - 1

Solvent - benzene

Gas Chromatograph Model - KD

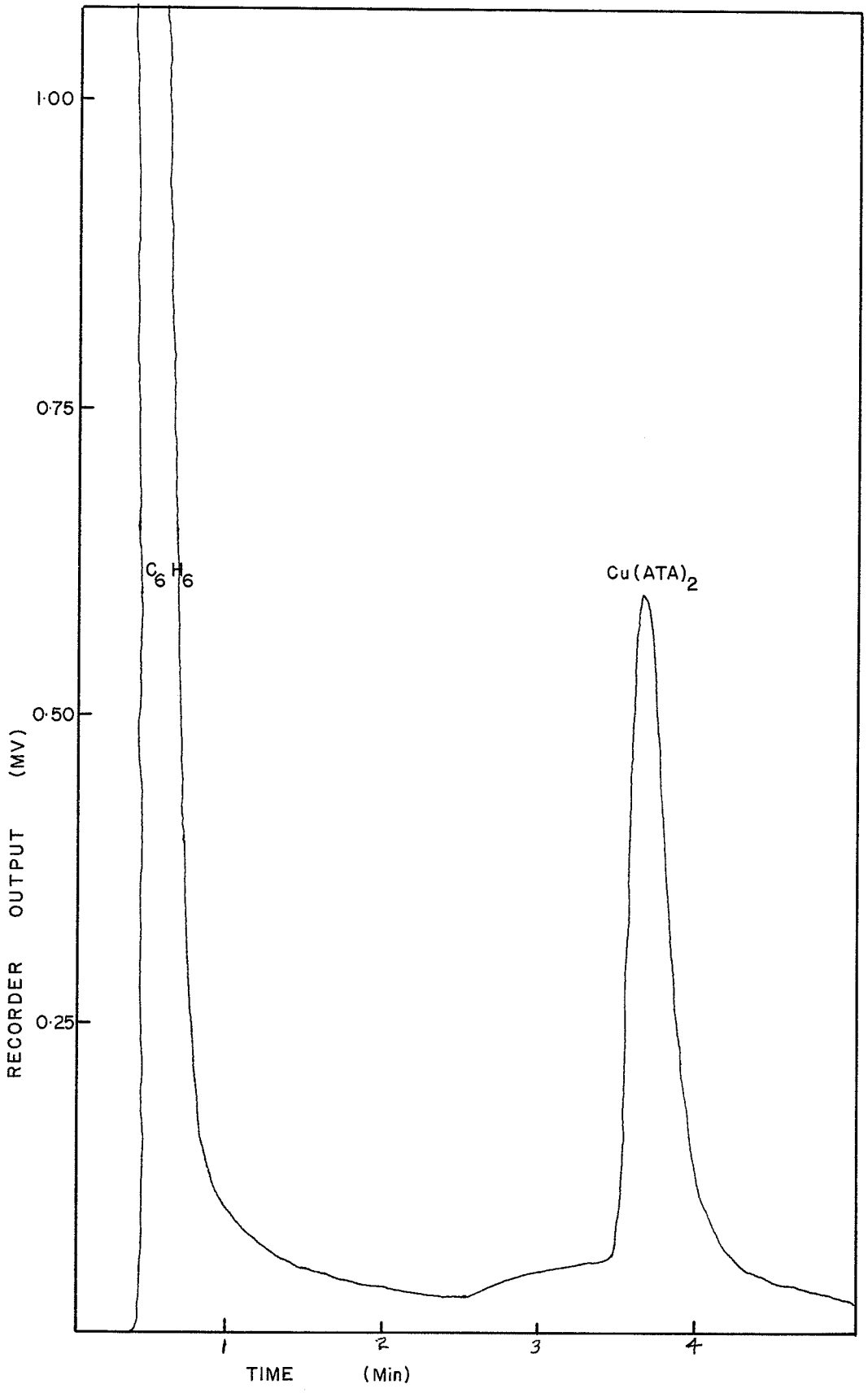

1·00
0·75
0·50
0·25
RECORDER OUTPUT (MV)
C6 H6
Cu(ATA)2
1
2
3
4
TIME (Min)

TABLE 10

ANALYSIS OF KNOWN AMOUNTS OF
Bis(1,1,1-trifluoro-2,4-pentanediono)-copper(II)

Sample Size(mg)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
0.0205	3.0	3.0	2.4 - 3.6
0.0410	6.0	5.9	5.6 - 6.8
0.0615	8.8	8.8	8.4 - 9.5
0.0820	11.4	11.7	11.0 - 11.8
0.102	14.9	14.6	14.4 - 15.5

FIGURE 15

Calibration Curve for
Copper Trifluoroacetylacetone

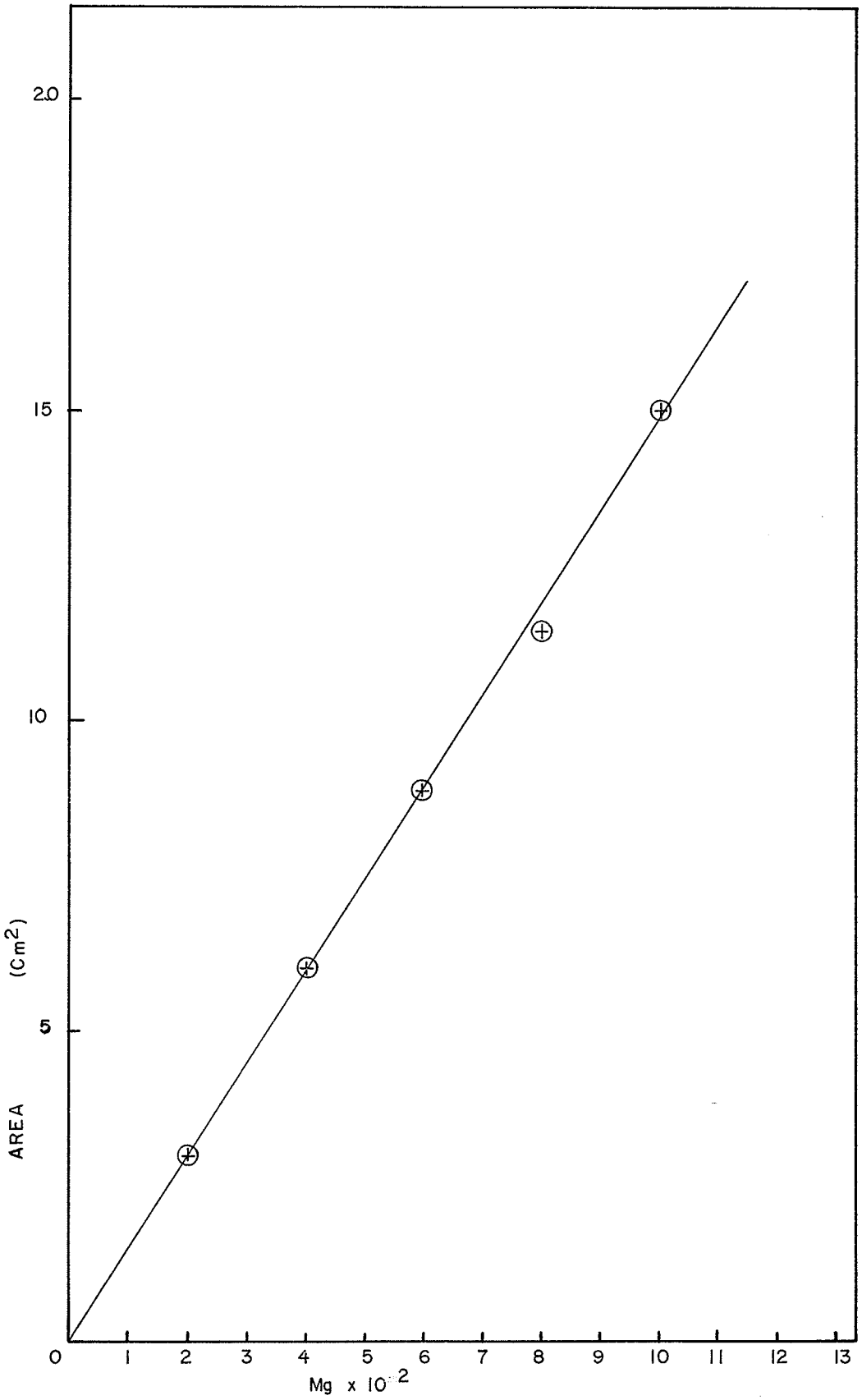

20
15
10
5
0
AREA (Cm2)
1
2
3
4
5
6
7
8
9
10
11
12
13
Mg x 10 2

FIGURE 16

A Typical Chromatogram of
Chromium Trifluoroacetylacetone

Conditions:

Column - #11 ie. 1/8" O.D. by 8' ss 7.5% SE 30 on 20/40 mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 170°C

Sample Size - 1-10 ul

Flow Rate - 44 ml min^{-1}

Detector Temperature - 188°C

Predetector Temperature - 176°C

Detector Current - 200 milliamperes

Attenuator Setting - 1

Solvent - benzene

Gas Chromatograph Model - KD

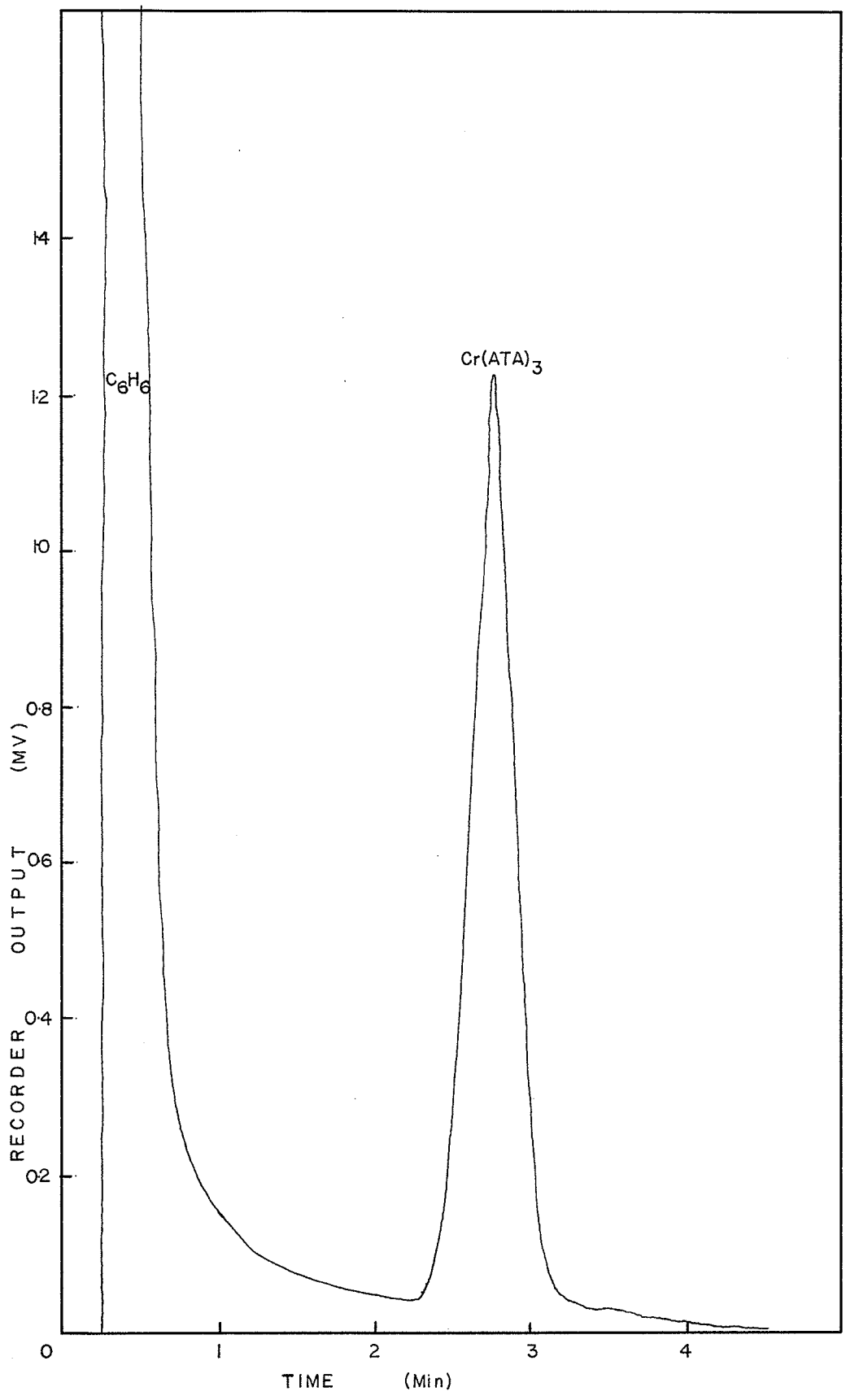

C6H6
Cr(ATA)3
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
1
2
3
4
RECORDER OUTPUT (MV)
TIME (Min)

TABLE 11

ANALYSIS OF KNOWN AMOUNTS OF
Tris-(1,1,1-trifluoro-2,4-pentanediono)chromium(III)

Sample Size(mg)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
0.0170	6.7	5.9	5.6 - 7.8
0.0340	8.8	8.8	8.0 - 10.2
0.0510	11.0	11.7	10.5 - 11.7
0.0680	14.4	14.6	13.6 - 15.6
0.0850	17.6	17.5	17.1 - 18.2
0.102	20.2	20.4	20.1 - 20.3
0.136	25.9	26.2	25.6 - 26.0
0.170	32.3	32.0	32.0 - 32.8

FIGURE 17

Calibration Curve for
Chromium Trifluoroacetylacetone

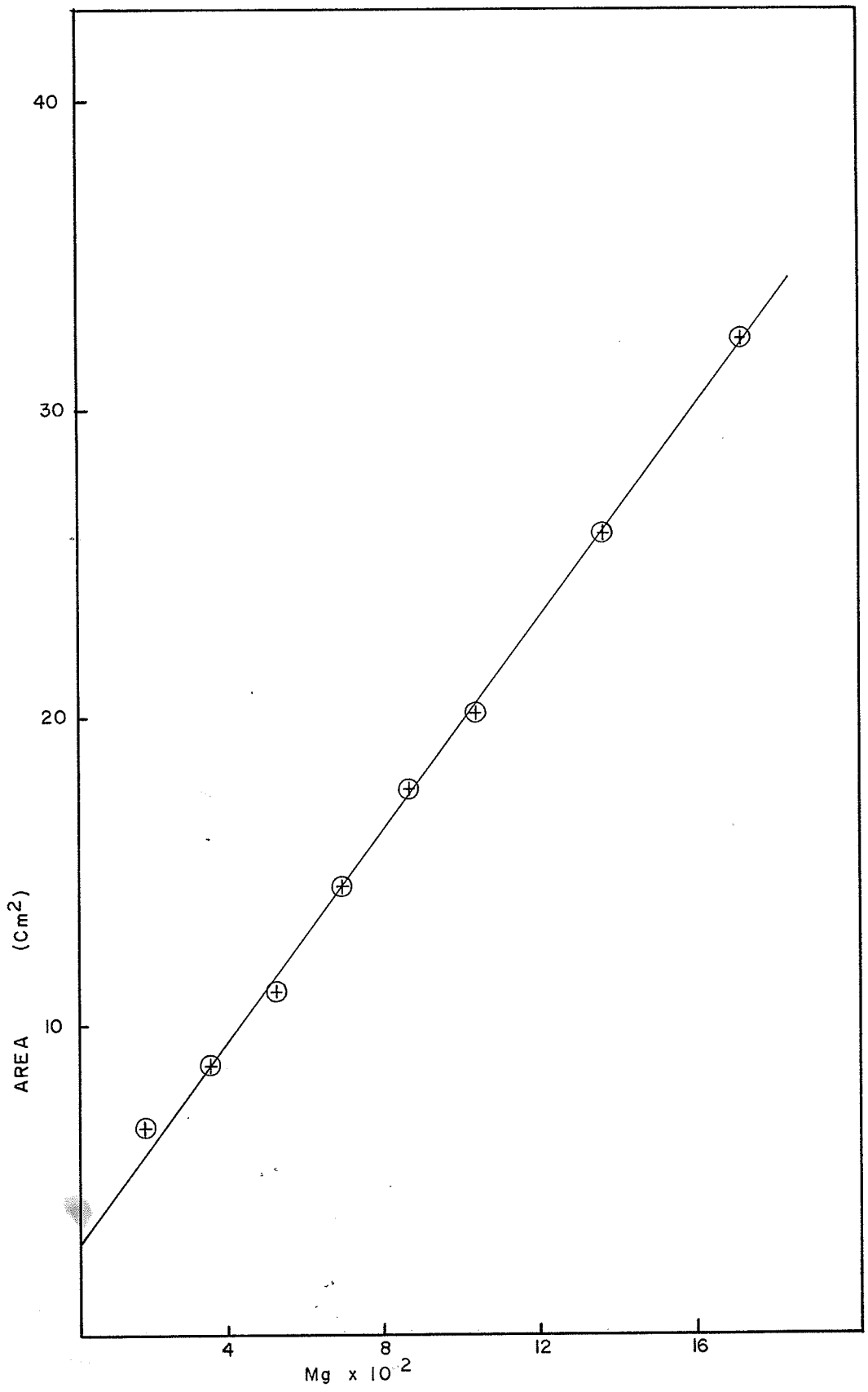

40
30
20
10
AREA (Cm2)
4
8
12
16
Mg x 10 2

FIGURE 18

A Typical Chromatogram of
Iron Trifluoroacetylacetone

Conditions:

