WRC RESEARCH REPORT NO. 94

# GAS CHROMATOGRAPHY OF VOLATILE METAL CHELATES: APPLICATION OF A NEW TECHNIQUE TO METAL ANALYSIS IN NATURAL WATERS

Roger A. Minear, Project Director
and
Steven Schneiderman

Department of Environmental Engineering
Illinois Institute of Technology
Chicago, Illinois

FINAL REPORT

Project No. A-064-ILL

The work upon which this publication is based was supported by funds provided by the U. S. Department of the Interior as authorized under Water Resources Act of 1964, P.L. 88-379. Agreement No. 14-31-0001-4013.

UNIVERSITY OF ILLINOIS
WATER RESOURCES CENTER
2535 Hydrosystems Laboratory
Urbana, Illinois 61801

September 1974

## ABSTRACT

### GAS CHROMATOGRAPHY OF VOLATILE METAL CHELATES: APPLICATION OF A NEW TECHNIQUE TO METALS ANALYSIS IN NATURAL WATERS

Originally, the application of commercially available monothiohexafluoroacetylacetone (HFAS) and its formation of volatile chelates with metals of environmental significance to rapid, multi-element analysis was under investigation. Inability to reproduce published results for the Nickel chelate led to critical examination of the chelating agent and ultimately to withdrawal of the compound from the commercial market when its identity and purity were found to be questionable. Independent synthesis of HFAS was unsuccessful and initial project objectives were abandoned. Project objectives were redirected to verification and extension of previous studies involving the lead chelate of 2,2,6,6-tetramethylheptane-3,5-dione (PIV). Extraction studies were conducted using flameless atomization atomic absorption for analysis but are of questionable value as a result of analytical inconsistencies. Gas chromatographic studies indicated previously reported synthesis of $Pb(PIV)_2$ had likely not been achieved. Both HFAS and PIV studies were unsuccessful and have resulted in programs of independent synthesis and continued research at The University of Tennessee where the Principal Investigator is now in residence.

Minear, Roger A. and Steven Schneiderman
GAS CHROMATOGRAPHY OF VOLATILE METAL CHELATES: APPLICATION OF A NEW TECHNIQUE TO METAL ANALYSIS IN NATURAL WATERS
Final Report to the Office of Water Resources Research, U. S. Department of the Interior, October 1974, Washington, D. C.
KEYWORDS--volatile metal chelates/heavy metals analysis/gas chromatography/cadmium/copper/iron/lead/nickel/zinc

# ACKNOWLEDGEMENT

Special appreciation is extended to Dr. James W. Patterson, Chairman of the Department of Environmental Engineering for assuming the administrative responsibility for the project after September 1, 1973, thus allowing continuation of the project upon the Principal Investigator's departure to The University of Tennessee. The contribution of Mr. Chen-Ming Su, graduate student in the Department of Environmental Engineering is acknowledged. Special appreciation is due Mr. Raymond Rose, graduate student at The University of Tennessee for unfunded effort contributed to the PIV studies at The University of Tennessee.

# TABLE OF CONTENTS

PAGE

I. INTRODUCTION

II. METHODOLOGY

III. HFAS STUDIES

IV. PIV STUDIES

## LIST OF FIGURES

# LIST OF TABLES

## I. INTRODUCTION

A. Objectives: The initial objectives of this research project were to investigate the use of the compound, monothiohexafluoroacetylacetone (HFAS) in the rapid, multi-element analysis of heavy metal concentrations in aqueous solution via gas chromatography. The proposed research was predicated on (1) previously reported research results (Bayer, et al.[1]) which demonstrated the formation of stable chelates of the metal ions, $Cu^{+2}$, $Fe^{+2}$, $Zn^{+2}$, $Ni^{+2}$, $Cd^{+2}$, $Pb^{+2}$, $Pt^{+2}$, and $Pd^{+2}$, directly from aqueous solution, (2) demonstrated gas chromatographic behavior of the platinum, palladium and nickel complexes (Bayer, et al.[1]) and (3) commercial availability of the HFAS chelating agent through Pierce Chemical Company, Rockford, Illinois.

The research was designed to determine (1) which of the metals forming chelates would react quantitatively or in constant proportion to allow establishment of a quantitative relationship, (2) optimum reaction conditions for chelate formation, (3) optimum solvent extraction conditions, (4) detectability by gas chromatography using both flame ionization and electron capture detectors, and (5) liquid phase and temperature conditions necessary to obtain component separations by gas chromatography requisite to multi-element analysis.

These objectives could not be accomplished because failure to duplicate published results (Bayer, et al.[1]) for nickel led to questions regarding the actual chemical identity of the commercial HFAS. The end result of several product replacements and exchange of information with Pierce Chemical Company was the withdrawal of the product from the commercial market. Pierce's action was the result of similar experience by numerous customers and taken after repeated attempts by their research staff to rectify the problem by alternate synthesis methods.

The project objectives were modified at this point to include an attempt to synthesize HFAS according to the original work of Bayer, et al.[1] Because project resources were limited and not initially oriented for the cost of organic synthesis, a one shot synthesis was planned and executed. Upon failure of the synthesis at an intermediate step, further work with HFAS was deemed fruitless and discontinued with respect to the project.

In order to effectively utilize previous project expenditures for chromatographic supplies and remaining funds available for student support, orientation was directed towards obtaining further information on the application of another volatile metal chelate, lead 2,2,6,6-tetramethylpentane-3,5-dionate, ($Pb(PIV)_2$) to aqueous lead analysis. This work was predicated on results obtained by Palesh[2] which indicated that the $Pb(PIV)_2$ could be gas chromatographed, and response could be quantitatively related to chelate concentration in the organic solvent phase. Preliminary studies (Minear and Palesh[3]) implied that direct chelate formation from aqueous lead ion solutions held promise as an analytical tool but additional data regarding reaction stoichiometry and optimum reaction conditions were needed. Confirmation of these previous findings, determination of quantitative relationships, minimum detectable concentration, optimum reaction conditions and verification that lead was passing through the gas chromatography were the objectives established for the final phase of the project.

B. Background: Developments in the formation of volatile metal chelates and their susceptibility to gas chromatography[4,5] led to the evolution of analytical techniques for ultratrace amounts of metals.

These methods, which represent the ultimate sensitivity, accuracy and precision for some metals, appear likely to find routine application in several disciplines. Water and wastewater analysis must certainly be included.

Many metals form volatile derivatives with various β-diketones, fluorinated β-diketones and their sulfur derivatives. Not all of these chelates have been separated by gas chromatography nor do they all react quantitatively. A number of the chelates have been formed from aqueous solutions resulting from the digestion of solid material (minerals, metals and biological substances) which demonstrates the potential application to water analysis. Notably the trifluoroacetylacetonates of beryllium[6-13], chromium[6,10,14-16], aluminum[6,17] have been utilized in the analytical determination of the respective metals from aqueous solutions. A review of gas chromatography of metals in general and metal chelates specifically is contained in a recent book by Guiochon and Pommier[18].

Formation of the chelates from aqueous solution and thermal stability of the chelate does not guarantee successful gas chromatographic separation. The alkali metal chelates of trifluoroacetylacetone; hexafluoroacetylacetone; 2,2,6,6-tetramethylheptane-3,5-dione and trifluoroacetyl-2,2,6,6-tetramethylheptane-3,5-dione[19] and the alkaline earth metal chelates of 2,2,6,6-tetramethylheptane-3,5-dione[20] are capable of being gas chromatographed individually in pure form but apparently exist as polymers in the gas phase and undergo metal exchange on the column to form mixed metal chelates

$$(\text{i.e. } [M_1L]_2 + [M_2L]_2 \rightleftharpoons 2\ M_1M_2\ [L]_2)$$

with the complexity increasing with increasing number of metal ion species.

However, this problem seems to have been overcome at least for the alkali metals with the use of penta and heptafluorodimethylheptane-3,5-dione[19].

Formation of chelates from aqueous solutions does not guarantee that a successful analytical method can be formulated. Frequently, less than 100 percent of the aqueous metal ion will react and be extracted into the organic phase[6,14,21]. This has been attributed primarily to the formation of the diketonate hydrate for hexafluoroacetylacetone[14,22]. A potential method of coping with this problem has been presented by Burgett[23] and Mitchell and Banks[24] whereby the hydrated water is replaced by another adduct species yielding a mixed ligand complex. Di-n-butylsulfoxide in conjunction with 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione for Ni, Co, Cu and Fe (Burgett[23]) and various triphosphate esters with trifluoro and hexafluoroacetylacetone for lanthanides and related elements (Mitchell and Banks[24]) have demonstrated this ability. Advantages were apparent both from the standpoint of chelate formation and thermal stability. In the latter case, water of hydration has been indicated as causing decomposition of the metal chelate in the gas chromatographic system.

Formation of the monothio derivative of hexafluoroacetylacetone (HFAS) seemed to overcome these limitations. Bayer, et al.[1] reported the formation of monothiohexafluoroacetylacetonates of copper, zinc, ferrous iron, nickel, gold, mercury, platinum, palladium, cadmium, lead and sodium. Of these, only the mercury and gold compounds were unstable to the point of decomposition during melting point determination. The metal chelates were formed directly from aqueous solution at 0.001 M concentration. Only the Pt, Pd, and Ni complexes have been investigated with respect to gas chromatographic behavior. The potential use of this compound is what prompted initiation of this investigation. Another modification of the β-diketones which yields volatile metal chelates has been recently reported by Uden, et al.[25] in which the ketoamine is formed. The copper and nickel chelates of the nitrogen analogs of TFA (amino and ethylenediamine) have been gas chromatographed and detected at picogram levels by electron capture.

Improvement in gas chromatographic detection systems has promoted the utility of this method of trace metals analyses. Earlier Investigations[17,26] using thermal conductivity detectors required high concentrations of metals and frequently this leads to overlapping of peaks. Use of flame ionization detectors (FID)[5,27] reduced detection of Be, Al, Cr, and Rh trifluoroacetylacetonates to $10^{-8}$ - $10^{-6}$ M. Electron capture detectors (ECD)[7-9,11,12,14,15] have allowed detection of as low as 0.01 μg/l of Be and Cr in the organic phase.