Column - #11 ie. 1/8" O.D. by 8' ss 7.5% SE 30 on 20/40 mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 170°C

Sample Size - 2-10 ul

Flow Rate - 64 ml min^{-1}

Detector Temperature - 187°C

Predetector Temperature - 175°C

Detector Current - 200 milliamperes

Attenuator Setting - 1

Solvent - benzene

Gas Chromatograph Model KD

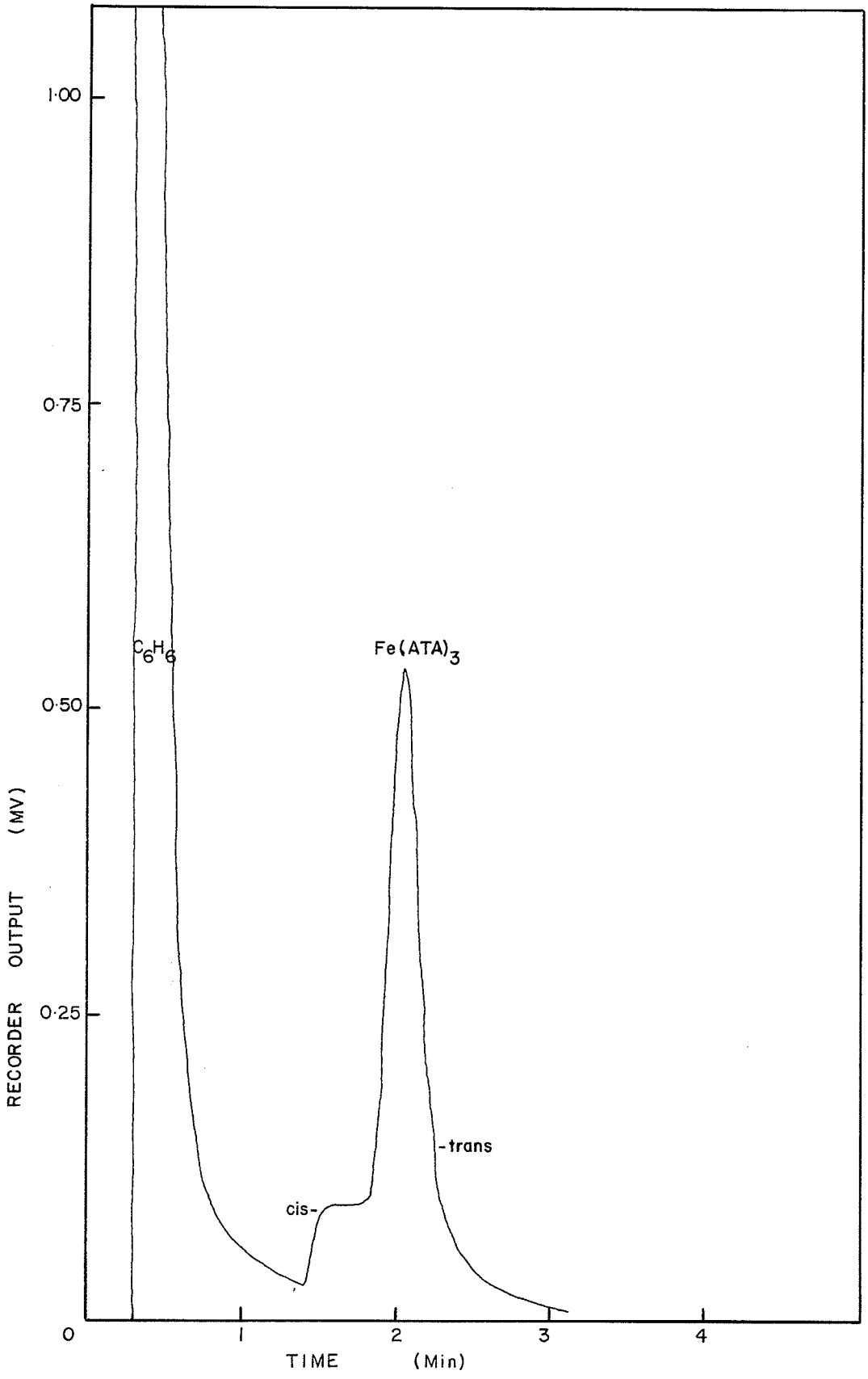

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
Fe(ATA)3
cis-
-trans
1
2
3
4
TIME (Min)

TABLE 12

ANALYSIS OF KNOWN AMOUNTS OF
Tris-(1,1,1-trifluoro-2,4-pentanediono)-iron(III)

Sample Size(mg)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
0.0266	2.0	2.2	2.0 - 2.0
0.0399	3.4	3.6	3.2 - 3.6
0.0532	5.2	5.0	5.1 - 5.3
0.0665	6.5	6.4	6.2 - 6.9
0.0798	8.0	7.8	7.8 - 8.2
0.0931	9.5	9.2	9.4 - 9.8
0.106	10.5	10.6	10.0 - 10.8
0.120	12.2	12.0	11.8 - 12.6
0.133	13.2	13.4	12.7 - 13.8

FIGURE 19

Calibration Curve for Iron Trifluoroacetylacetone

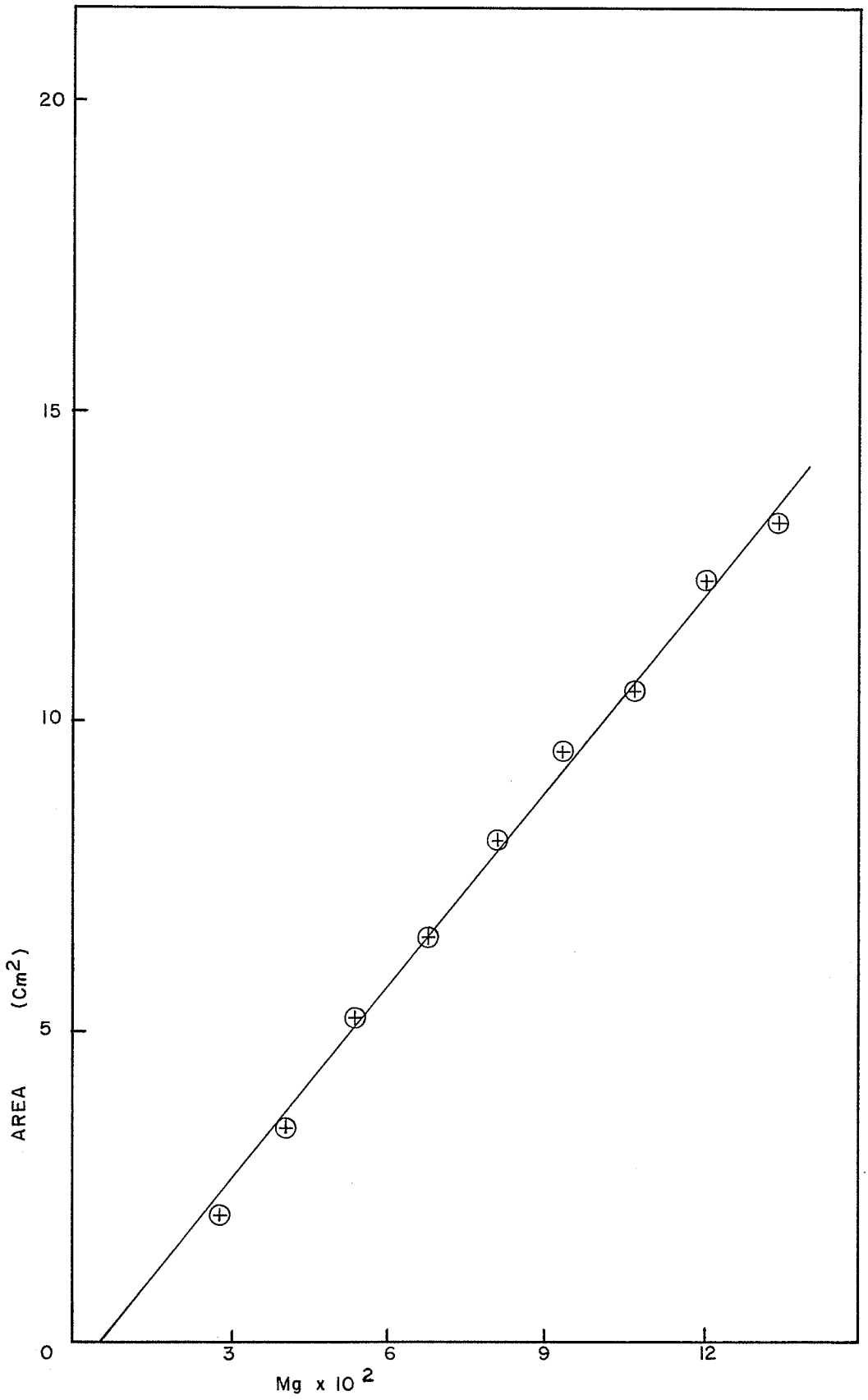

20
15
10
5
0
AREA (Cm2)
3
6
9
12
Mg x 10 2

FIGURE 20

A Typical Chromatogram of
Cobalt Trifluoroacetylacetone

Conditions:

Column - #12 ie, 1/8" O.D. by 4'ss 7.5% SE 30 on 42/60 mesh fire brick acid washed

Column Temperature - 175°C

Flash Vaporizer Temperature - 205°C

Sample Size - 4.0 ul

Flow Rate - 51 ml min^{-1}

Detector Temperature - 232°C

Predetector Temperature - 210°C

Detector Current - 200 milliamperes

Attenuator Setting - 2

Solvent - carbon tetrachloride

Gas Chromatograph Model-KD

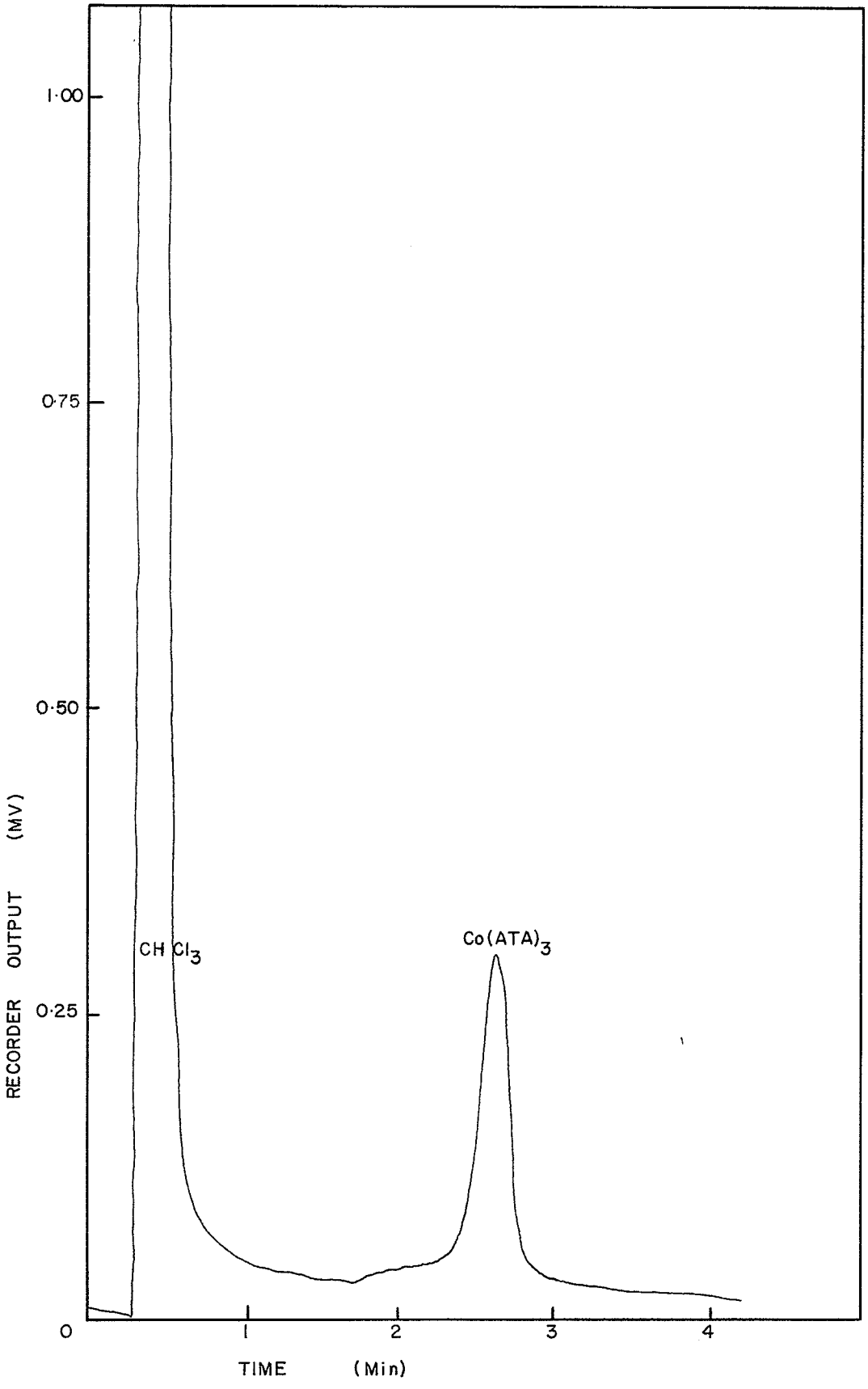

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
CH Cl3
Co(ATA)3
1
2
3
4
TIME (Min)

TABLE 13

ANALYSIS OF KNOWN AMOUNTS OF
Tris-(1,1,1-trifluoro-2,4-pentanediono)cobalt(III)

Sample Size(mg)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
0.175	27.1	26.5	27.0 - 27.2
0.0875	13.3	13.2	13.1 - 13.8
0.0438	6.6	6.6	6.3 - 7.1
0.0219	2.9	2.9	2.6 - 3.1

FIGURE 21

Calibration Curve for
Cobalt Trifluoroacetylacetone

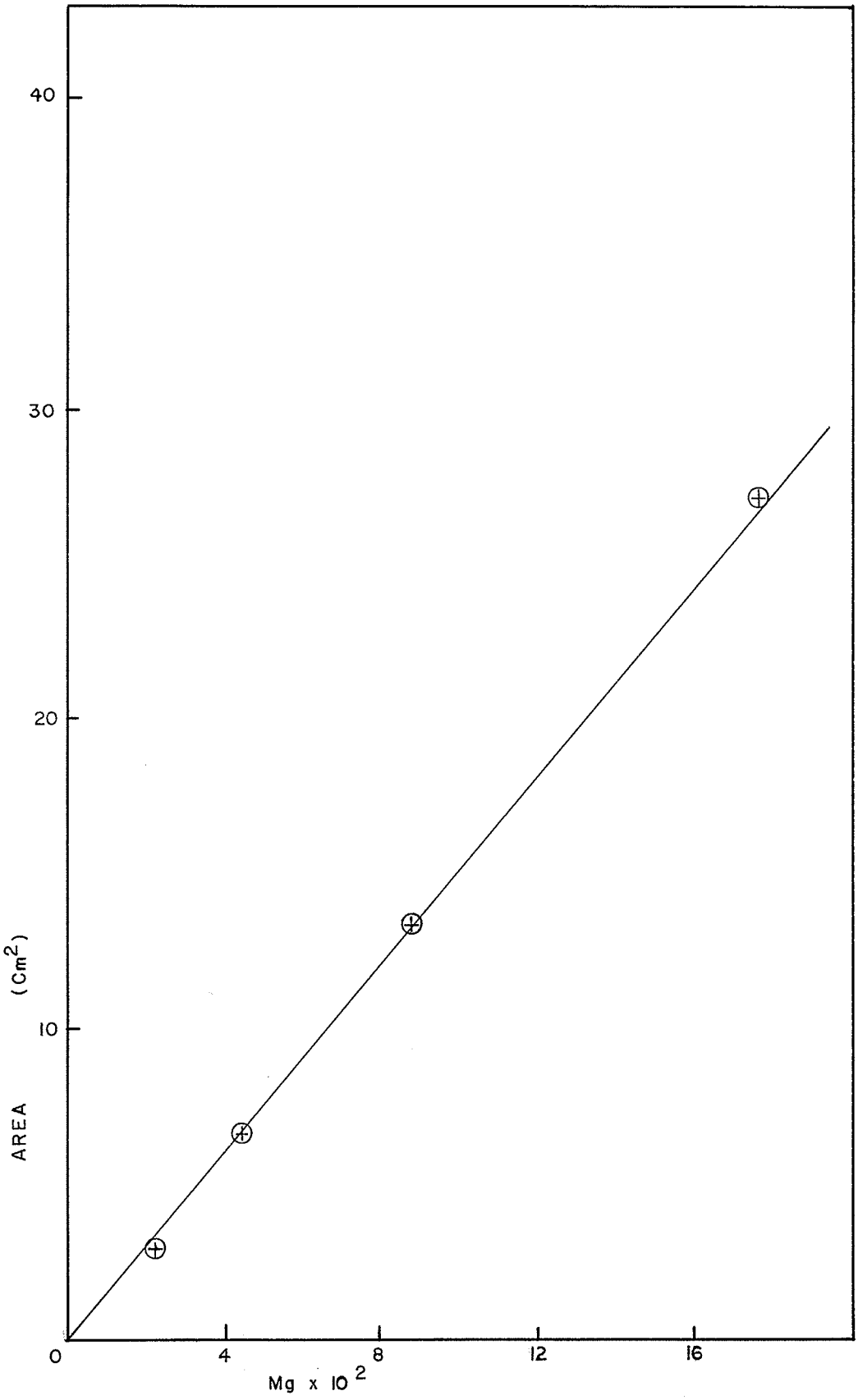

40
30
20
10
0
AREA (Cm2)
4
8
12
16
Mg x 10 2

FIGURE 22

A Typical Chromatogram of
Indium Trifluoroacetylacetone

Conditions:

Column - #12 ie. 1/8" O.D. by 4' ss 7.5% SE 30 on 42/60 mesh fire brick acid washed

Column Temperature - 175°C

Flash Vaporizer Temperature - 198°C

Sample Size - 2.0 - 8.0 ul

Flow Rate - 32 ml min^{-1}

Detector Temperature - 220°C

Predetector Temperature - 200°C

Detector Current - 200 milliamperes

Attenuator Setting - 1

Reference Flow Rate - 9.6 ml min^{-1}

Solvent - carbon tetrachloride

Gas Chromatograph Model - KD

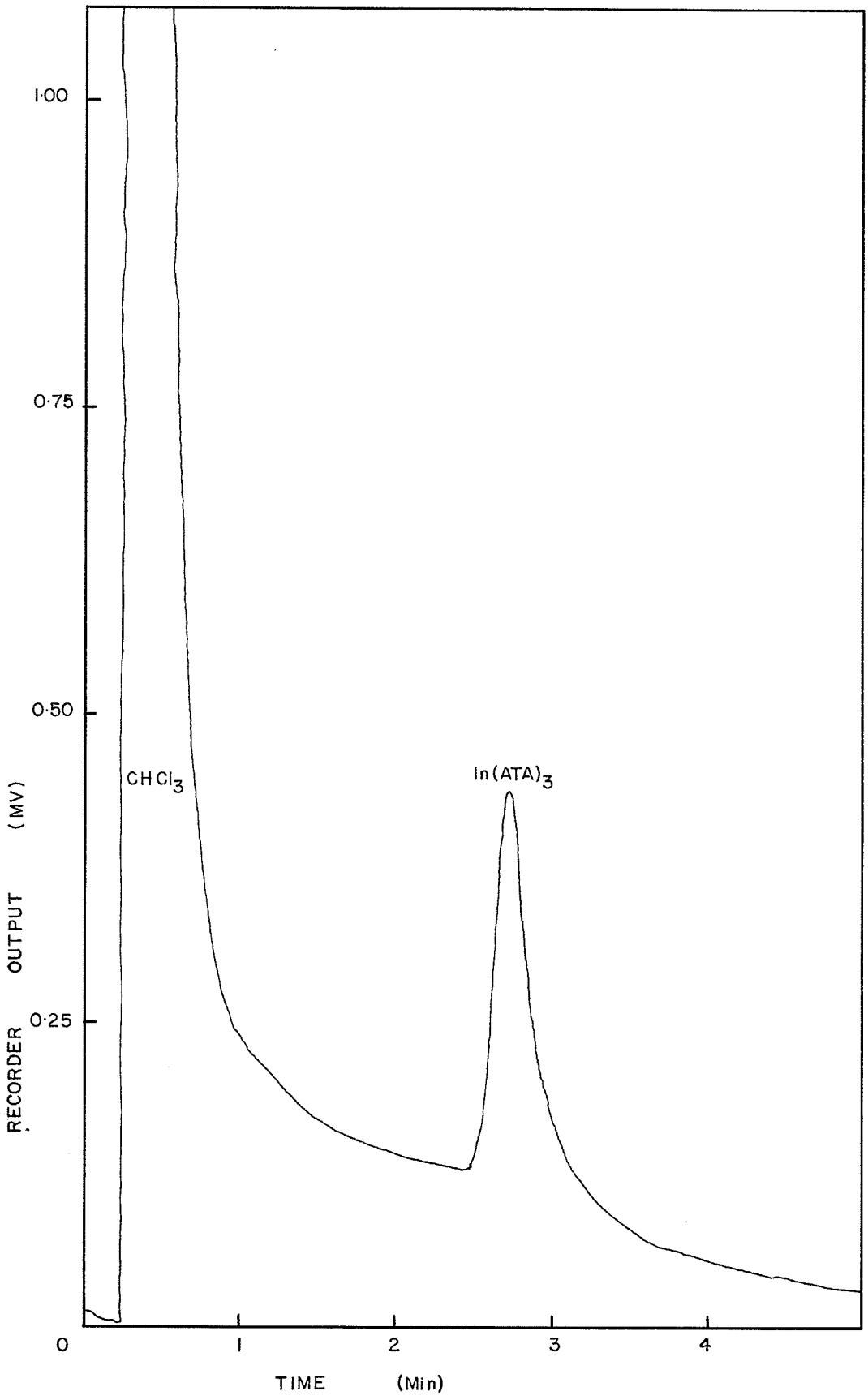

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
CHCl3
In(ATA)3
1
2
3
4
TIME (Min)

TABLE 14

ANALYSIS OF KNOWN AMOUNTS OF
Tris-(1,1,1-trifluoro-2,4-pentanediono)indium(III)

Sample Size(mg)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
0.0312	3.8	4.1	3.5 - 4.2
0.0468	6.1	5.9	5.8 - 6.5
0.0624	7.6	7.7	7.3 - 7.8
0.0780	9.2	9.5	9.0 - 9.4
0.0936	11.1	11.3	10.7 - 11.6
0.109	12.8	13.1	12.4 - 13.0
0.125	14.8	14.9	14.5 - 15.2

FIGURE 23

Calibration Curve for
Indium Trifluoroacetylacetone

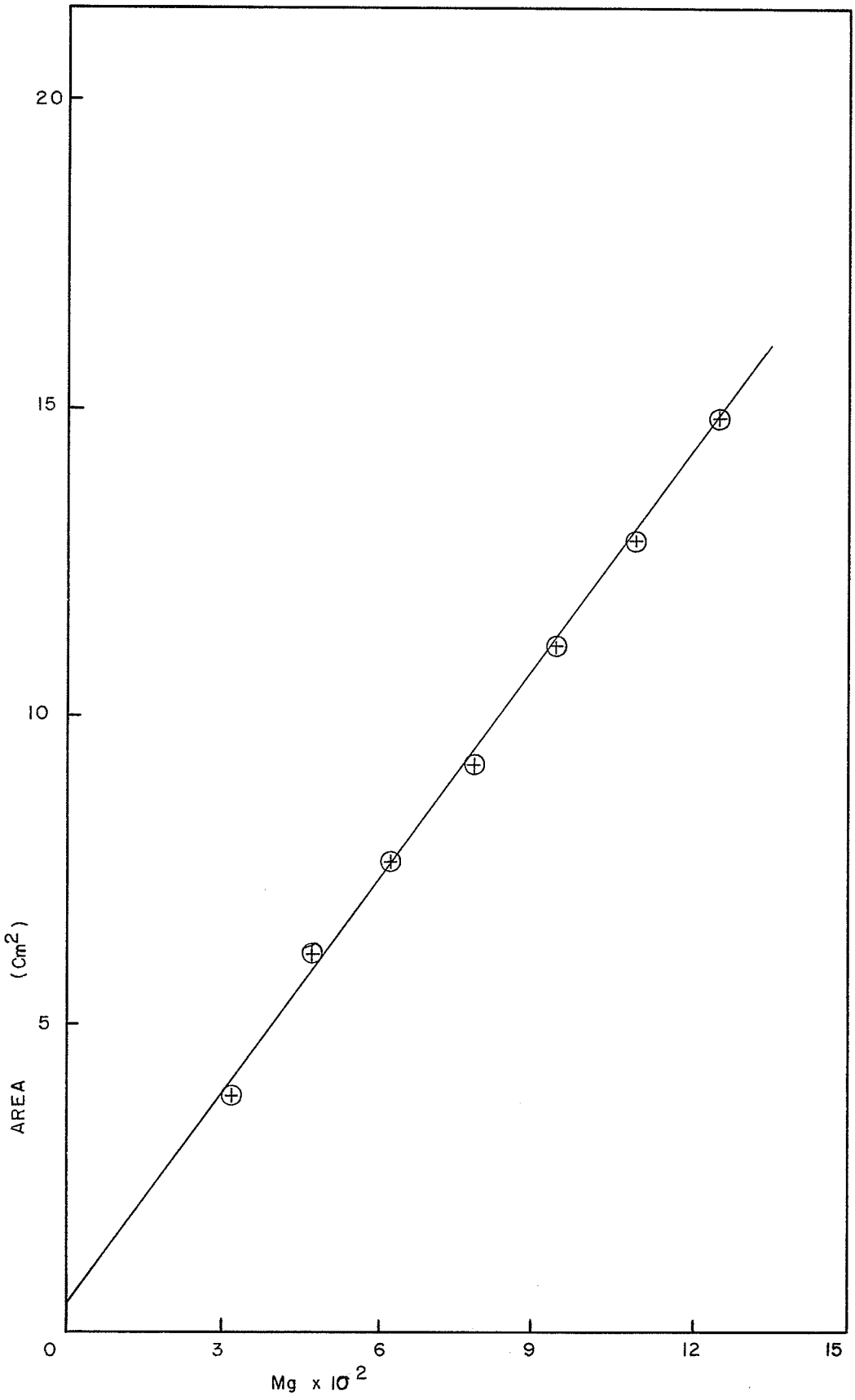

20
15
10
5
0
AREA (Cm2)
3
6
9
12
15
Mg x 10 2

FIGURE 24

A Typical Chromatogram of Thorium Acetylacetone

Conditions:

Column - #12 ie. 1/8" O.D. by 4' ss 7.5% SE 30 on 42/60 mesh fire brick acid washed

Column Temperature - 140°C

Flash Vaporizer Temperature - 190°C

Sample Size - 1.0 - 6.0 ul

Flow Rate - 41 ml min^{-1}

Reference Flow Rate - 9 ml min^{-1}

Predetector Temperature - 220°C

Detector Temperature - 238°C

Detector Current - 200 milliamperes

Attenuator Setting - 2

Solvent - carbon tetrachloride

Gas Chromatograph Model - KD

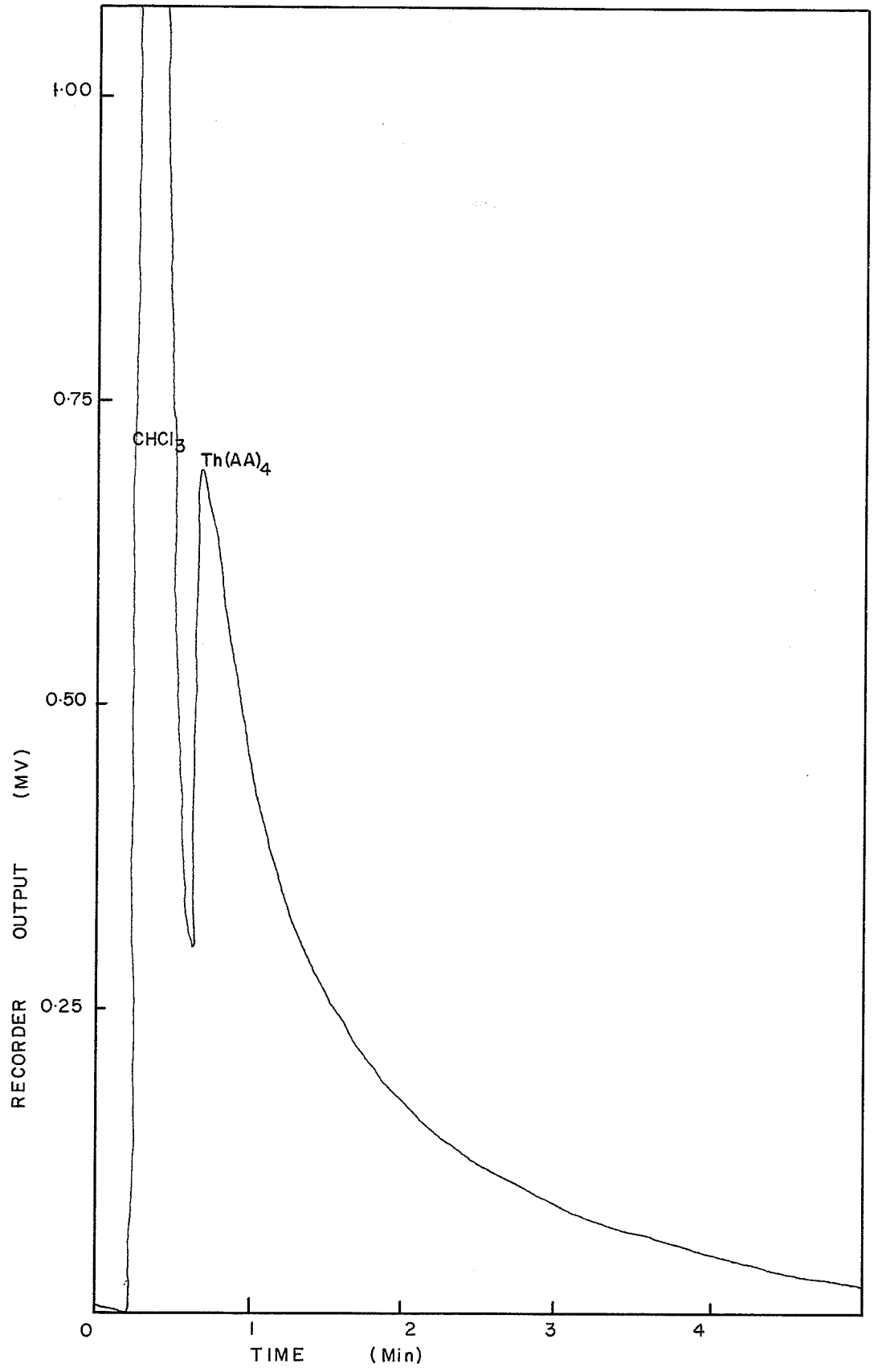

1·00
0·75
0·50
0·25
RECORDER OUTPUT (MV)
CHCl3
Th(AA)4
0
1
2
3
4
TIME (Min)

TABLE 15

ANALYSIS OF KNOWN AMOUNTS OF
Tetrakis-(2,4-pentanediono)thorium(IV)

Sample* Size(μl)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
1.0	3.7	4.8	2.8 - 4.5
2.0	9.7	10.0	8.0 - 11.9
3.0	15.6	15.2	14.9 - 16.0
4.0	20.2	20.4	19.0 - 21.1
5.0	24.6	25.6	23.7 - 26.0
6.0	30.8	30.8	29.2 - 31.6