Such an increase in sensitivity is not without attendant problems, most notably interference from the unreacted β-diketone which also extracts into the organic phase. With trifluoroacetylacetone, back extraction with aqueous NaOH selectively removes the β-diketone[8,9,11,12,14,15]. However, not all chelating agents appear to be so easily removed and results in greatly reduced sensitivity of the electron capture detector[27]. Clean up procedures similar to those used in pesticide analysis could also be implemented. Work with Cr and Be acetylacetonates in serum and plasma[11] has demonstrated the use of gas chromatography mass spectrometry interfacing to provide absolute specificity of the response while sensitivities comparable to those of electron capture detectors are obtained. The attractive feature of this technique is that the gas chromatographic peaks need not be resolved at all since observation of one mass is not interferred with by the other metal species.

## II. METHODOLOGY

A. Analytical: In-lab analyses were conducted by atomic absorption and gas chromatographic techniques using a Varian Techtron AA-120 atomic absorption spectrophotometer and a Varian Aerograph 1740 gas chromatograph, respectively. Conventional atomic absorption analysis was supplemented where small sample volumes and low concentrations dictated by use of the Varian Model 63 Carbon Rod flameless atomizer. Background correction was obtained by duplicate analysis employing a hydrogen continuum lamp. Representative standard curves are presented in Figures 1, 2, and 3 for Nickel and Copper. Lead analyses were conducted in similar fashion.

Gas chromatographic determinations were made using all pyrex systems. Operating conditions and the detector employed are given in conjunction with the individual data presentations.

Infrared and Nuclear Magnetic Resonance spectra were obtained through the Chemistry Department at IIT. Specific details pertaining to these data are included in the appropriate sections as provided in the report.

B. Reagents: General reagents were of ACS grade or better [pesticide (Fisher) or nanograde (Malinkrodt) grade solvents used for reactions and subsequent gas chromatographic studies]. The specific chelating agents, monothiohexafluoroacetylacetone (HFAS) and 1,1,6,6-tetramethylpentane-3,5-dione (PIV) were purchased from Pierce Chemical Company, Rockford, Illinois as was the hexafluoroacetylacetone used in the attempted synthesis of HFAS when commercial marketing of the latter product was discontinued by Pierce Chemical Company.

C. Chelation and Synthesis: Due to variation of technique during the project period, individual procedures are included within the narrative.

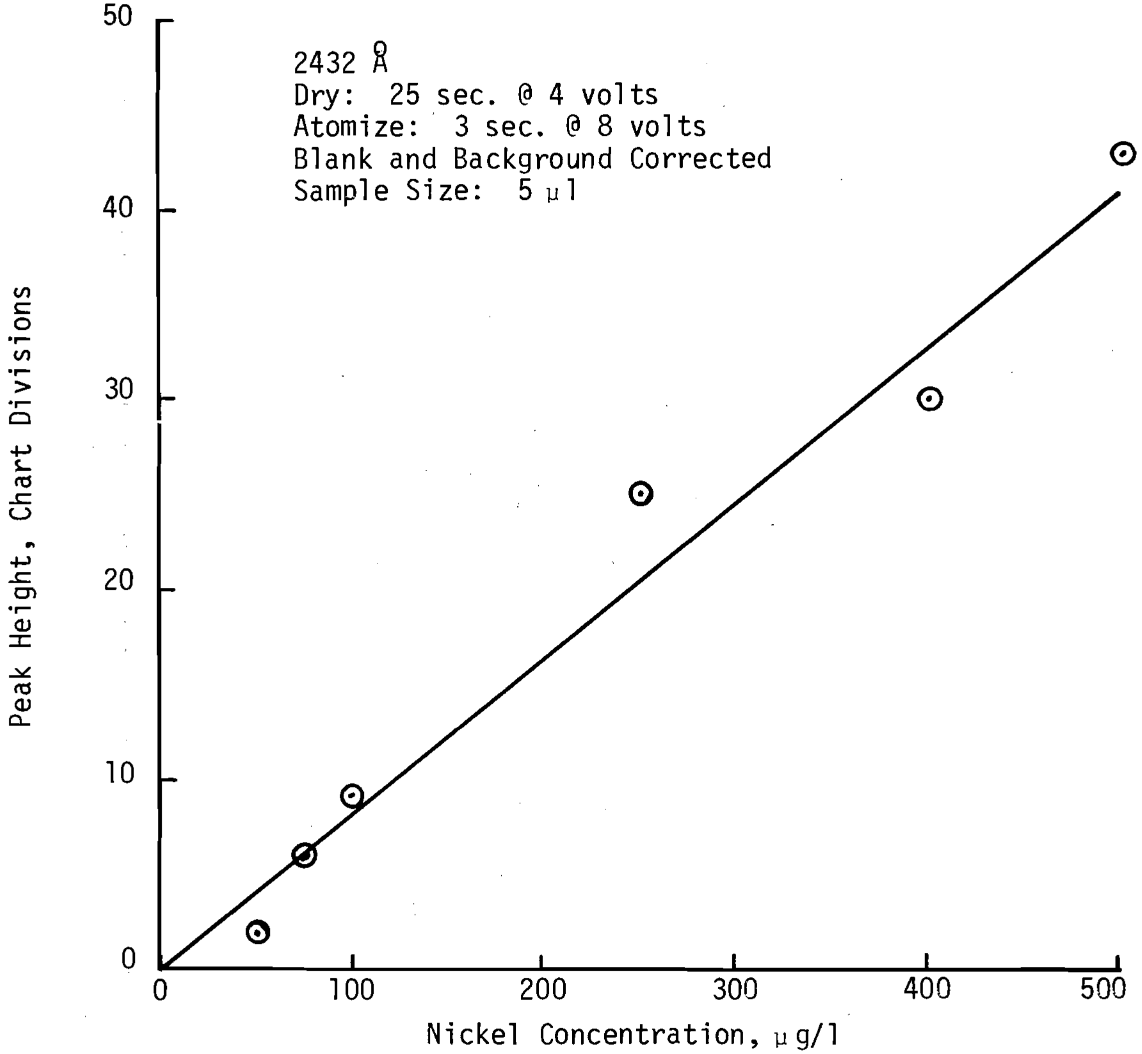


Figure 1. Nickel Standard Curve Using MS-63
Carbon Rode without Scale Expansion

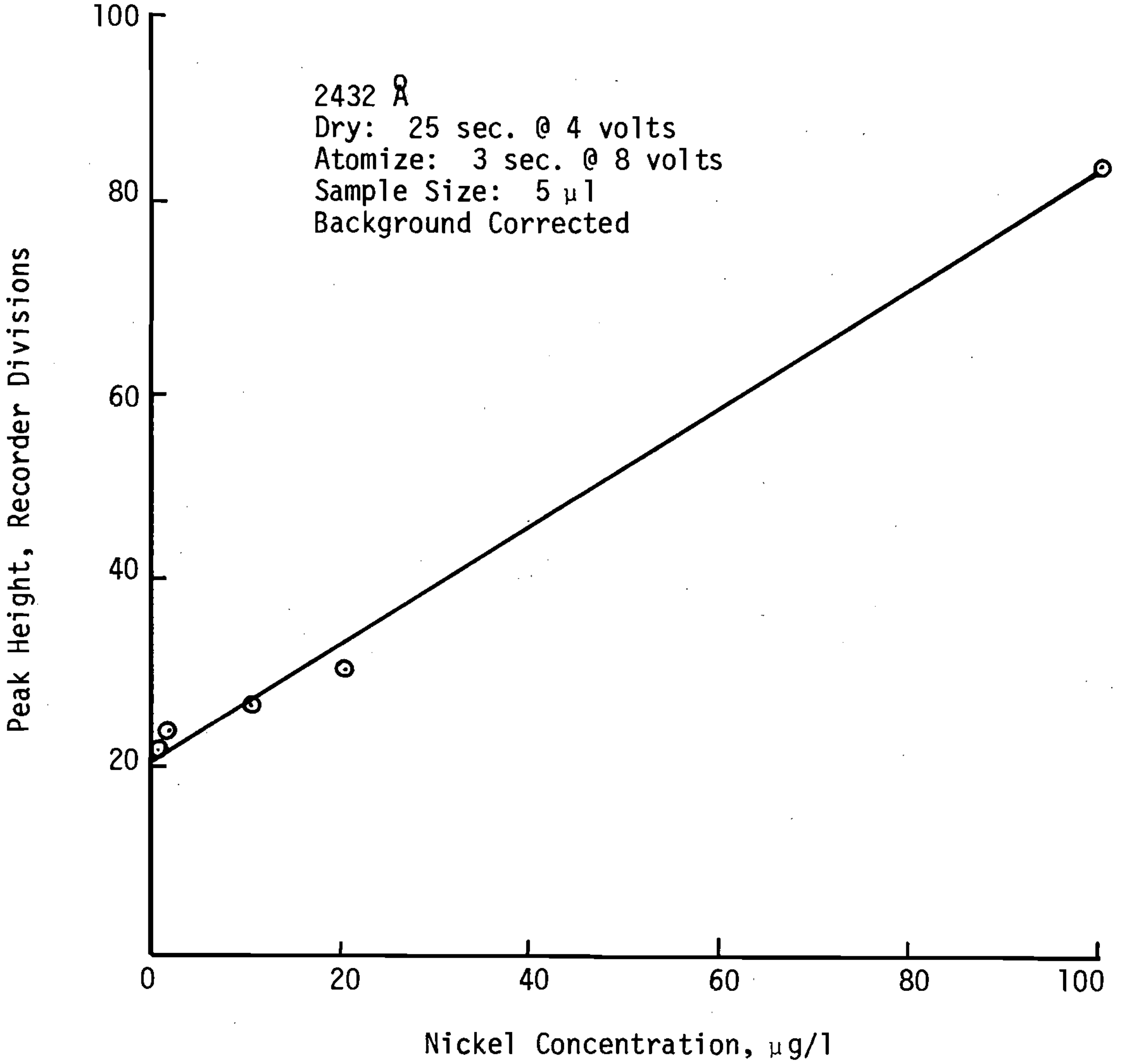


Figure 2. Nickel Standard Curve Using MS-63 Carbon Rod with Scale Expansion

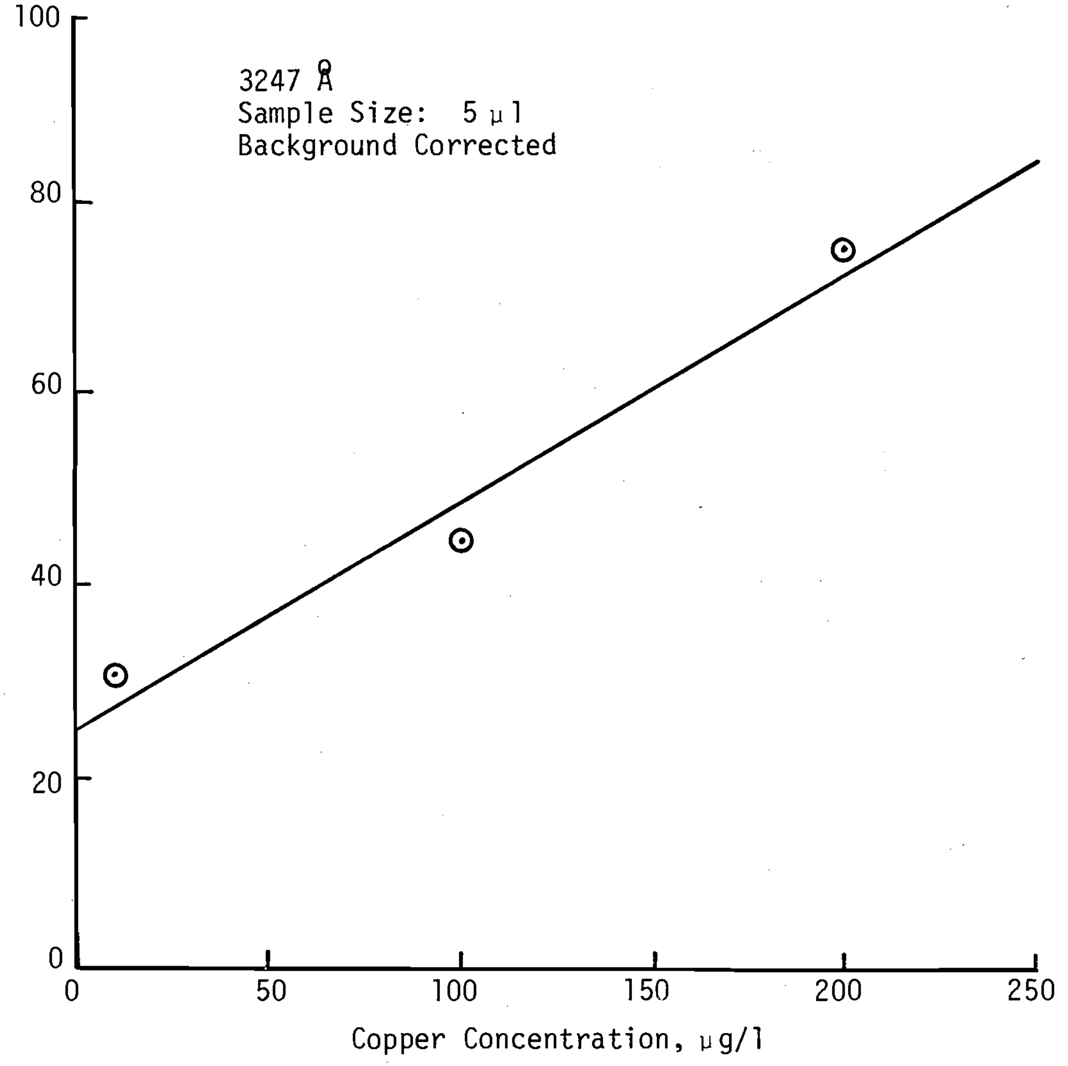


Figure 3. Copper Standard Curve Using MS-63 Carbon Rod

## III. HFAS STUDIES

A. Preliminary: Based upon published research involving HFAS[1] and the commercial availability of the compound, the initial focus of the project was to form the individual metal chelates; assess optimum reaction conditions and preferred organic solvents. Preliminary qualitative results are summarized in Table 1. Two of the chelates were further examined with respect to alternative solvent systems for purposes of changing the solvent peak elution position upon gas chromatographic analysis. These qualitative data are presented in Table 2.

In conjunction with the preliminary studies, quantitative evaluations were started to determine the extent of metal reaction and transfer into the organic phase for varying concentrations of the aqueous metal ion. Results are given in Table 3.

B. Gas Chromatography of HFAS Chelates: The chelates formed in the above studies were injected onto gas chromatographic columns (5% SE-30 on Chromosorb W, 5% SE-52 on Chromosorb W and 5% QF-1 on Varaport 30) under various injector, column and detector temperatures and various carrier gas flow rates using both flame ionization and electron capture detectors. Temperature programming was also utilized. In no case was a clean chromatogram obtained. Furthermore, injections of HFAS solutions and pure HFAS liquid yielded complex chromatograms indicative of mixtures and/or compound decomposition on the column. No definitive difference could be discerned between chelate solutions and HFAS solutions. These difficulties were puzzling since the chelates had been precipitated and redissolved and atomic absorption analysis substantiated the presence of the metals in the organic phase.

Table 1. Summary of Preliminary HFAS Chelate Formation Studies.

| Metal | Procedure | Observation |
|---|---|---|
| Cu | 5 ml 0.001 M $CuSO_4$ in 1 N $H_2SO_4$ + 1 ul HFAS | Slightly visible brown precipitate formed. |
| Cu | 5 ml 0.01 M $CuSO_4$ in 1 N $H_2SO_4$ + 20 ul HFAS | Brown precipitate formed immediately. |
| Cu | 1 ul 0.01 M $CuSO_4$ + 10 drops 1 N $H_2SO_4$ + 0.5 ml HFAS·Na solution (0.1 ml HFAS in 6 N NaOH) | Red-brown color appeared instantly. Filtered precipitate soluble in $CHCl_3$, less soluble in hexane. |
| Cu | 5 ml 0.001 M $CuSO_4$ + 15 ml 0.001 M HFAS·Na | No precipitate formed. |
| Cu | 1 ml 0.01 M $CuSO_4$ + 1 ml 0.01 M HFAS·Na + 1 drop 1 N $H_2SO_4$ + 2 ml $CHCl_3$ or Hexane | Chelate formed upon shaking with transfer into organic phase. |
| Zn | 5 ml 0.01 M $ZnSO_4$ in 1 N $H_2SO_4$ + 20 ul HFAS | Yellow precipitate formed. |
| ZN | 1 ml 0.01 M $ZnSO_4$ ml HFAS·Na + 10 drops 1 N $H_2SO_4$ | Reddish precipitate formed. Filtered precipitate dissolved in $CHCl_3$ to yield yellow-orange color. |
| Pb | 1 ml 0.01 M $Pb(NO_3)_2$ + 0.5 ml HFAS·Na + 10 drops 1 N $HNO_3$ | Reddish precipitate formed. Filtered precipitate only slightly soluble in $CHCl_3$ and hexane. |

Table 1. (continued)

| | | |
|---|---|---|
| Fe | 2 ml 0.01 M $FeSO_4$ + 1 ml HFAS·Na + 15 drops 1 N $H_2SO_4$ | Reddish precipitate formed. Filtered precipitate soluble in $CHCl_3$ but not in hexane. |
| Cd | 1 ml .01 M $CdCl_2$ + 0.5 ml HFAS·Na + 10 drops 1 N $H_2SO_4$ | Yellow precipitate formed. |

Table 2. Qualitative Solubility Rating of Copper and Zinc HFAS Chelates in Selected Organic Solvents.

| Solvent | Subjective Solubility Rating* | |
|---|---|---|
| | Cu | Zn |
| Methyl Isobutyl Ketone | 1 | 1 |
| 2-Octanol | 1 | 2 |
| Benzene | 1 | 1 |
| Cyclohexane | 3 | 3 |
| 1-Butanol | 2 | 1 |
| N-Amyl Alcohol | 1 | 1 |

* 1 = very soluble
2 = moderately soluble
3 = slightly soluble

Table 3. Distribution of Copper and Zinc between Aqueous and Hexane Phases.

| Metal | Initial Conc., M Aqueous≠ | Final Aqueous Conc., M | Final Organic Conc., M | $K_d$* |
|---|---|---|---|---|
| Cu | 0.005 | 0.0039 | 0.0011 | 0.29 |
| | 0.0005 | 0.00038 | 0.0012 | 0.33 |
| | 0.00005 | 0.000042 | 0.00008 | 0.18 |
| Zn | 0.005 | 0.0040 | 0.0010 | 0.25 |
| | 0.0005 | 0.00038 | 0.0012 | 0.31 |
| | 0.00005 | 0.000045 | 0.00005 | 0.10 |

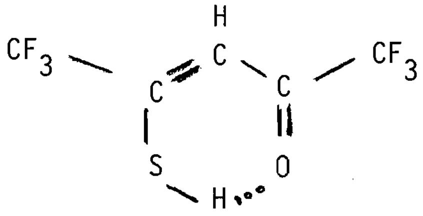
Procedure: 1 ml aqueous metal solution + 1 ml 0.01 M HFAS·Na + 0.03 (1 drop) 1 N $H_2SO_4$ + 2 ml Hexane. Reaction vial shaken and phases analyzed for metal concentration by atomic absorption with Carbon Rod Atomizer, corrected for background.

≠ Includes dilution by addition of HFAS·Na and acid solutions.

* $K_d$ = Final Organic Phase Concentration/Final Aqueous Phase Concentration.

It was apparent at this point that the commercial compound was not purified by the distillation procedure and previously reported results for successful chromatographing of the nickel chelate could not be duplicated.

C. Examination of Commercial HFAS: The initial quantity of HFAS received from Pierce Chemical Company was vacuum distilled prior to use and the constant boiling fraction at 60° C and 70 mm Hg was collected. Upon reaction with 6 N NaOH, the organic layer dissolved yielding a red solution as expected. However, upon obtaining the results mentioned above, close examination of the compound was made. A nuclear magnetic resonance (NMR) spectrum of the compound was obtained (Figure 4). In light of NMR spectra obtained for other β-diketone structures (Trifluoroacetylacetone, Figure 5, and 2,2,6-Tetramethylpentane-3,5-dione, Figure 6) the spectrum for the commercial product shows strong evidence of highly impure HFAS, indicating a mixture of compounds. This conclusion was substantiated upon consultation with several chemists (Robert Rickert, IIT, Chester Vandergriff and Dr. James Kinstle, The University of Tennessee). Based upon Bayer, *et al.*[1] for HFAS and several other authors for other monothio-β-diketones (Ho, *et al.*[28], Chaston, *et al.*[29], Chaston and Livingstone[30], Barraclough, *et al.*[31]) the structure expected is given below:



which would imply a relatively simple NMR spectrum. Certainly, nothing as complex as that given in Figure 4 is to be expected from the molecular structure above.