*concentration = 0.109 mg per μl

FIGURE 25

Calibration Curve for Thorium Acetylacetone

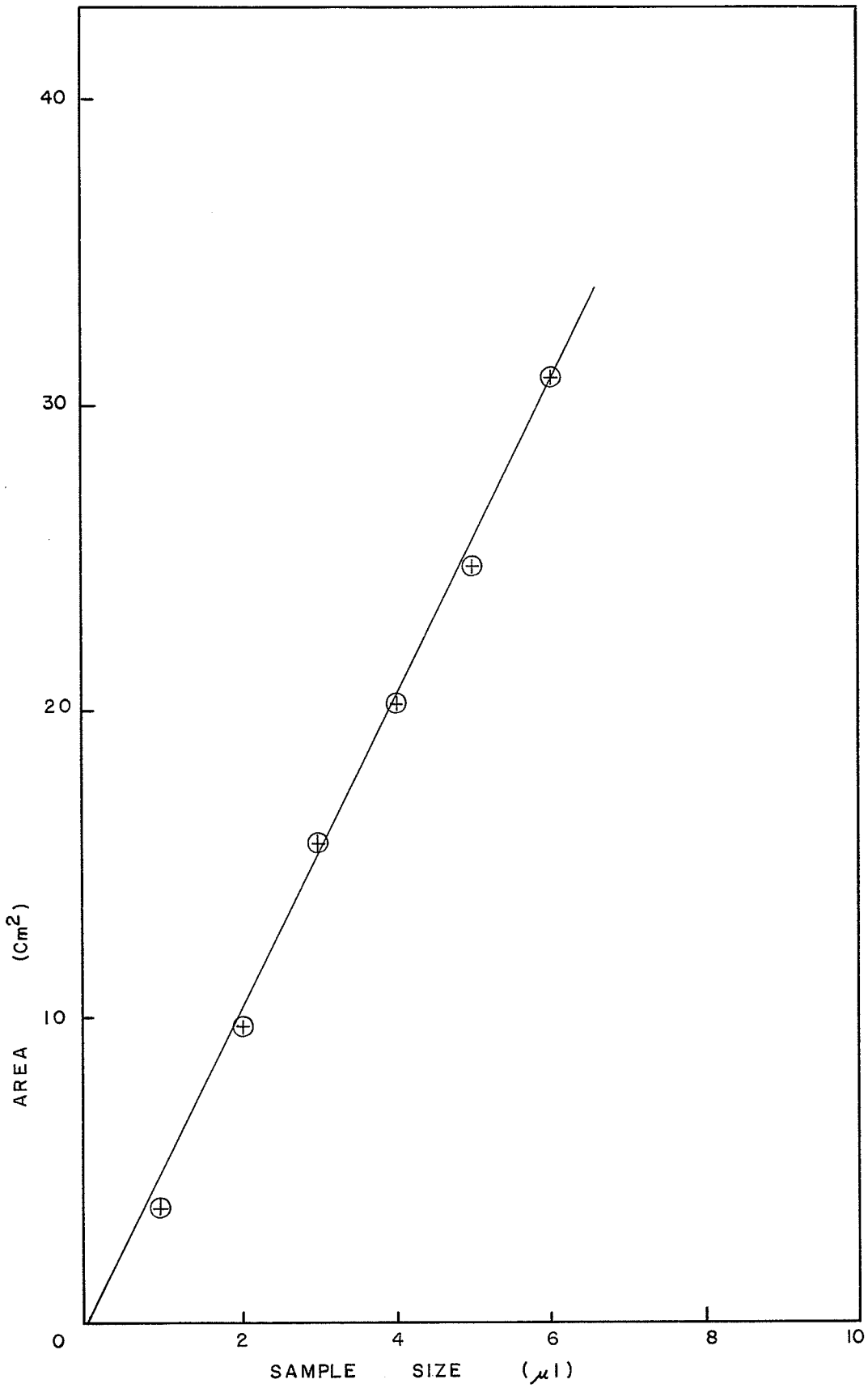

40
30
20
10
0
AREA (Cm²)
2
4
6
8
10
SAMPLE SIZE (μl)

FIGURE 26

A Typical Chromatogram of
Rhodium Trifluoroacetylacetone

Conditions:

Column - #12 ie. 1/8" O.D. by 4'ss 7.5% SE 30 on 42/60 mesh fire brick acid washed

Column Temperature - 150°C

Flash Vaporizer Temperature - 207°C

Sample Size - 3.0 - 10.0 ul

Flow Rate - 66 ml min^{-1}

Reference Flow Rate - 11 ml min^{-1}

Predetector Temperature - 189°C

Detector Temperature - 203°C

Detector Current - 200 milliamperes

Attenuator Setting - 1

Solvent - carbon tetrachloride

Gas Chromatograph Model - KD

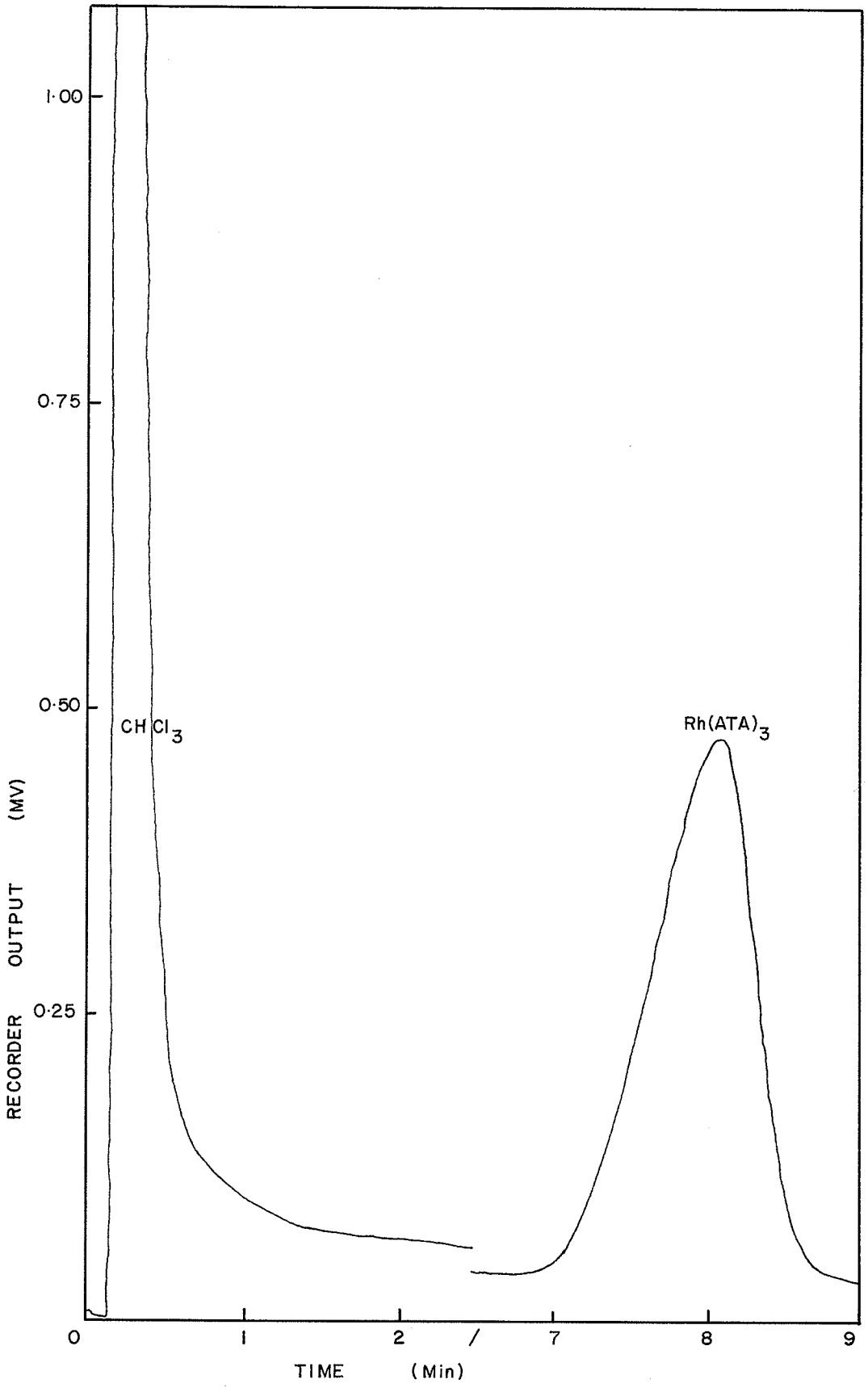

1·00
0·75
0·50
0·25
RECORDER OUTPUT (MV)
CHCl3
Rh(ATA)3
0
1
2
/
7
8
9
TIME (Min)

TABLE 16

ANALYSIS OF KNOWN AMOUNTS OF
Tris-(1,1,1-trifluoro-2,4-pentanediono)rhodium(III)

Sample* Size(μl)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
3.0	22.6	20.2	22.6 - 22.6
4.0	27.0	27.1	25.5 - 28.2
5.0	34.2	34.2	34.2 - 34.2
6.0	40.8	41.3	40.6 - 41.2
7.0	48.4	48.4	47.6 - 49.2
8.0	55.2	55.5	54.8 - 55.9
9.0	63.4	62.6	61.0 - 66.2
10.0	67.0	69.7	66.7 - 67.2

*concentration $\sim$ 0.2 mg per μl

FIGURE 27

Calibration Curve for
Rhodium Trifluoroacetylacetone

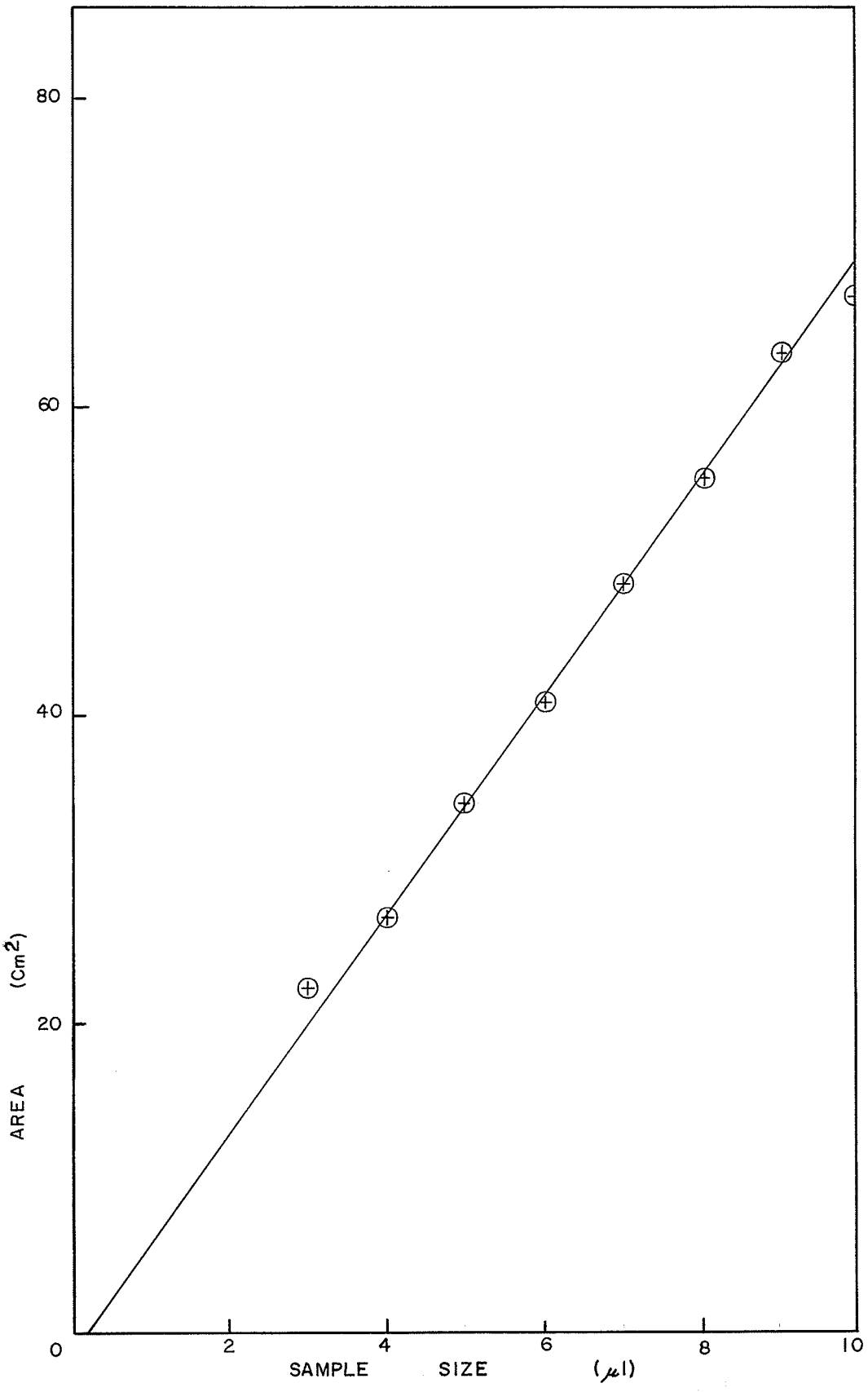

80
60
40
20
0
AREA (Cm²)
2
4
6
8
10
SAMPLE SIZE (µl)

FIGURE 28

A Typical Chromatogram of
Zirconium Acetylacetone

Conditions:

Column - #12 ie. 1/8" O.D. by 4' ss 7.5% SE 30 on 42/60 mesh fire brick acid washed

Column Temperature - 103°C

Flash Vaporizer Temperature - 227°C

Sample Size - 2.0 - 7.0 µl

Flow Rate - 11 ml min^{-1}

Reference Flow Rate - 12 ml min^{-1}

Predetector Temperature - 206°C

Detector Temperature - 237°C

Attenuator Setting - 4

Solvent - carbon tetrachloride

Gas Chromatograph Model - KD

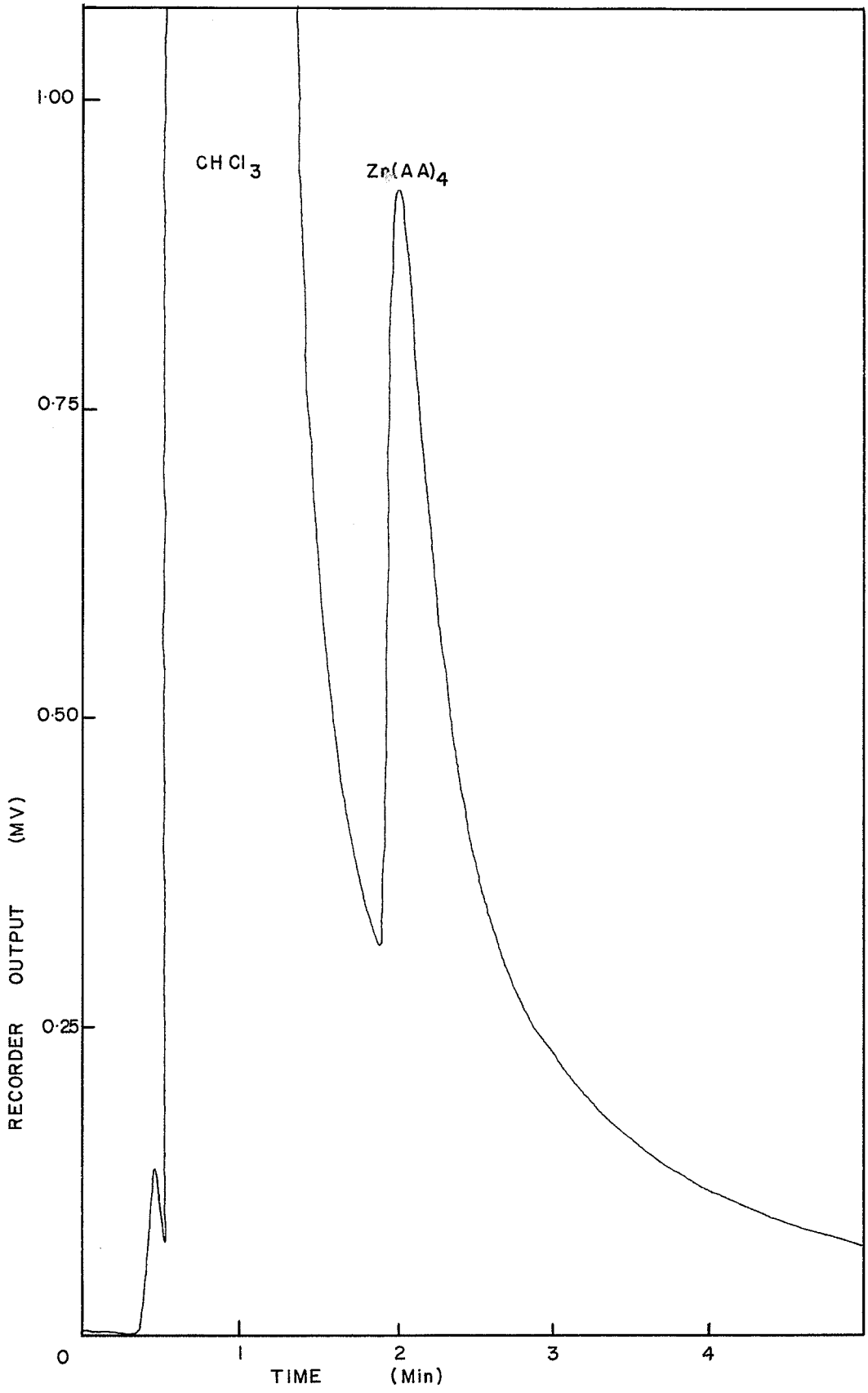

1·00
0·75
0·50
0·25
0
CHCl3
Zr(AA)4
RECORDER OUTPUT (MV)
1
2
3
4
TIME (Min)