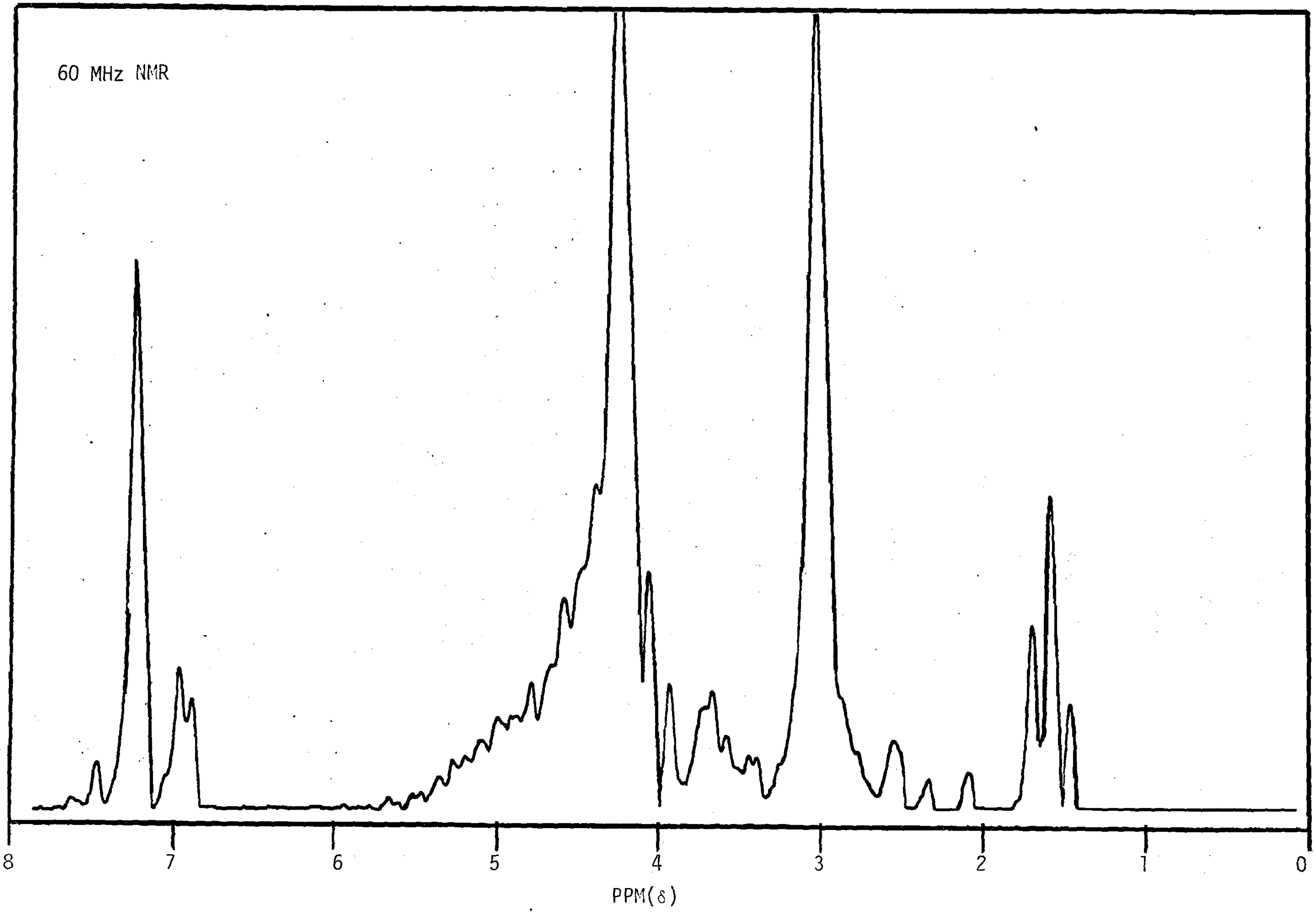


Figure 4. NMR Spectrum of Initial Batch of HFAS after Distillation

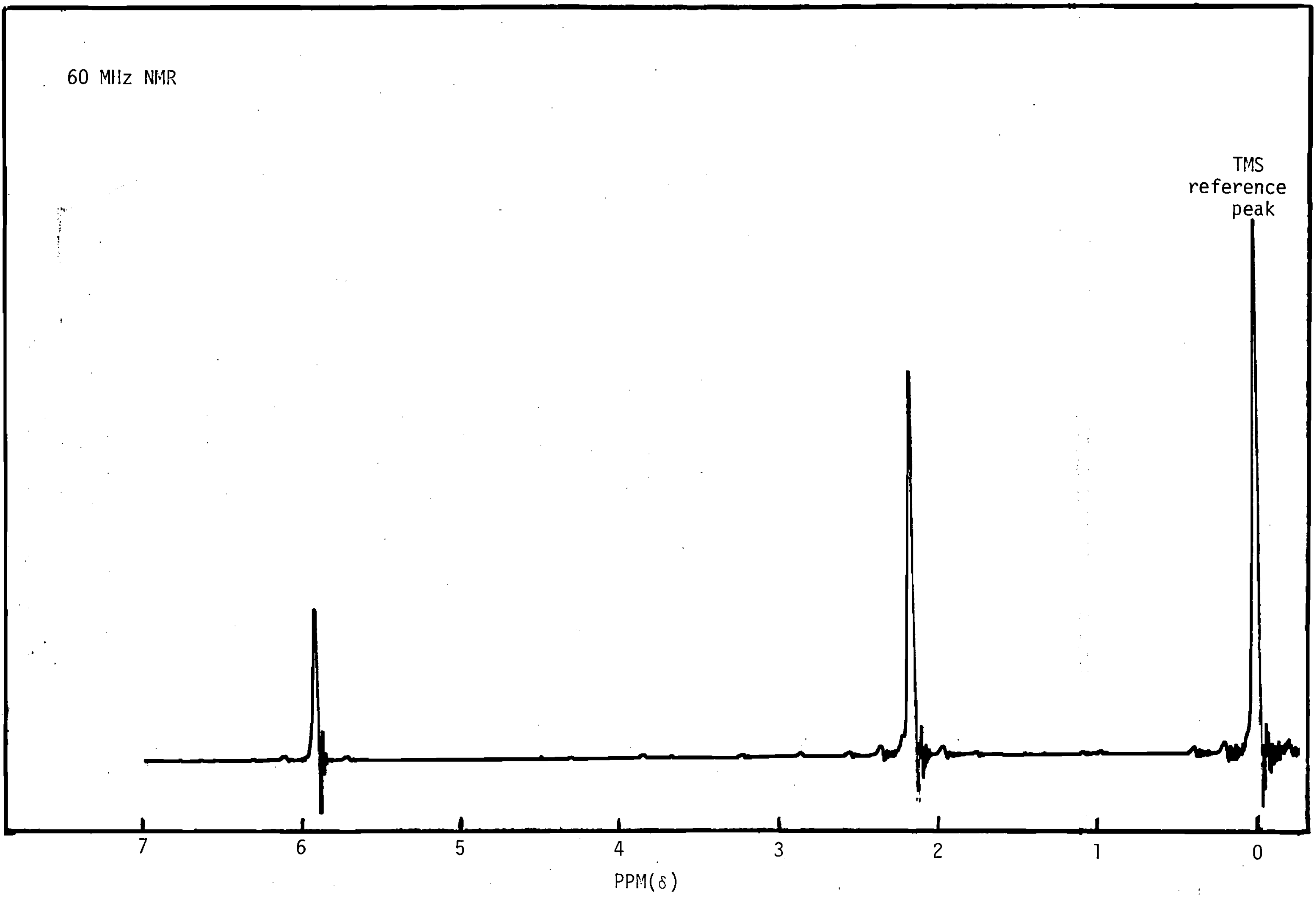


Figure 5. NMR Spectrum of 1,1,1,-Trifluoroacetylacetone

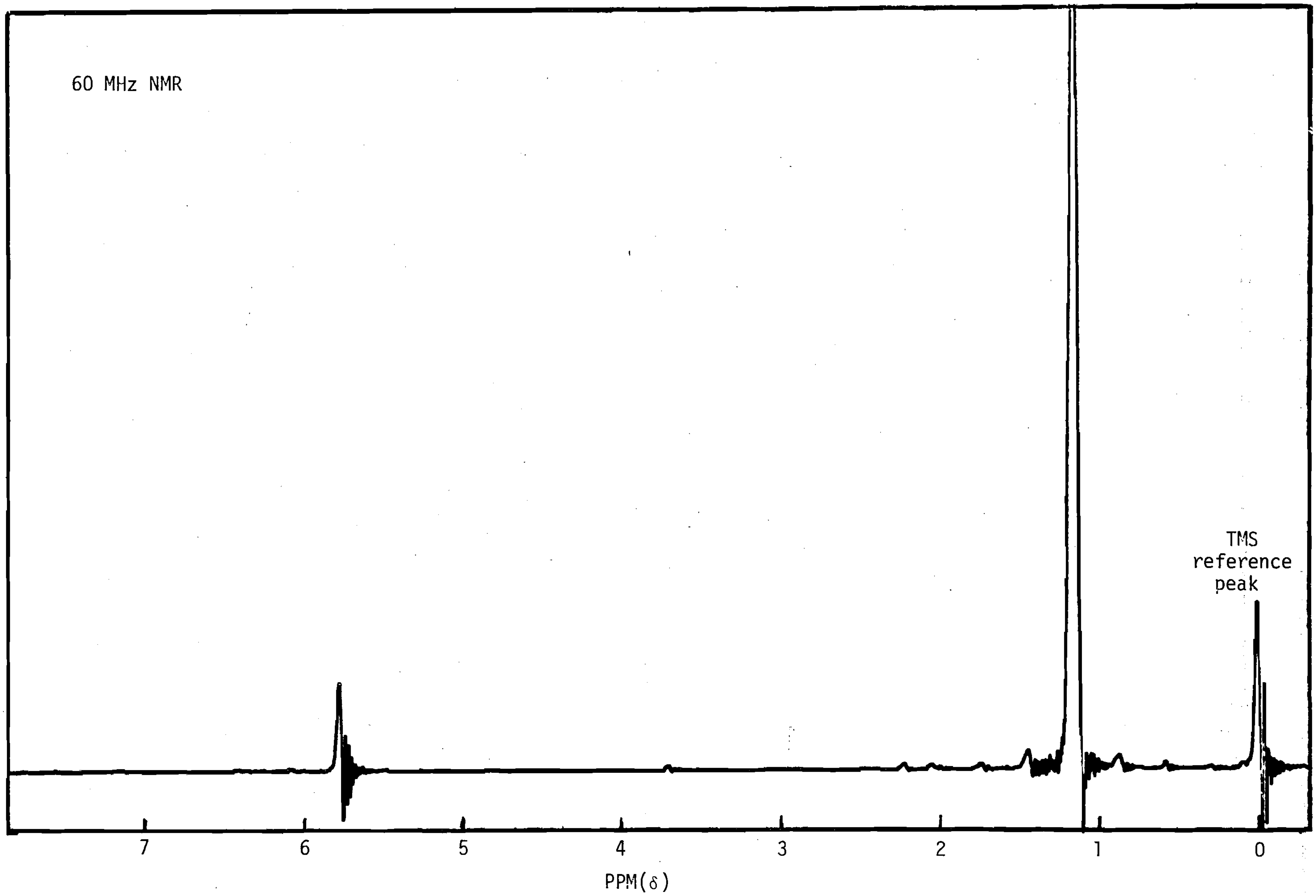


Figure 6. NMR Spectrum of 2,2,6,6-Tetramethylheptane 3,5,-dione

Communication with Pierce Chemical Company at this point resulted in shipment of a replacement of the original purchase. This material contained crystals and upon purification by vacuum distillation yielded the NMR spectrum of Figure 7. At this point, further communication with Pierce revealed that our complaint regarding product identity was not an isolated incident, and, in fact, the company was in the process of removing the product from the market. As a gesture of good faith, Pierce contributed their remaining stock free of charge for investigative purposes. The NMR spectrum of this material as received is shown in Figure 8.

This material was vacuum distilled and a constant boiling fraction at 52-54$^{o}$ C was collected. The NMR spectrum was messy as before (Figure 9) and gas chromatographic analysis on SE-30 yielded multiple peaks (Figure 10). Thin layer chromatograms were obtained on silica gel and alumina layers. These results, summarized in Figure 11, generally yielded single mobile spots with another spot remaining at the point of application.

Large scale separations were performed with alumina columns. One ml of HFAS on the column separated into four distinct regions. The uppermost was yellow, followed by green, yellow orange and purple upon passage of acetone through the column. These bands were not eluded.

To another column, 1 ml of HFAS was eluted with absolute Methanol. Three bands formed on the column which were orange, green-blue and yellow respectively from the top of the column. The yellow band remained at the top of the column upon continued elution. The collected eluent was evaporated on a steam table and the residue redissolved in Methanol. Chromatography of the residue on SE-30 yielded multiple peaks.

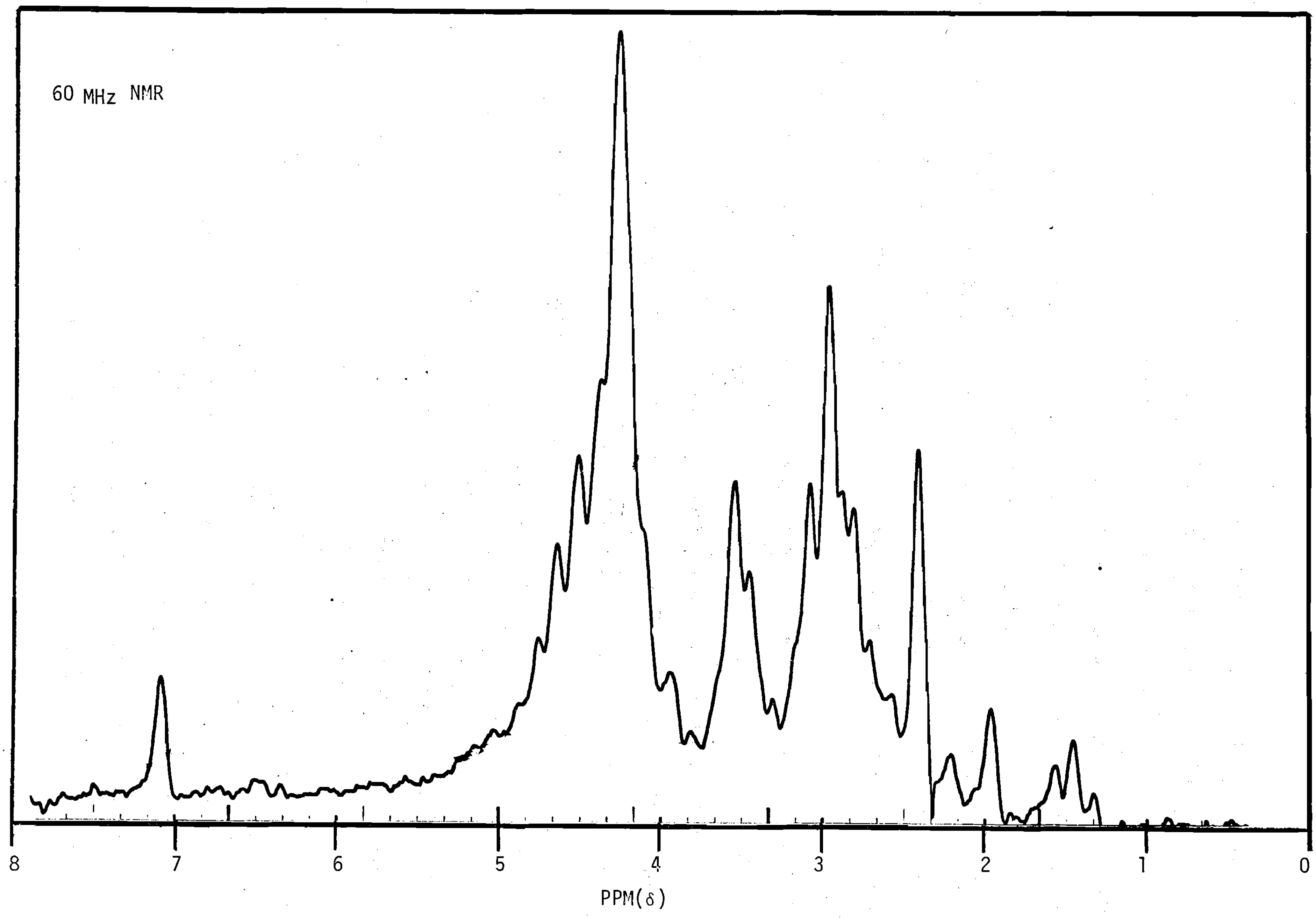


Figure 7. NMR Spectrum of Second Batch of HFAS after Distillation

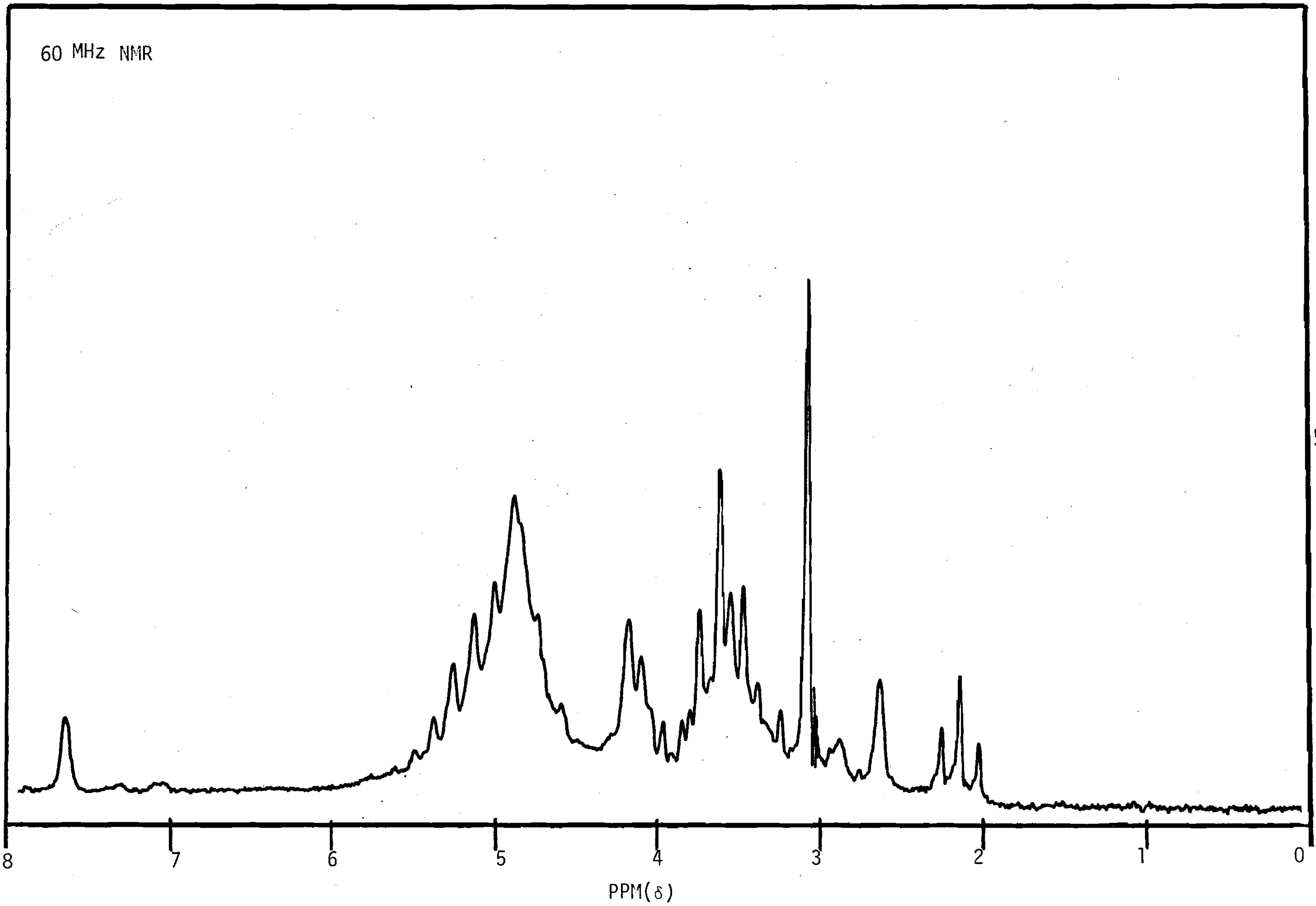


Figure 8. NMR Spectrum of Pierce Remaining HFAS Stock Donated upon Removal of Product from Market (Prior to Distillation)