TABLE 17

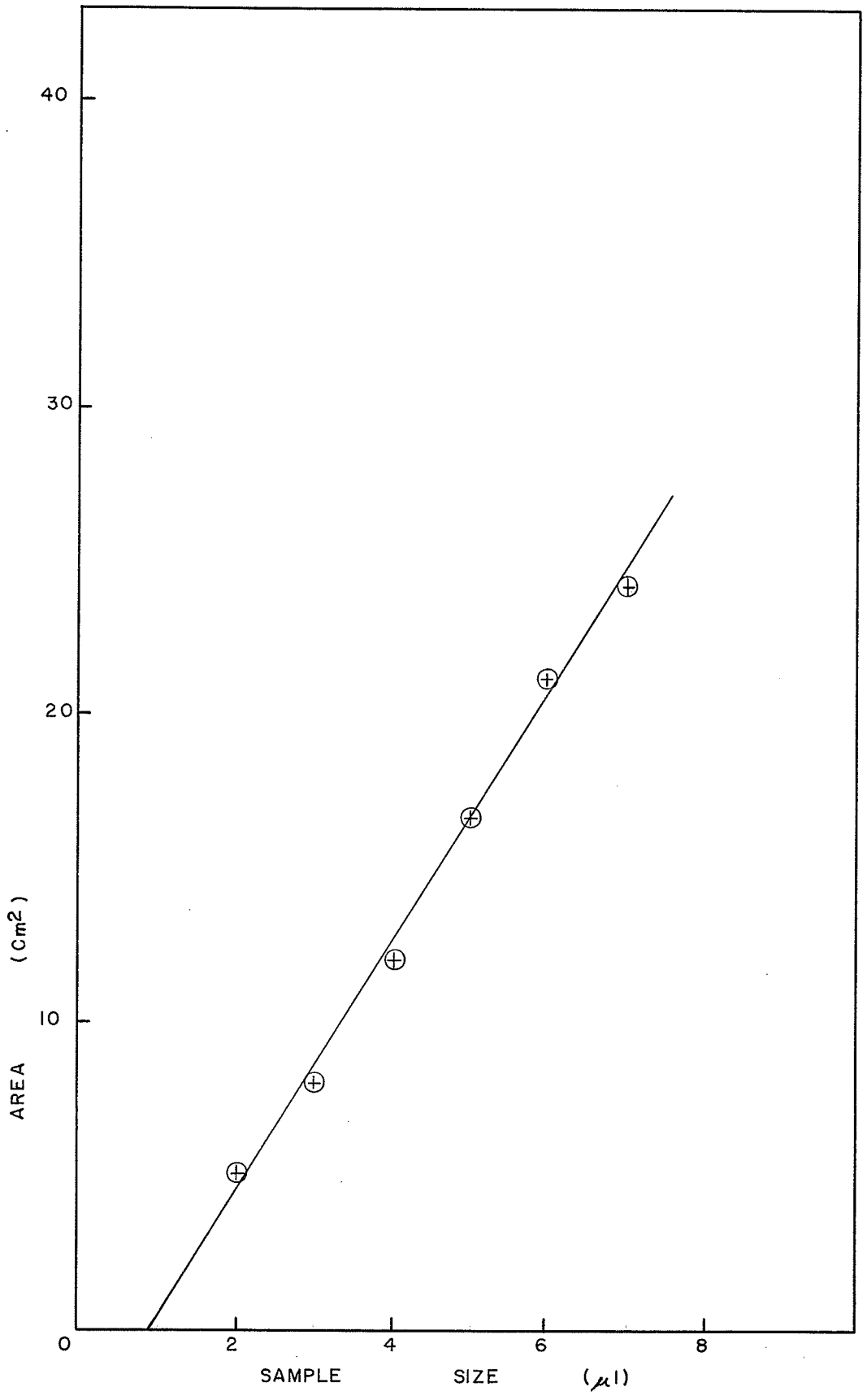
ANALYSIS OF KNOWN AMOUNTS OF
Tetrakis(2,4-pentanediono)zirconium(IV)

Sample* Size(µl)	Average area(cm^2)	Calculated area(cm^2)	Range of areas(cm^2)
2.0	5.0	4.3	4.8 - 5.2
3.0	8.0	8.4	7.3 - 8.4
4.0	12.0	12.5	11.6 - 12.8
5.0	16.6	16.6	15.9 - 17.1
6.0	21.2	20.7	18.8 - 22.8
7.0	24.2	24.8	24.1 - 24.3

*concentration is 0.0282 mg per µl

FIGURE 29

Calibration Curve for
Zirconium Acetylacetone


40
30
20
10
0
AREA (Cm2)
2
4
6
8
SAMPLE SIZE (µl)

Analysis and Separation of Mixtures

The following mixtures were separated and quantitatively analyzed:

(1) Beryllium and aluminum acetylacetonates

(2) Beryllium and aluminum trifluoroacetylacetonates

(3) Aluminum and copper trifluoroacetylacetonates

(4) Beryllium, aluminum and copper trifluoroacetylacetonates.

For each mixture there is given a Table of Conditions, a typical chromatogram showing the separation of the chelates, a Table giving the quantity of each chelate in the sample and comparing the measured areas with the areas calculated from the "Method of Averages" and a Figure showing the calibration curves of the components in the mixture.

Figures 30 (page 107), 32 (page 111), 34 (page 113) and 36(page 115) show that multicomponent mixtures of metal chelates were separated rapidly and efficiently by gas chromatography. Figures 31 (page 109), 33 (page 113), 35 (page 117) and 37 (page 121) show that these mixtures were quantitatively analyzed.

TABLE 18

Conditions for the Separation of $Be(AA)_2$ and $Al(AA)_3$

Column - #9 ie. $\frac{1}{4}$" O.D. by 4' Cu, 0.5% apiezon L on 50 mesh glass beads

Column Temperature - 129°C

Flash Vaporizer Temperature - 150°C

Sample Size - 1.0 - 9.0 µl

Flow Rate - 50 ml min^{-1}

Detector Temperature - 200°C

Detector Current - 145 milliamperes

Attenuator Setting - 2

Solvent - benzene

Instrument - KD

Concentration = 0.0694 mg $Be(AA)_2$ and

0.0504 mg $Al(AA)_3$ per µl solution.

FIGURE 30

A Typical Chromatogram Showing the Separation of Beryllium and Aluminum Acetylacetonates

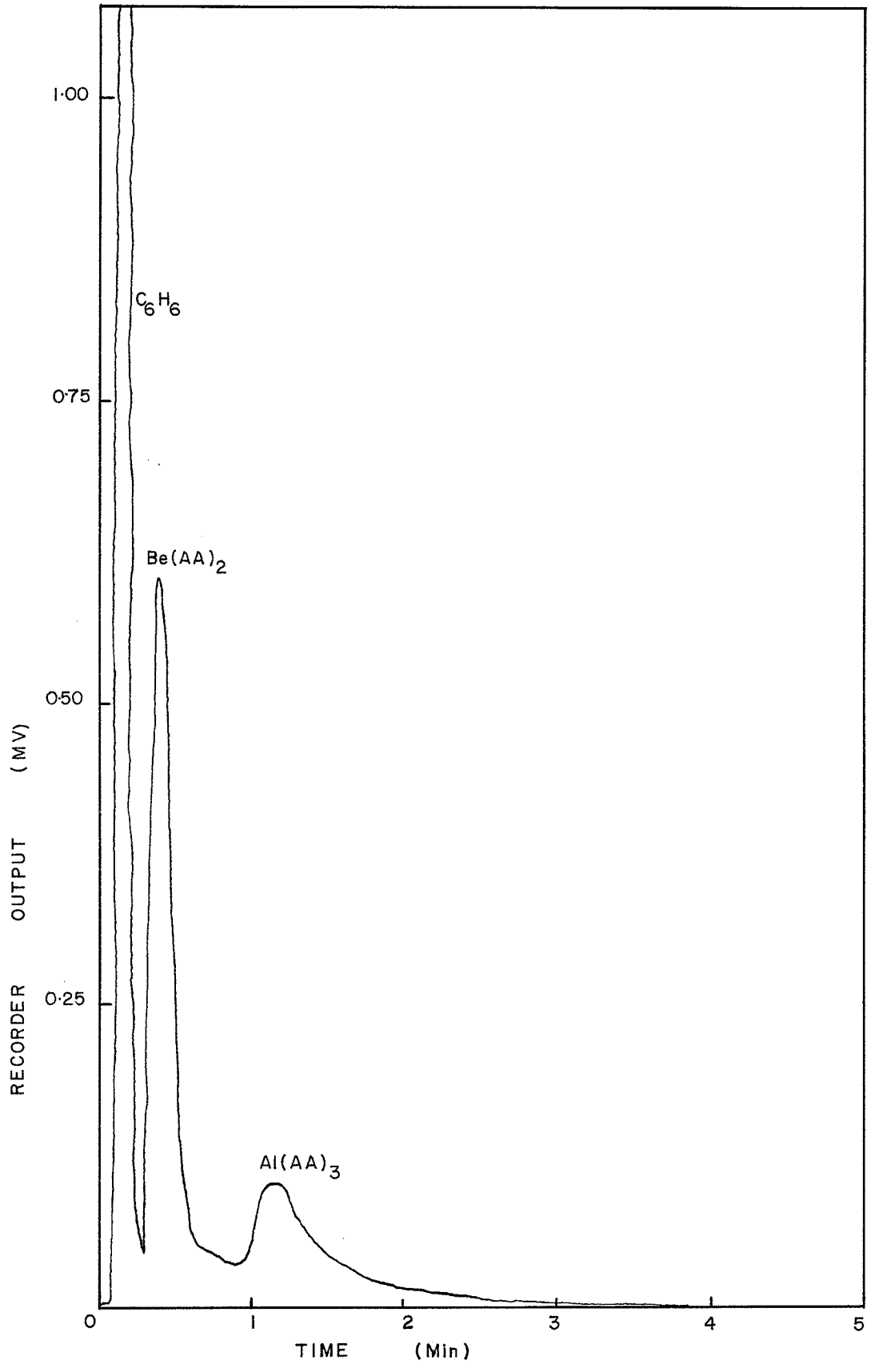

1·00
0·75
0·50
0·25
RECORDER OUTPUT (MV)
C6H6
Be(AA)2
Al(AA)3
0
1
2
3
4
5
TIME (Min)

TABLE 19

ANALYSIS OF A MIXTURE OF
Bis(2,4-pentanediono)beryllium(II) and
Tris(2,4-pentanediono)aluminum(III)

$Be(AA)_2$			$Al(AA)_3$		
Mg	Average area(cm^2)	Calc. area	Mg	Average area(cm^2)	Calc. area
0.0694	2.3	2.3	0.0504	1.0	1.0
0.139	4.4	4.2	0.101	2.0	2.0
0.208	6.6	6.1	0.151	3.2	3.1
0.278	7.7	8.0	0.202	4.0	4.1
0.347	9.4	9.8	0.252	5.0	5.1
0.416	11.8	11.7	0.302	6.2	6.2
0.486	13.1	13.6	0.353	7.8	7.3
0.555	15.1	15.5	0.403	8.6	8.3
0.625	18.4	17.4	0.454	9.6	9.4

FIGURE 31

Calibration Curves for Beryllium Acetylacetone
and Aluminum Acetylacetone Mixtures

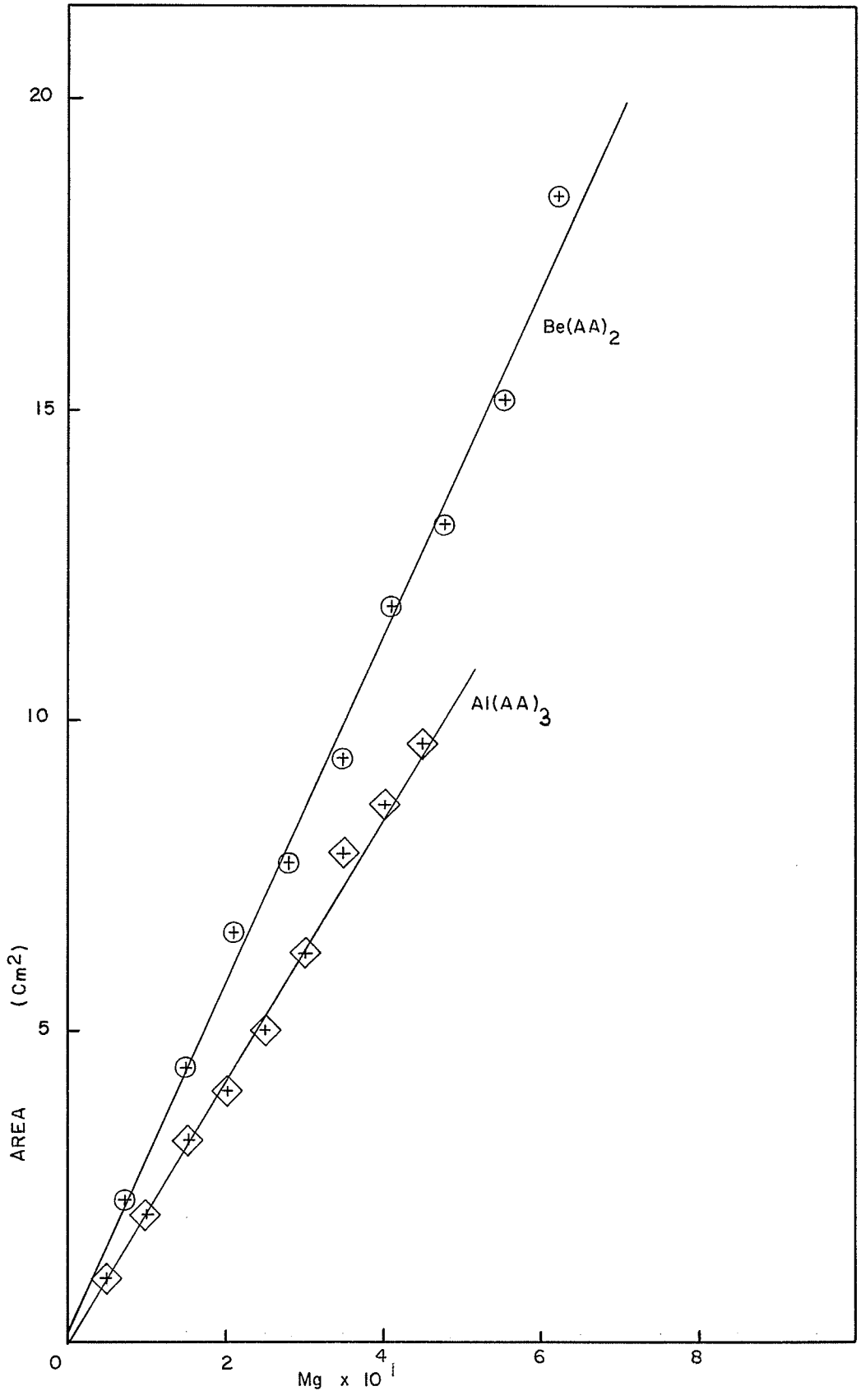

20
15
10
5
0
2
4
6
8
AREA (Cm2)
Mg x 10 i
Be(AA)2
Al(AA)3

TABLE 20

Separation of $Be(ATA)_2$ and $Al(ATA)_3$

Conditions:

Column - #10 ie. ¼" by 40" Cu. 7.5% SE 30 on 20/40 mesh fire brick

Column Temperature - 148°C

Flash Vaporizer Temperature - 180°C

Sample Size - 1.0 ul to 6.0 µl

Flow Rate - 10 ml min^{-1}

Detector Temperature - 200°C

Detector Current - 145 milliamperes

Attenuator Setting - 5

Solvent - 50/50 carbon tetrachloride and benzene

Instrument - KD

Concentration = 0.0428 mg of $Be(ATA)_2$ and
0.0403 mg of $Al(ATA)_3$ per µl solution.