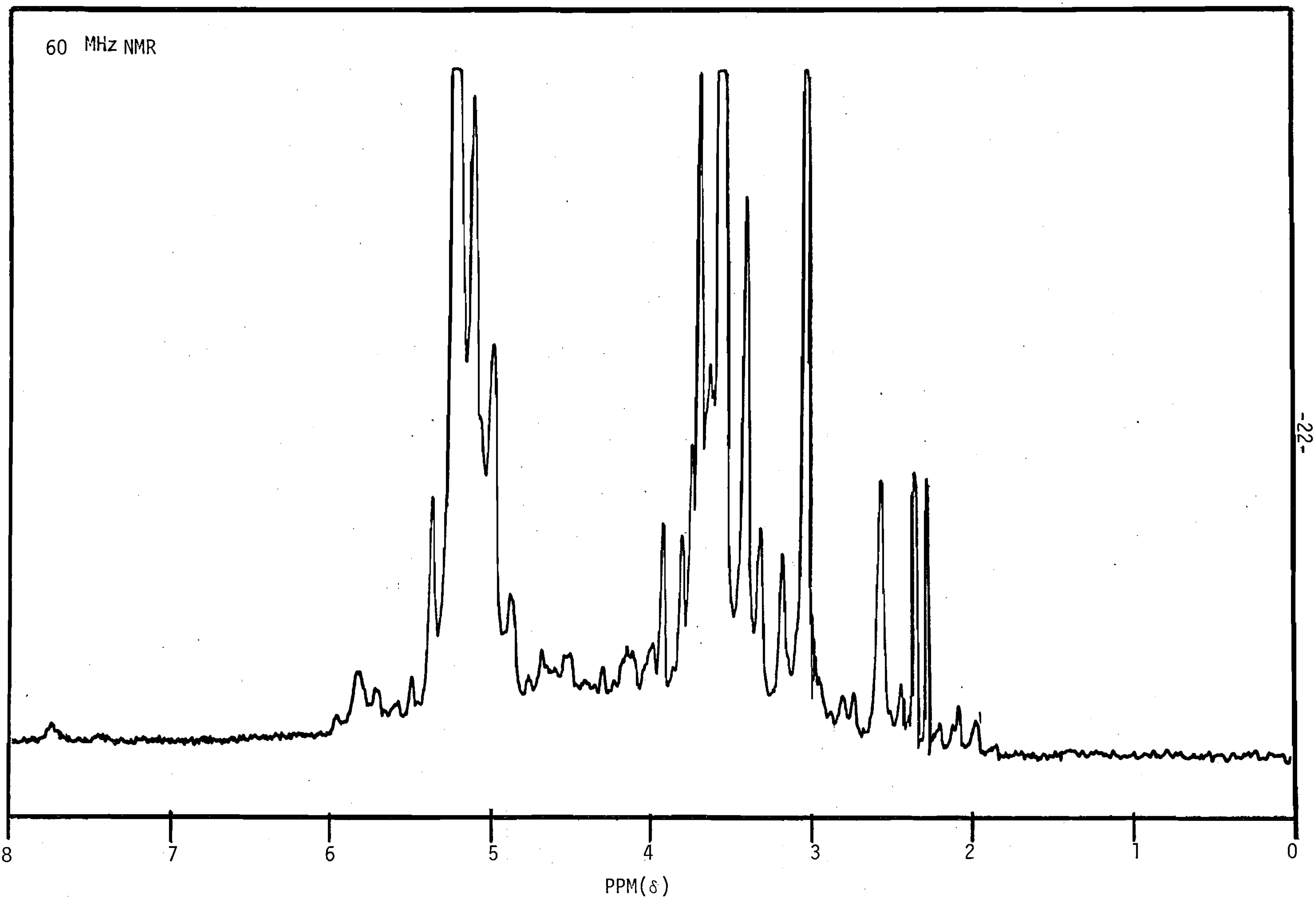
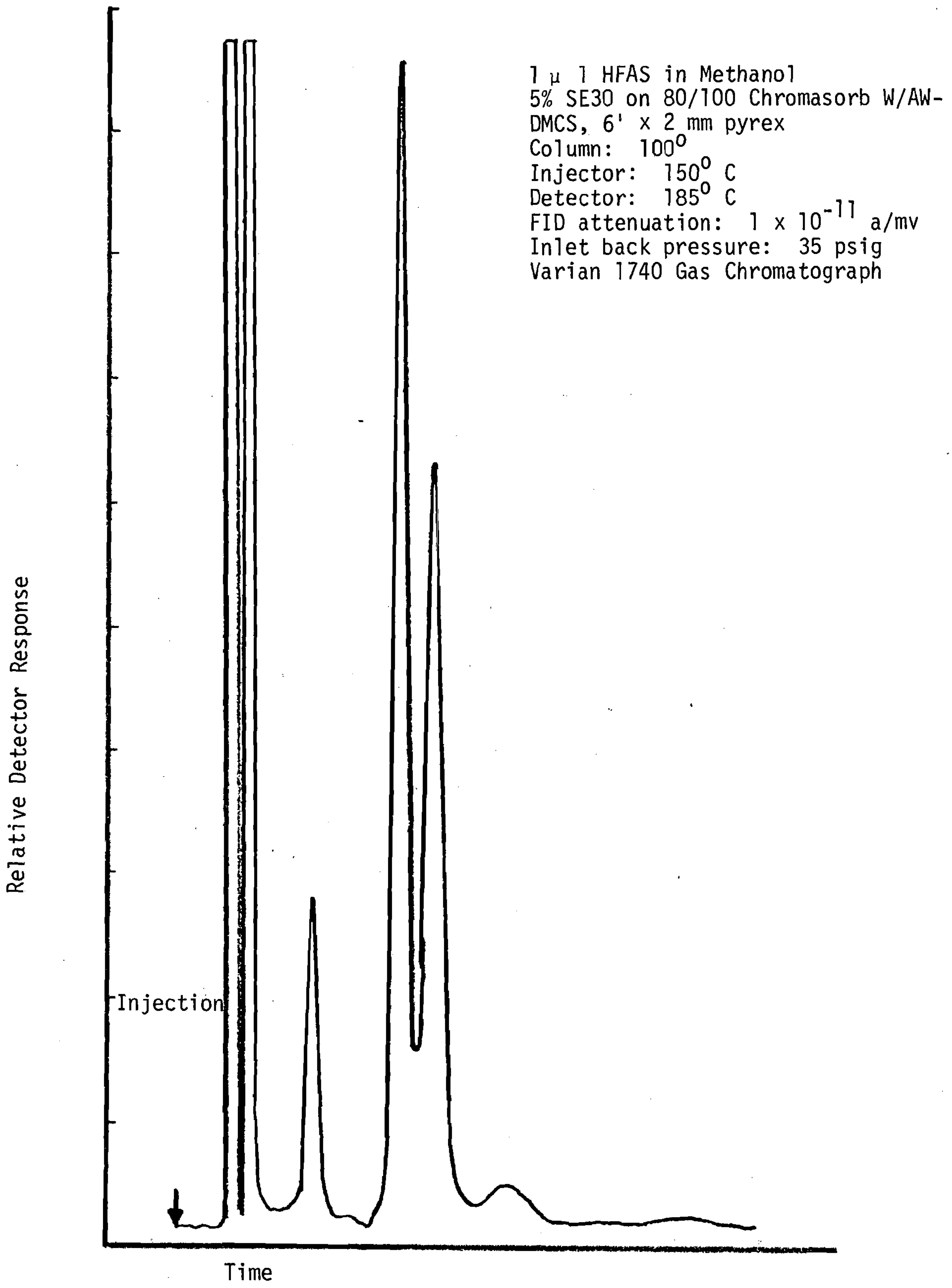
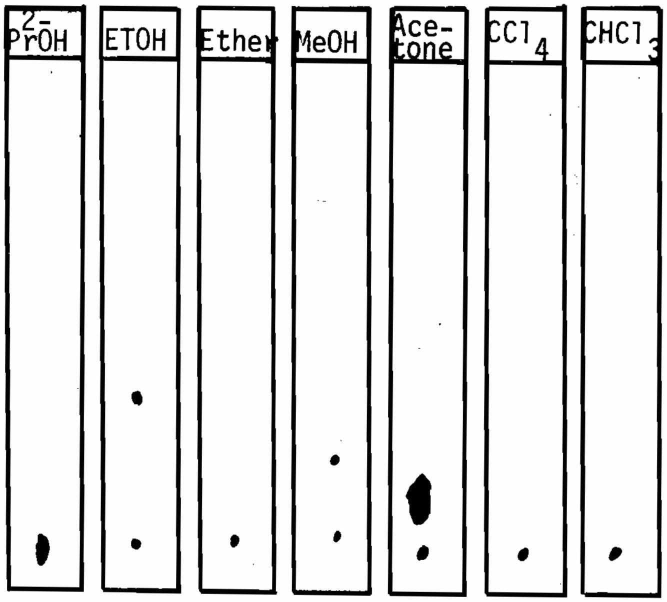


Figure 9. NMR Spectrum of Donated HFAS after Distillation

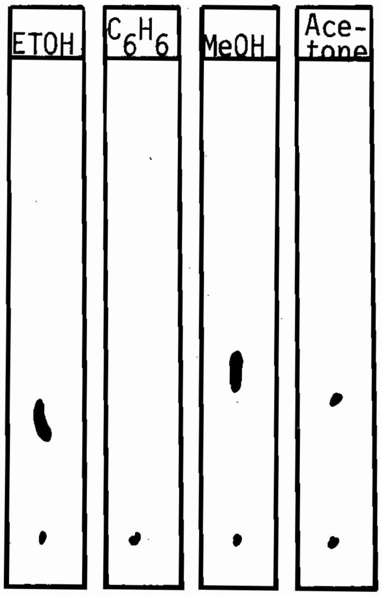


1 μ l HFAS in Methanol
5% SE30 on 80/100 Chromasorb W/AW-DMCS, 6' x 2 mm pyrex
Column: 100°
Injector: 150° C
Detector: 185° C
FID attenuation: 1 x $10^{-11}$ a/mv
Inlet back pressure: 35 psig
Varian 1740 Gas Chromatograph

Figure 10. Chromatograph of Distilled HFAS (Donalted Stock)



Silica Gel



Alumina

Figure 11. Thin-Layer Chromatograms of Donated HFAS Stock

A finer fractionation was made on 0.5 ml of HFAS with the methanol-acetone eluent. Three fractions were collected. The first was yellow, the second red and the third a lighter red. Upon evaporation on a steam table, the yellow fraction turned dark red.