FIGURE 32

A Typical Chromatogram Showing the Separation of Beryllium and Aluminum Trifluoroacetylacetonates

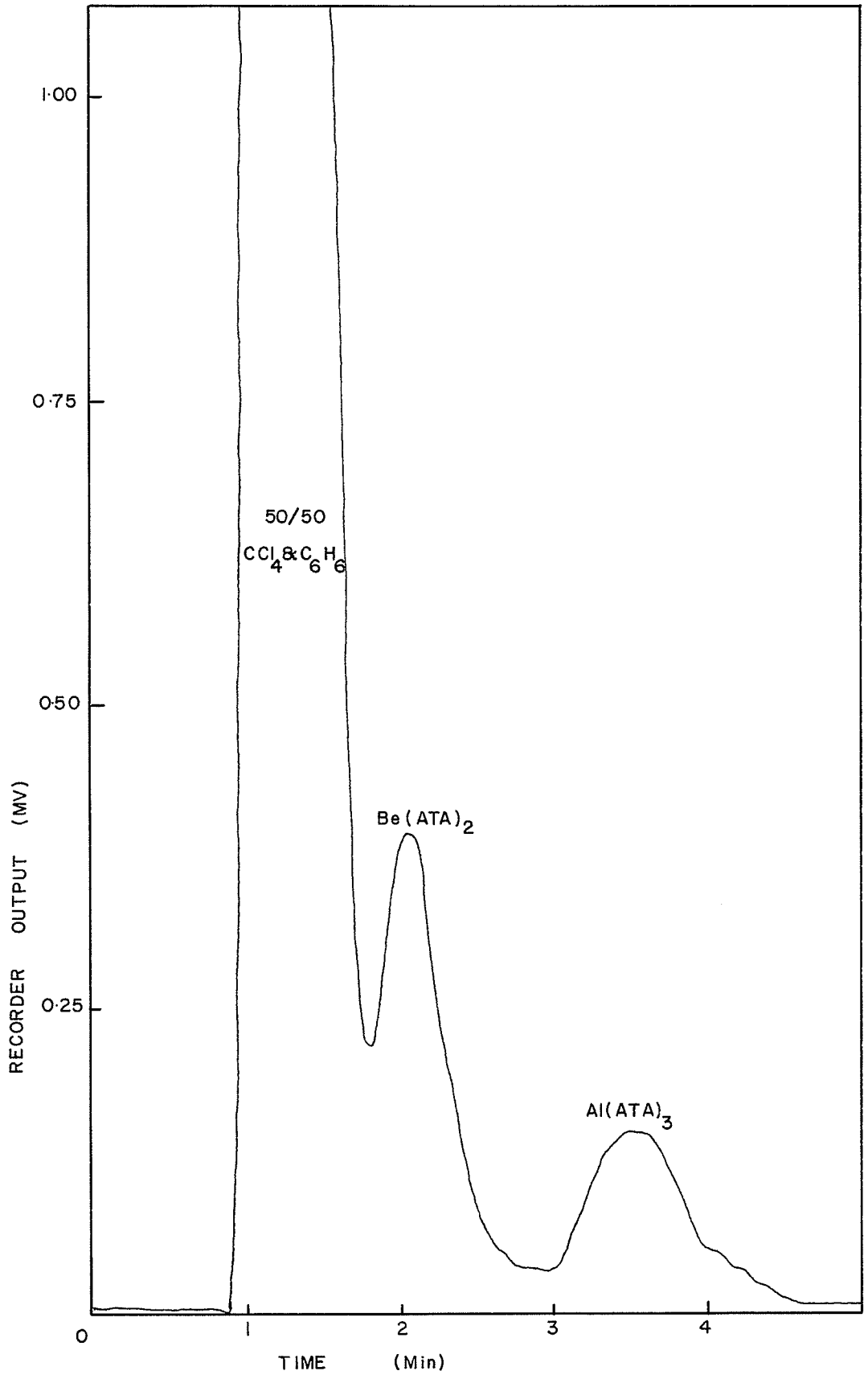

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
50/50
CCl4&C6H6
Be(ATA)2
Al(ATA)3
1
2
3
4
TIME (Min)

TABLE 21

ANALYSIS OF $Be(ATA)_2$ AND $Al(ATA)_3$ MIXTURE

$Be(ATA)_2$			$Al(ATA)_3$		
Mg	Average area(cm^2)	Calc. area	Mg	Average area(cm^2)	Calc. area
0.0428	5.5	5.2	0.0403	*	-
0.0855	11.0	10.9	0.0806	6.3	6.4
0.128	16.2	16.6	0.121	10.2	10.2
0.171	22.3	22.5	0.161	14.0	14.0
0.214	28.0	28.0	0.202	17.2	17.8
0.256	33.6	33.7	0.242	22.3	21.6

* area too small to measure accurately

FIGURE 33

Calibration Curves for
Beryllium Trifluoroacetylacetonate
and Aluminum Trifluoroacetylacetonate

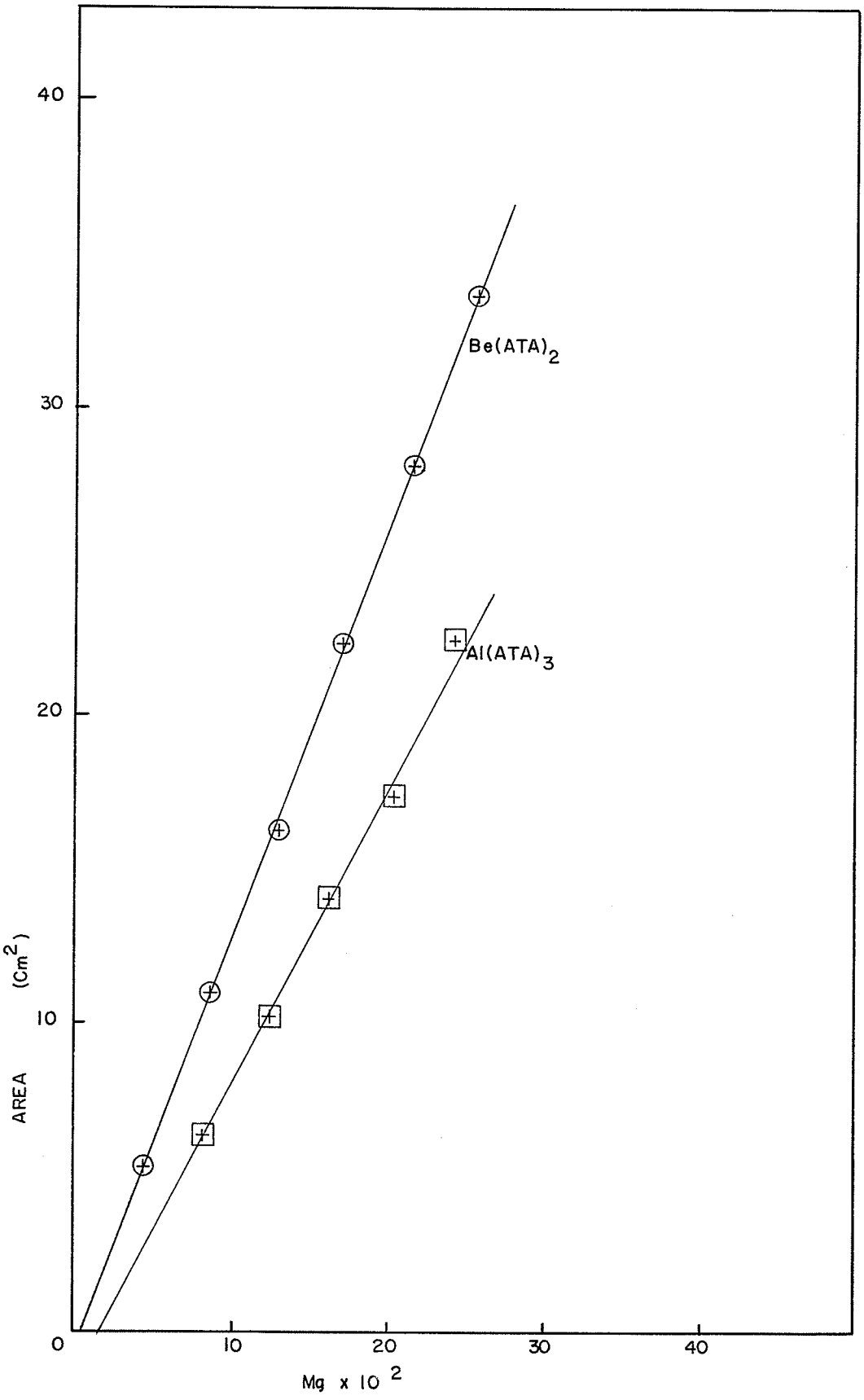

40
30
20
10
0
AREA (Cm^2)
10
20
30
40
Mg x 10^2
Be(ATA)$_2$
Al(ATA)$_3$

TABLE 22

Separation of $Al(ATA)_3$ and $Cu(ATA)_2$

Conditions:

Column - #11 ie. 1/8" O.D. by 8'ss, 7.5% SE 30 on mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 170°C

Sample Size - 1.0 - 3.0 ul

Flow Rate - 29 ml min^{-1}

Reference Flow Rate - 23 ml min^{-1}

Predetector Temperature - 176°C

Detector Temperature - 188°C

Detector Current - 200 milliamperes

Attenuator Setting - 2

Solvent - 50/50 benzene and carbon tetrachloride

Gas Chromatographic Instrument - KD

Concentration = 0.0249 mg of $Al(ATA)_3$ and
0.0180 mg of $Cu(ATA)_2$ per ul solution

FIGURE 34

A Typical Chromatogram Showing the Separation
of Aluminum and Copper Trifluoroacetylacetonates

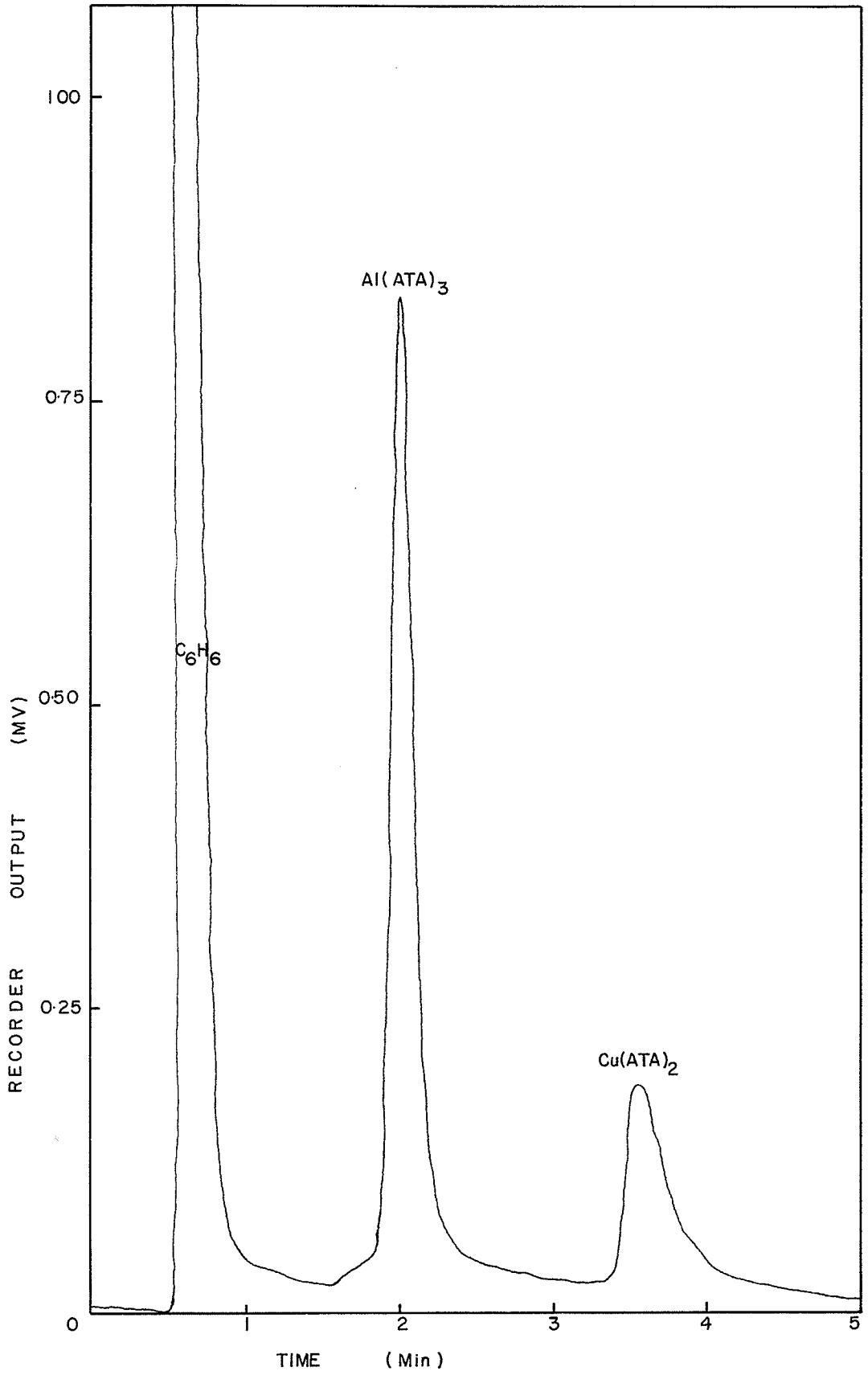

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
Al(ATA)3
Cu(ATA)2
1
2
3
4
5
TIME (Min)

TABLE 23

ANALYSIS OF $Al(ATA)_3$ AND $Cu(ATA)_2$ MIXTURE

$Al(ATA)_3$			$Cu(ATA)_2$		
Mg	Average area(cm^2)	Calc. area	Mg	Average area(cm^2)	Calc. area(cm^2)
0.0249	11.9	11.0	0.0180	4.5	4.5
0.0374	13.3	14.2	0.0269	6.0	6.2
0.0498	18.5	17.4	0.0359	8.2	8.0
0.0622	19.6	20.6	0.0449	10.0	9.8
0.0747	*		0.0538	11.4	11.6

*chromatographic peak went off scale

FIGURE 35

Calibration Curves for Aluminum Trifluoroacetylacetonate and Copper Trifluoroacetylacetonate Mixture

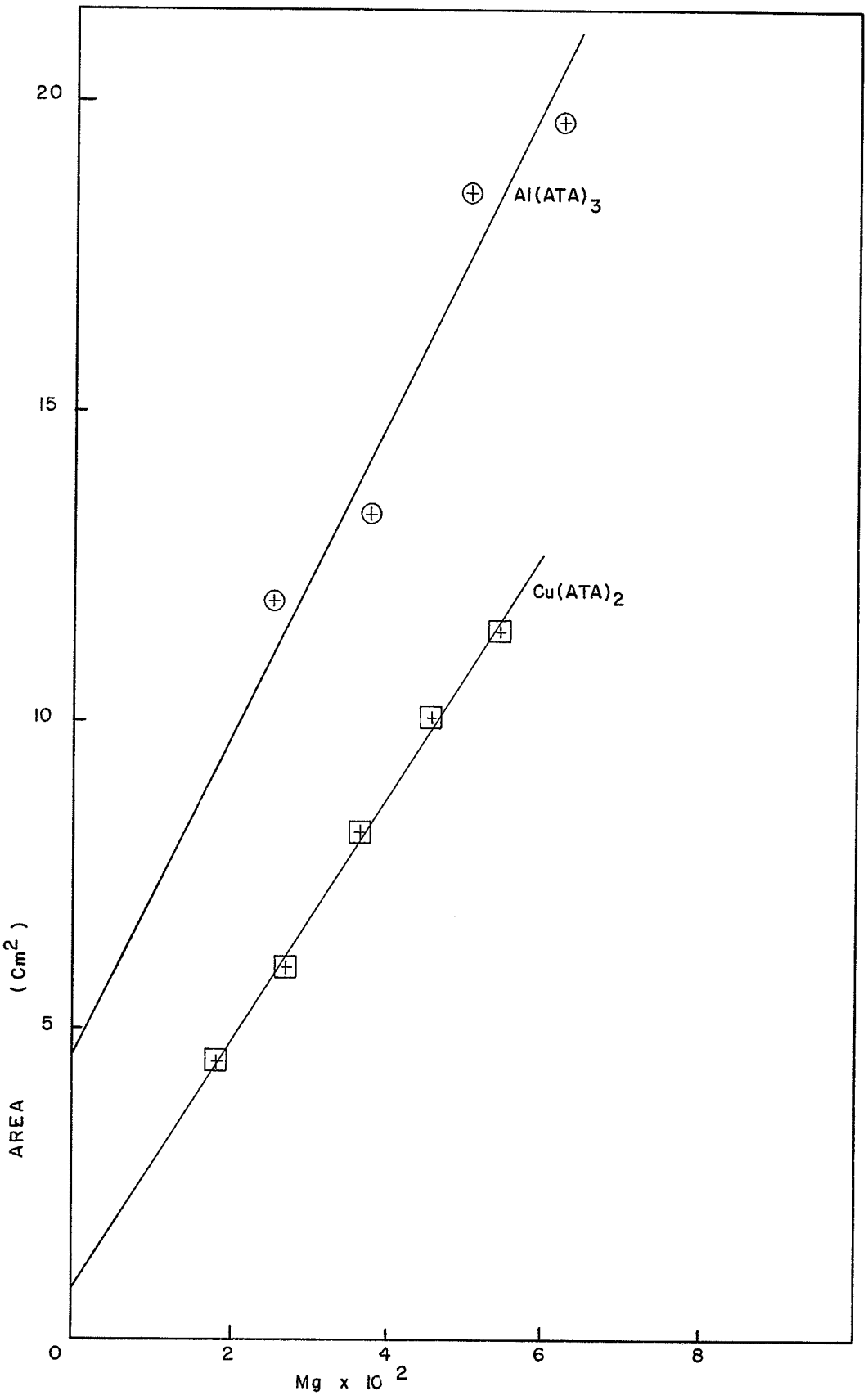

20
15
10
5
0
AREA (Cm2)
2
4
6
8
Mg x 10 2
Al(ATA)3
Cu(ATA)2

TABLE 24

Conditions for the Separation of $Be(ATA)_2$, $Al(ATA)_3$ and $Cu(ATA)_2$

Column - #12 ie. 1/8" O.D. by 4'ss, 7.5% SE 30 on 42/60 mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 192°C