D. Attempt to Synthesize HFAS: In spite of Pierce Chemical Company's failure with HFAS, an attempt was made to synthesize the compound in-house. The procedure of Bayer, et al.[1] was followed in speculation that the compound was perhaps sufficiently unstable that storage and shipment of the compound represented the major problem. The procedure followed is presented in Table 4. The synthesis failed at step A-5. The addition of the crude HFACl mixture to ice water, an exothermic reaction, yielded a cloudy white solution rather than the expected two phase system. Success of the synthesis prior to this point was substantiated by a NMR spectrum of the crude HFACl product prior to excess $SOCl_2$ destruction in ice water (Figure 14). Continuation of the procedure beyond this step failed to yield a product.

The chemical cost of additional synthesis attempts contrasted with the project budget status at this point prohibited continuation of in-house synthesis of HFAS. Since the commercial compound obtained was of questionable identity and could not be satisfactorily purified, continued investigation was deemed meaningless. In fact, the remaining Pierce stock donated to the project would not dissolve in sodium hydroxide. Instead, cloudy solutions were obtained upon mixing yielding a light yellow precipitate indicative of loss of sulfur from the parent molecule.

## Table 4. Synthesis of HFAS*

A. HFAS·Cl 3 neck flask with condenser and drying tube, dropping funnel, and thermometer

1. 4 ml Dimethyl Formamide, 194 ml $SOCl_2$ added with stirring and heated to 40° C.
2. 80 ml HFAE (Hexafluoroacetylacetone, Pierce Chemical) added dropwise over 3 hours.
3. Heated for 3 hours at 75° C which was the maximum attainable temperature.
4. HCl gas produced on heating, solution remained yellow throughout.
5. Stirred overnite at room temperature under $N_2$.
6. Distilled, yielding 102 ml green liquid at 65-75° C - G.C., NMR, IR show correct product. (See Figures 12-14).
7. Added to 150 ml ice water.
8. Semi-violent exothermic reaction occurred yielding a cloudy white solution.
9. Extracted 5 times in diethyl ether.
10. Dried over $MgSO_4$ overnite.
11. Filter, distilled.

No product obtained.

B. NaSH (under $N_2$)

1. 12 g Sodium metal added slowly to 120 ml 99 percent ETOH. Three 50 ml portions of ETOH added as needed to continue dissolving Na.
2. Yellow liquid results.
3. Bubbled $H_2S$ for 1 hour - no rxn.
4. Add 300 ml dry ether
   White p'tate (dense) formed.
5. Filtered on No. 1 Qual. Filter w. vacuum
   Store in vacuum desiccator
   To supernatant added ether, reprecip. 5 times.

   Last 4 products slightly yellow.

---

*All done under N atmosphere.