Sample Size - 1.0 to 7.0 µl

Flow Rate - 37 ml min^{-1}

Reference Flow Rate - 8 ml min^{-1}

Predetector Temperature - 216°C

Detector Temperature - 246°C

Detector Current - 200 milliamperes

Attenuator Setting - 2

Instrument - KD

Solvent - benzene

Concentration = 0.00405 mg of $Be(ATA)_2$, 0.0116 mg of $Al(ATA)_3$ and 0.0143 mg of $Cu(ATA)_2$ per µl solution

FIGURE 36

A Typical Chromatogram Showing the Separation of Beryllium, Aluminum and Copper Trifluoroacetylacetonates

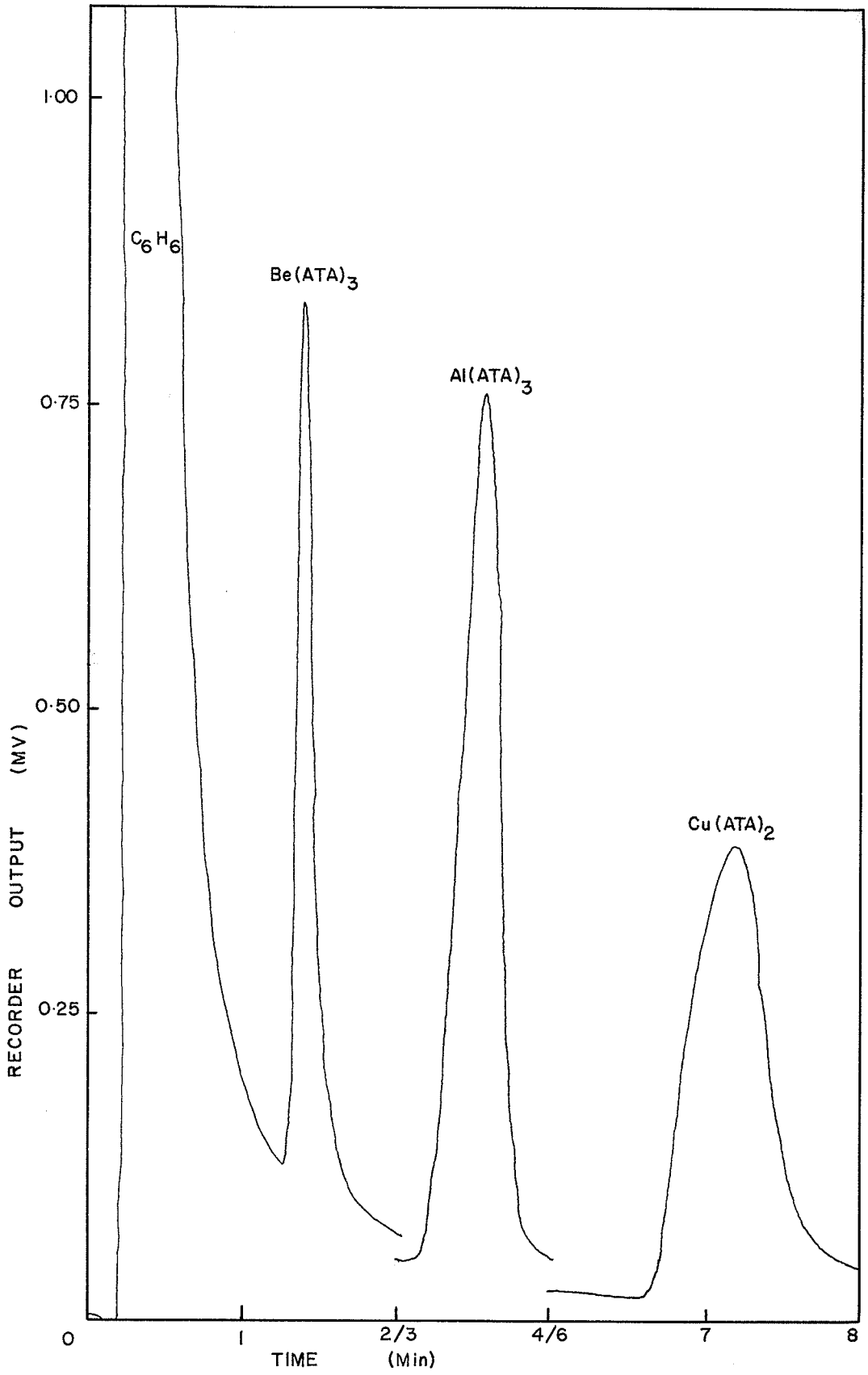

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
Be(ATA)3
Al(ATA)3
Cu(ATA)2
1
2/3
4/6
7
8
TIME (Min)

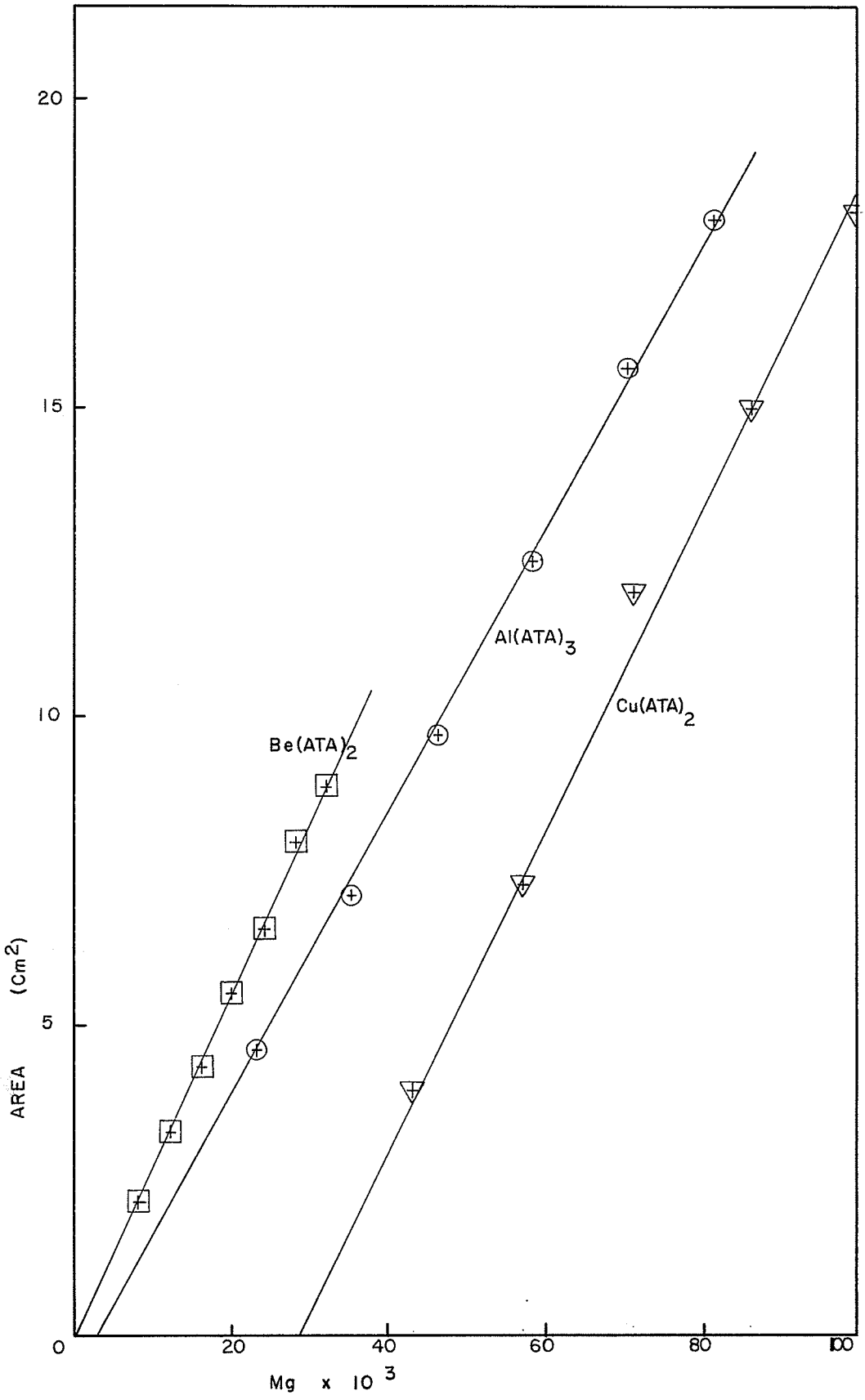
TABLE 25

ANALYSIS OF A $Be(ATA)_2$, $Al(ATA)_3$ and $Cu(ATA)_2$ MIXTURE

	Mg	Average area(cm^2)	Calc. area(cm^2)
$Be(ATA)_2$	0.0081	2.2	2.2
	0.0121	3.4	3.4
	0.0162	4.4	4.5
	0.0202	5.6	5.6
	0.0243	6.6	6.7
	0.0284	8.1	7.9
$Al(ATA)_3$	0.0232	4.6	4.6
	0.0348	7.1	7.2
	0.0464	9.7	9.8
	0.0580	12.5	12.5
	0.0696	15.1	15.2
	0.0812	17.9	17.8
$Cu(ATA)_2$	0.0429	4.0	4.4
	0.0572	7.3	7.8
	0.0715	12.1	11.3
	0.0858	14.6	14.7
	0.100	18.3	18.1

FIGURE 37

Calibration Curves for Beryllium Trifluoroacetylacetone, Aluminum Trifluoroacetylacetone and Copper Trifluoroacetylacetone and Mixture


20
15
10
5
0
AREA (Cm²)
20
40
60
80
100
Mg x 10³
Be(ATA)₂
Al(ATA)₃
Cu(ATA)₂

The preceeding Tables, calibration curves and chromatograms have shown that many metal β-diketones can be determined quantitatively by gas-liquid chromatography. Under the experimental conditions of the present work it appeared that when the retention times for two peaks differ by one minute or more, they were separated and the individual metal chelates quantitatively determined.

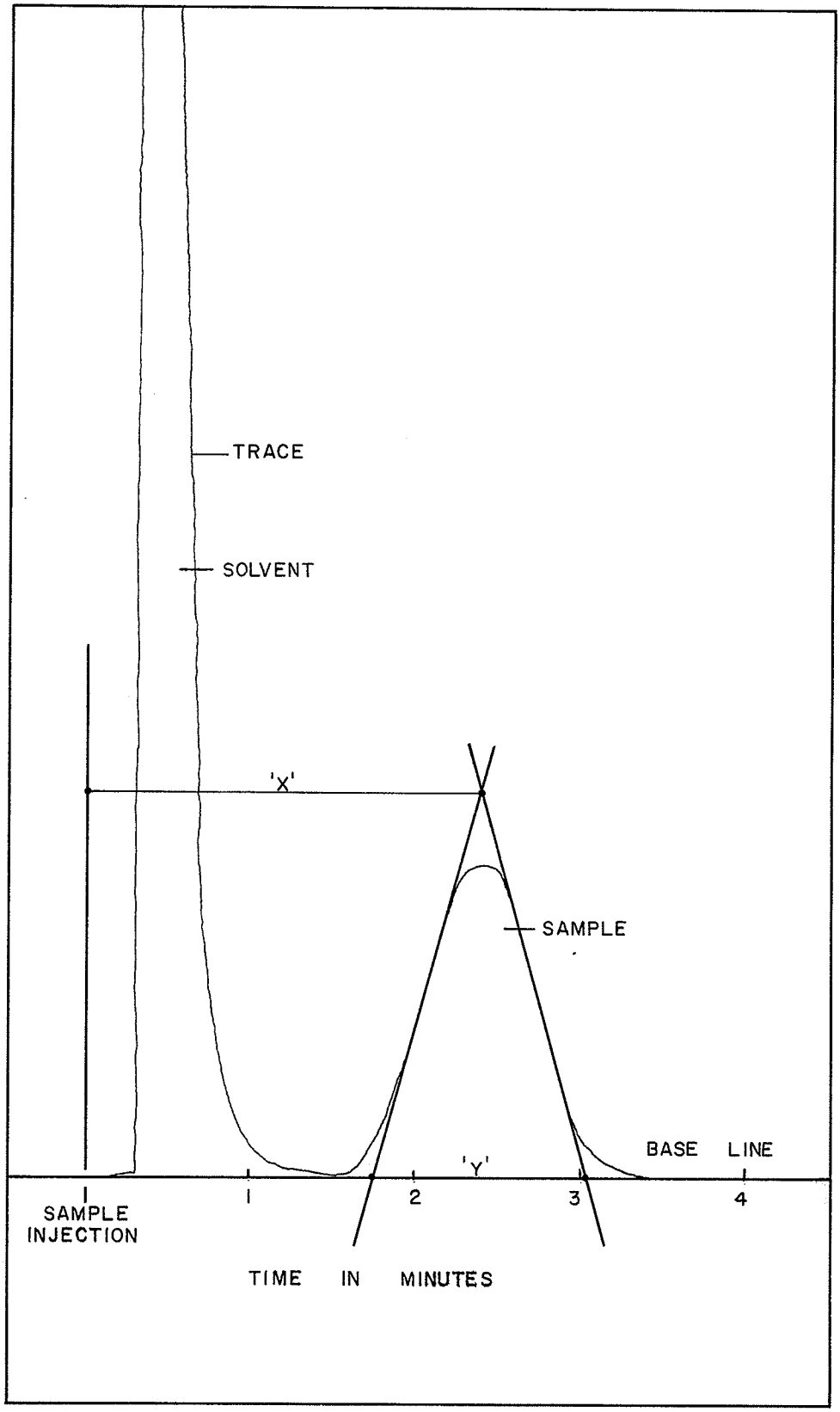
Whether a separation of any two peaks is adequate for analysis is determined by separation factor and the efficiency of the column (42). Separation factor is equal to the ratio of the two retention times (43). Efficiency is usually expressed in the number of theoretical plates. The more theoretical plates a column would have, the more efficient it is. The number of theoretical plates is calculated from the formula

$$N = 16(x/y)^2$$

where x is the retention time and y is the width of the baseline intercepted by the tangents to the inflection points of the peak, (See Figure 38, page 123) which is defined as the peak width.

FIGURE 38

A Chromatogram for Defining Terms


TRACE
SOLVENT
'X'
SAMPLE
'Y'
BASE LINE
SAMPLE INJECTION
1
2
3
4
TIME IN MINUTES

As an example, the component peak in Figure 38 has retention time x of 2.50 minutes, and has a peak width of 1.25 minutes. Therefore, the number of theoretical plates is

$$N = 16\left(\frac{x}{y}\right)^2 = 16\left(\frac{2.50}{1.25}\right)^2 = 64$$

Now it was noticed that a difference in retention time of one minute was all that was needed for enough separation for analysis. So, if two peaks, A and B, whose retention time differ by one minute (for example x for A = 3 minutes and x for B = 4 minutes) and if each has a peak width of one minute, then separation factor is 4 divided by 3, or 1.3. The number of theoretical plates in each case is:

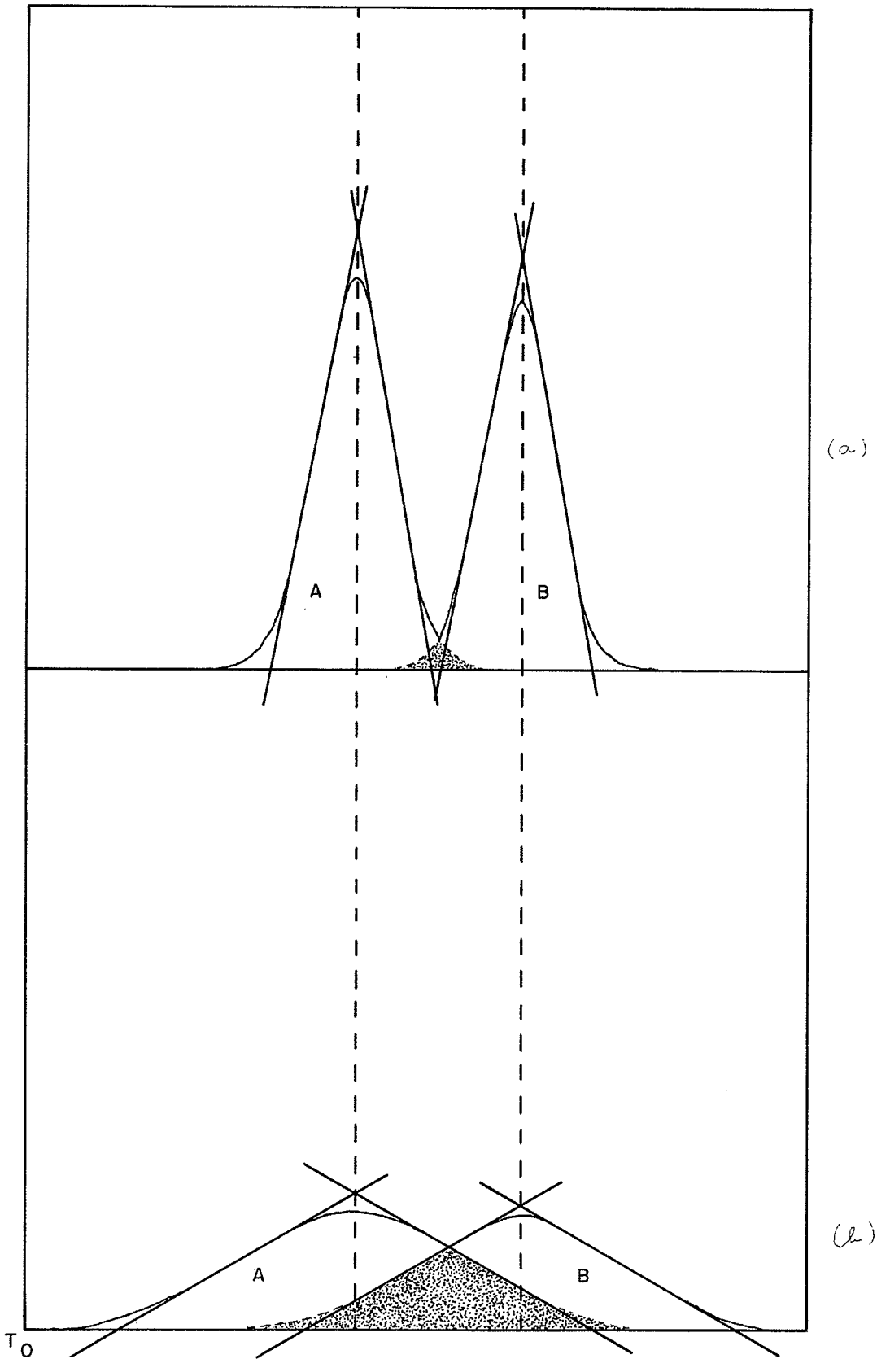
for peak A - $N = 16\ \frac{3^2}{1^2} = 144$ and

for peak B - $N = 16\ \frac{4^2}{1^2} = 256$

From Figure 39 (a), page 125 we see that the overlap of the peaks is small and analysis is possible.

FIGURE 39

Illustration Showing Effect of the Number of Theoretical Plates in a Gas Chromatographic Resolution


A
B
(a)
A
B
(b)
T0

If the separation factor was the same, but the efficiency of the column less; say peak width was two minutes, then we have:

for Peak A - $N = 16\frac{3^2}{2^2} = 36$ and

for Peak B - $N = 16\frac{4^2}{2^2} = 64$

Figure 39 (b), page 125 shows a much larger error due to overlap of the peaks.

Also, analysis of the two neighboring components would be a function of the difference in their retention times (Δx) and the average of their peak widths($\bar{y}$). The further apart the peaks, the easier the analysis; the smaller the peak widths the easier the analysis.

Therefore, $\Delta x = K \bar{y}$

where K is a constant $K = \Delta x \div \bar{y}$

if K is equal to or larger than a certain number analysis is possible. Assume that the number is one. Then if Δ x is equal to or greater than $\bar{y}$ an analysis is possible.

Figure 39, page 125.

Case one: analysis = $\frac{1}{1}$ = 1

therefore, analysis is possible

Case two: analysis = $\frac{1}{2}$ = 0.5

therefore, analysis is not possible.

Theoretically there is agreement, now lets see if it holds for the data in this research.

By examining the chromatogram showing the separation of beryllium and aluminum trifluoroacetylacetonates(i.e. Figure 32, page 111); it is seen that the difference between peaks is 1.5 minutes. The peak width for $Be(ATA)_2$ is 0.8 minute and 1.2 minutes for $Al(ATA)_3$, so the average value of peak width is 1.0 minute.

Therefore, $K = \frac{\Delta x}{\bar{y}} = \frac{1.5}{1.0} = 1.5 > 1$

so analysis is possible; this our experimental data confirms. (See Table 21, page 112). This is further substantiated from Figures 30, 34 and 37.

Therefore, if difference in retention times between two peaks is larger than average of their peak widths, the peaks can be separated adequately to be analyzed.

The Quantitative Gas Chromatographic Analysis of a Beryllium-Copper Alloy

The final part of this research was concerned with studies of the applicability of gas-liquid chromatography to the analysis of metal alloys, of which beryllium-copper alloy is an example. The beryllium-copper alloy was chosen as an example for analysis of a metal alloy because both beryllium and copper trifluoroacetylacetonates had been analyzed earlier in this work and a known analysis of this alloy was available (15). (See Table 28, page 133).

When following Baldwin's procedure for the gas chromatographic analysis of the alloy, only the beryllium could be measured (See Figure 40, page 129). When a buffer was used, both beryllium and copper could be measured, (See Figure 41, page 131) showing that chelation of these metals is pH dependent. Table 26, page 130 lists the conditions for the analysis and Table 27, page 132 shows the results obtained.

FIGURE 40

A Typical Chromatogram of Beryllium-Copper Alloy
Without Buffer

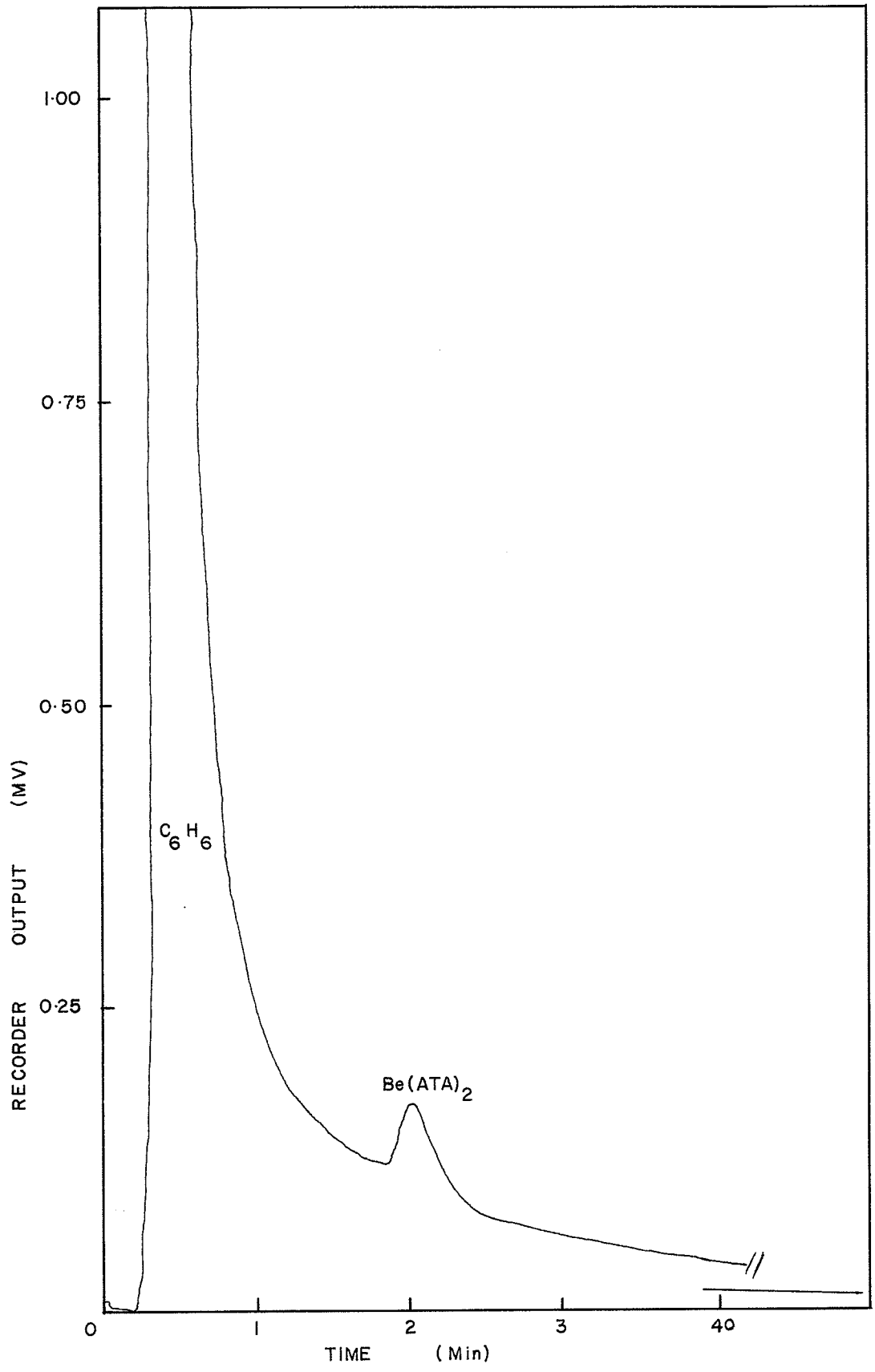

1·00
0·75
0·50
0·25
RECORDER OUTPUT (MV)
C_6H_6
$Be(ATA)_2$
0
1
2
3
40
TIME (Min)

TABLE 26

Analysis of a Beryllium-Copper Alloy

Conditions:

Column - #12 ie. 1/8" O.D. by 4' ss, 7.5% SE 30 on 42/60 mesh fire brick

Column Temperature - 150°C

Flash Vaporizer Temperature - 210°C

Sample Size - 1.0 - 10.0 ul

Flow Rate - 32 ml min^{-1}

Reference Flow Rate - 10 ml min^{-1}

Detector Temperature - 210°C

Detector Current - 200 milliamperes

Attenuator setting - 2

Gas Chromatographic Insturment - KD

Solvent - benzene

FIGURE 41

A Typical Chromatogram of Beryllium-Copper Alloy with Buffer

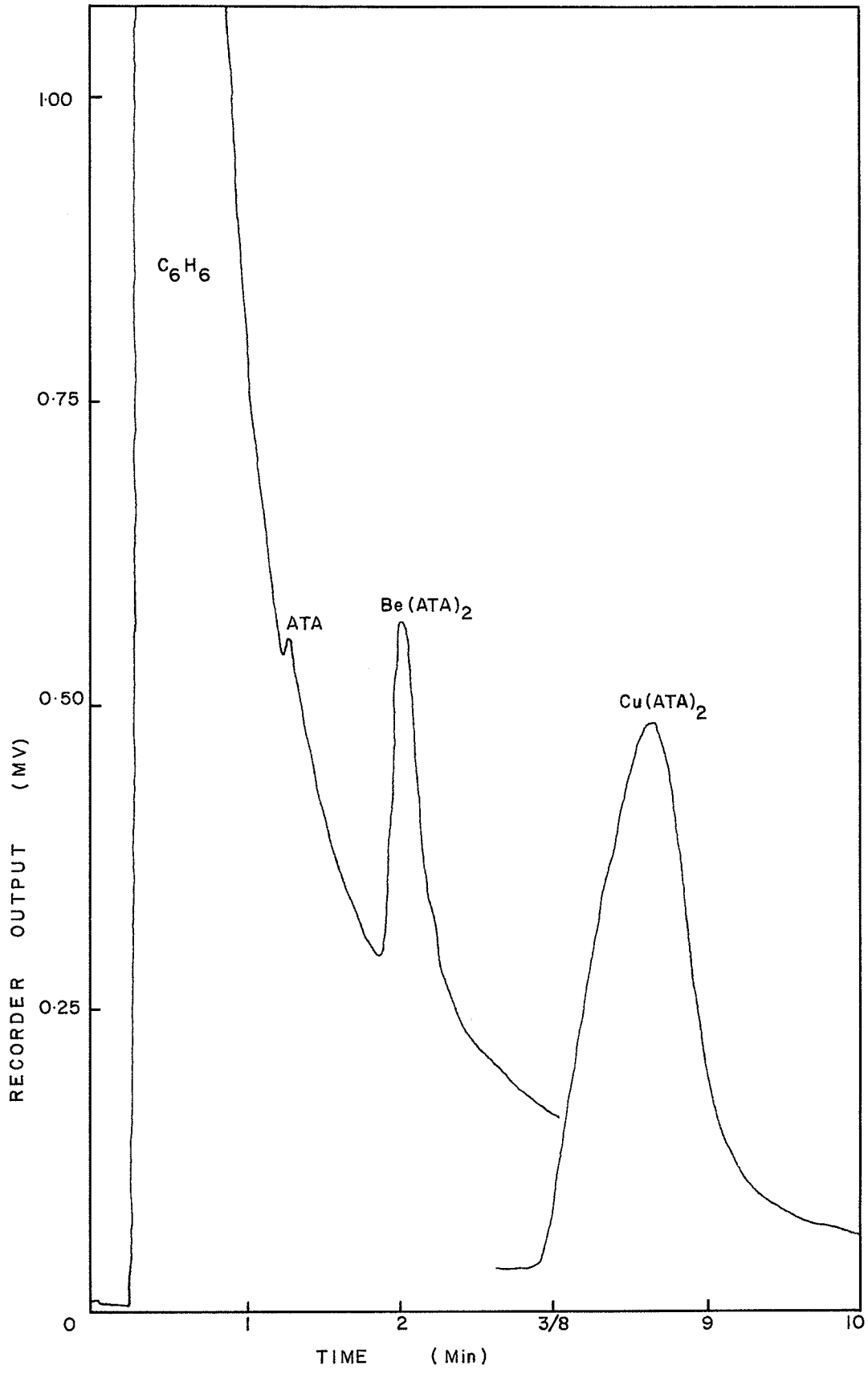

1·00
0·75
0·50
0·25
0
RECORDER OUTPUT (MV)
C6H6
ATA
Be(ATA)2
Cu(ATA)2
1
2
3/8
9
10
TIME (Min)

TABLE 27

Analysis of a beryllium-copper alloy

	% Be	%Cu
I	1.84%	98.5%
II	1.87%	98.3%
Average	1.86%	98.4%

TABLE 28

Results of Chromatographic Analysis*

% Be Found Chromat.	% Be Found Gravimet.	% Be Found Fluorimet.
1.99	1.85	1.83
1.79	1.60	1.79
1.49	1.68	1.83
1.71	1.75	1.58

*Taken from reference 15, page 38

The accurate determination of most metal alloys is tedious and time consuming. The method followed depends on what metals are being analyzed but are usually gravimetric, colorimetric, fluorometric, specthrochemical or activation or combinations of these. The use of gas chromatography could make these analysis easier and quicker. The quantity of sample being measured is limited only by the sensitivity of the detector. The feasibility of this technique has been demonstrated with the analysis of the beryllium-copper alloy. This method may be extended to more complicated alloys that is containing three or more metals or even to the analysis of ore samples. There may be no limit to what can be analyzed with the gas chromatograph when this technique is used in conjunction with other methods as pyrolysis, solvent extraction etc. Solvent extraction and complex formation combined with gas chromatography would make a useful method of metal analysis and should be further investigated.

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