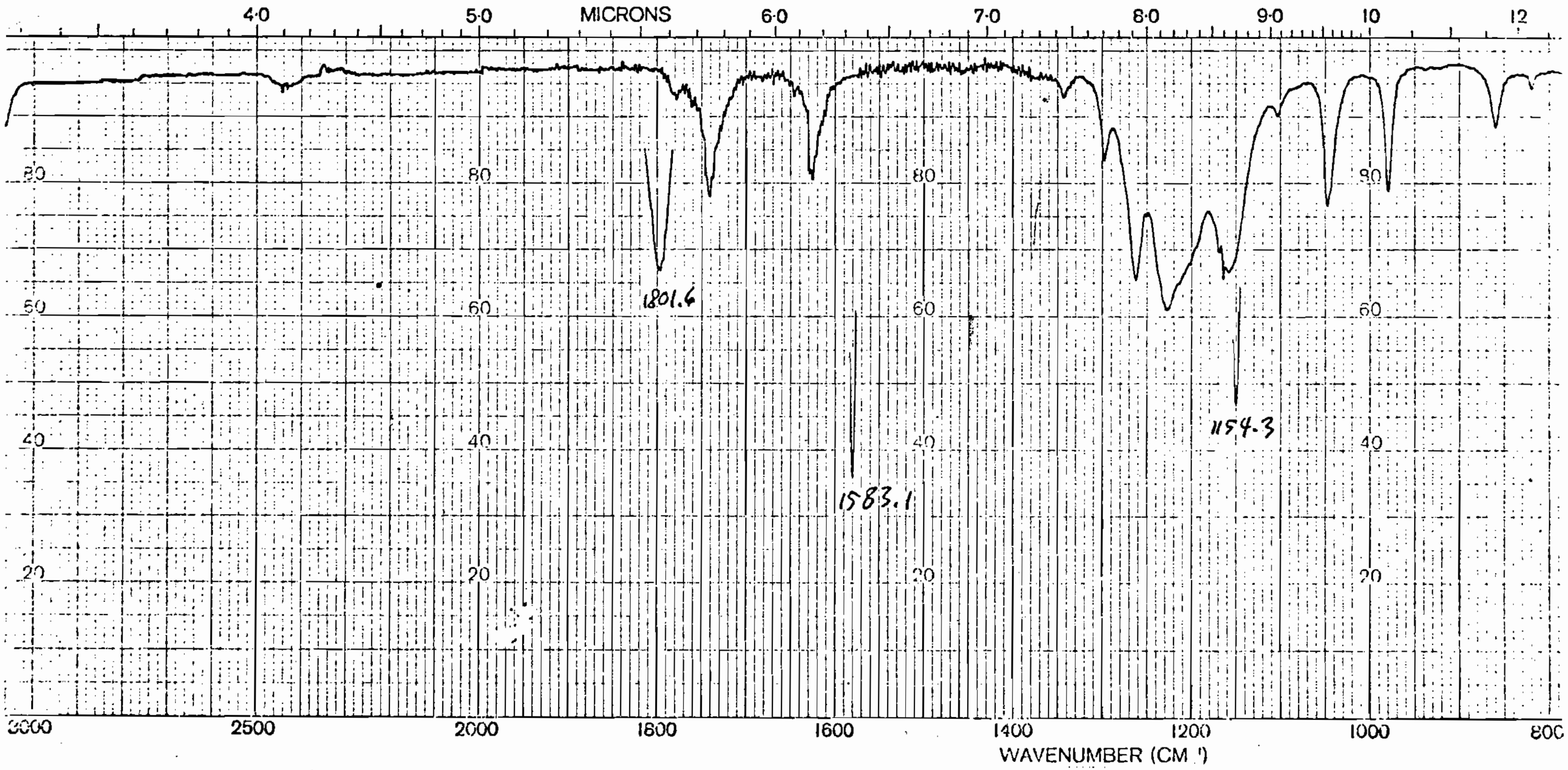


Figure 12. I.R. Spectrum of Crude HFACl Product

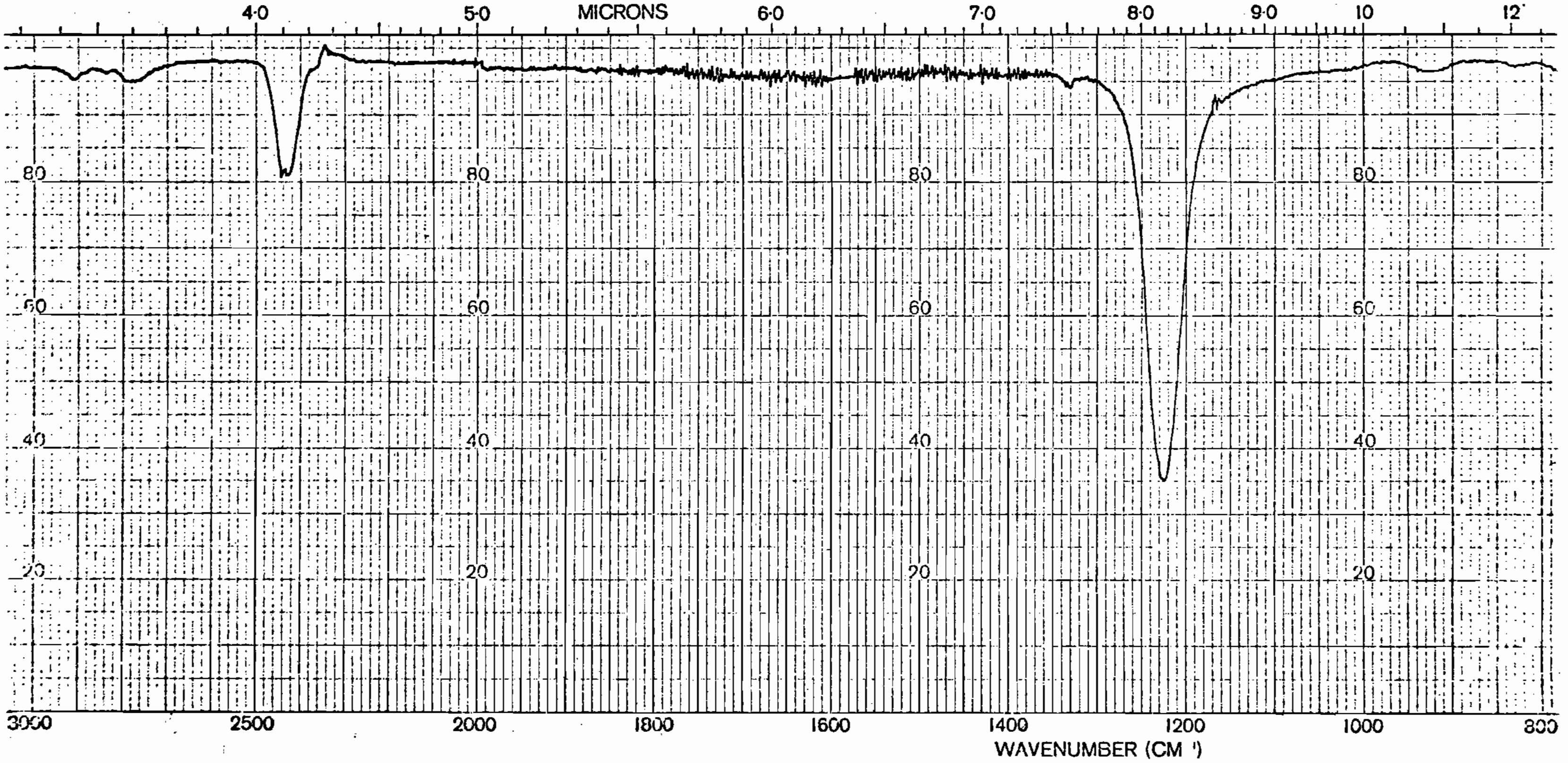


Figure 13. I.R. Spectrum of Thionyl Chloride

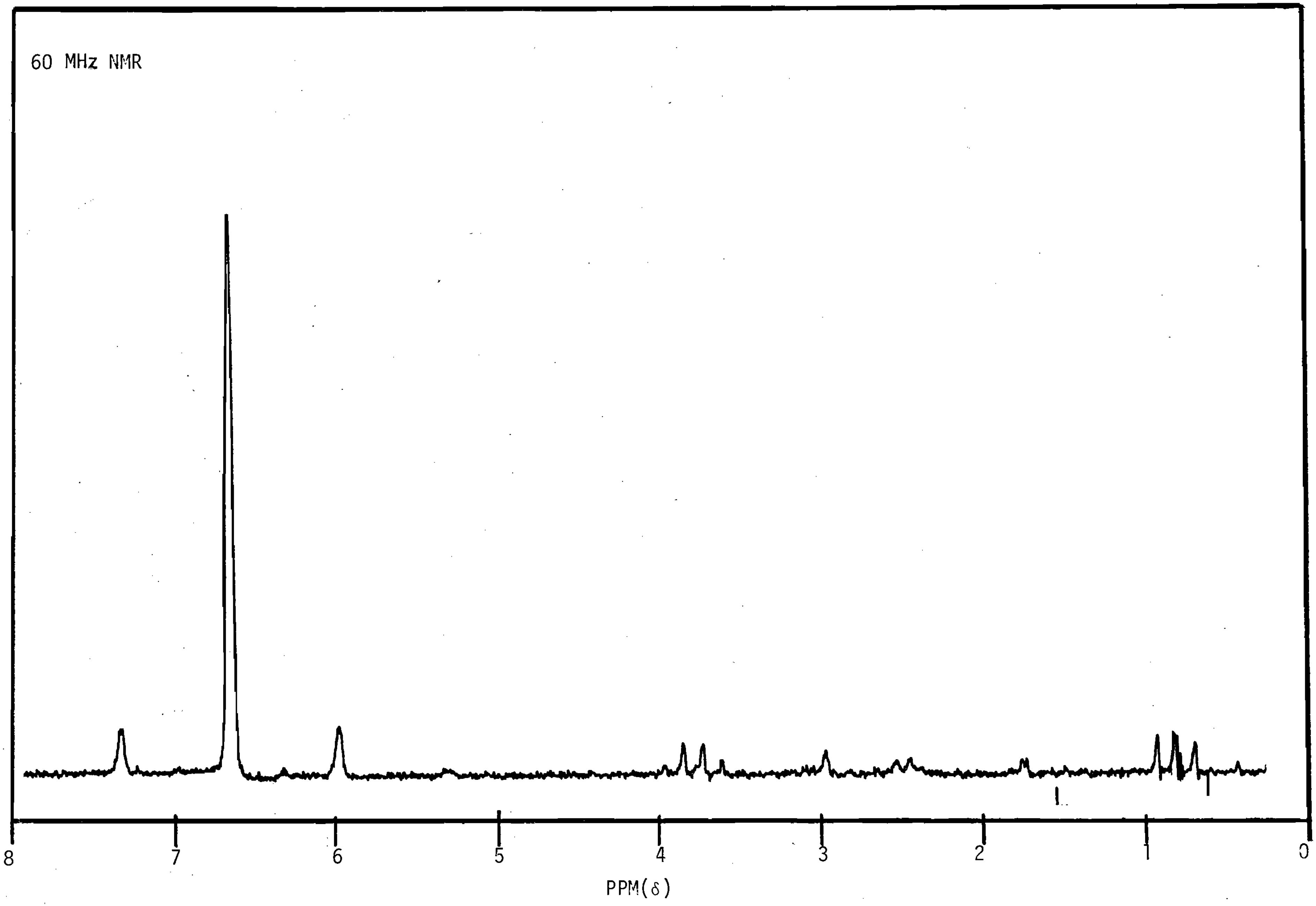


Figure 14. NMR Spectrum of Crude HFACl Product

E. Discussion: The potential utility of HFAS for metals analysis was not determined because of difficulties associated with obtaining the chelating agent in pure form. Preliminary studies with what was ultimately determined to be impure HFAS did indicate formation of metal chelates as described by Bayer, *et al.*[1]. Inability to duplicate the gas chromatographic behavior for Nickel HFAS cannot be considered *prima facie* evidence that the reported work was in error for several reasons. (1) The presence of impurities may have resulted in the formation of a different metal chelate which was not thermally stable to gas chromatography. (2) The presence of impurities may have led to decomposition of the Nickel HFAS upon injection into the gas chromatograph. (3) The presence of impurities in the HFAS may have yielded peaks that co-eluted with any HFAS in the mixture, thus, masking the chelate.

Before a final judgement can be made, the chelating agent must necessarily be prepared in its purity confirmed. The research conducted did, in part, lead to the discontinuance of the commercial distribution of the chelating agent and in a sense must be considered to have contributed to the scientific community in this regard. An attempt to synthesize HFAS by modified routes is being initiated through unsponsored research at The University of Tennessee, Department of Chemistry as a result of this project and interaction by the Principal Investigator. Although motivated by entirely different interests relating to basic research, a by-product of this interest will be a reinstitution of the original project goals, albeit, without formal funding. Successful synthesis of HFAS and even demonstration of chelate formation and gas chromatographic separation are overshadowed by potential problems of HFAS stability.

To be a viable analytical technique for routine use, HFAS must be readily and easily obtained either through stability once obtained or through reasonably simple synthesis if unstable. These questions are unresolved at present demonstrated by the problems encountered with the commercial product on this project.

## IV. PIV STUDIES

A. Extraction Studies: A series of aqueous lead solutions ($Pb(NO_3)_2$) ranging from 100 mg/l to 0.01 mg/l lead were contacted with equal volumes of 0.1 and 0.01 M PIV in benzene and agitated in a sonic bath in sealed vials for varying time periods to assess transfer of lead into the organic phase. The organic layer was analyzed for lead content by flameless atomic absorption with the MS-63 carbon rod. At lower Pb concentrations, analysis was also performed on the aqueous layer. Molar ratios of PIV to Pb ranged from $2.07 \times 10^6$ to 20.7 for the entire series of extractions. Duration of extraction was 1, 2, 4 and 6 hours for each combination of lead and PIV solutions.

The data presented in Tables 5 and 6 were the reported results of this study which unfortunately were obtained continuously without communication of experimental progress before completion in spite of strong demands for such communication. The net result is that these data are meaningless for several reasons:

(1) The minimum detectable quantity of Pb was 40 ppb as illustrated by the "standard" curve of Figure 15.

(2) The curve does not pass through 0.

(3) Reported minimum detectable quantity by the method used should be 1 ppb.

## Table 5. Lead Extraction Studies with 0.1 M PIV

| Original Aqueous Lead Conc., mg/l | Final Benzene Lead Conc., μg/l | Original Aqueous Lead Conc., mg/l | Final Benzene Lead Conc., μg/l | Final Aqueous Lead Conc., μg/l |
|---|---|---|---|---|
| | | 10 (1) | 70 | |
| 100 (1)* | 45 | 10 (1) | 115 | |
| 100 (1) | <40 | 10 (1) | 50 | |
| 100 (2) | 53 | 10 (2) | >400 | |
| 100 (2) | 53 | 10 (2) | 197 | |
| 100 (6) | 50 | 10 (4) | <40 | |
| 100 (6) | 50 | 10 (4) | <40 | |
| 50 (1) | 50 | 10 (6) | <40 | |
| 50 (1) | 53 | 10 (6) | <40 | |
| 50 (2) | 45 | 5 (1) | <40 | |
| 50 (2) | 48 | 5 (1) | 48 | |
| 50 (4) | 47 | 5 (2) | 50 | |
| 50 (4) | 45 | 5 (2) | 45 | |
| 50 (6) | 48 | 5 (4) | 65 | |
| 50 (6) | 48 | 5 (4) | 45 | |
| 25 (1) | <40 | 5 (6) | <40 | |
| 25 (1) | 50 | 5 (6) | <40 | |
| 25 (2) | <400 | 5 (6) | <40 | |
| 25 (2) | <400 | 5 (6) | 60 | |
| 25 (4) | 58 | 1 (1) | <40 | 400 |
| 25 (4) | 46 | 1 (1) | 45 | 375 |
| 25 (6) | 47 | 1 (2) | <40 | 230 |
| 25 (6) | 48 | 1 (2) | <40 | 158 |
| | | 1 (4) | 45 | 138 |
| | | 1 (4) | 60 | 290 |
| | | 1 (6) | <40 | >400 |
| | | 1 (6) | <40 | >400 |
| | | .5 (1) | no data | 210 |
| | | 15 (2) | no data | 122 |
| | | | | 145 |
| | | .5 (4) | 45 | 55 |
| | | .5 (4) | 55 | 105 |
| | | .5 (6) | <40 | 55 |
| | | .5 (6) | 58 | 45 |
| | | .1 (1) | no data | <40 |
| | | .1 (1) | no data | 50 |
| | | .1 (2) | no data | 45 |
| | | .1 (4) | <40 | <40 |
| | | .1 (4) | <40 | <40 |
| | | .1 (6) | <40 | <40 |
| | | .1 (6) | 45 | <40 |
| | | all 0.05<br>and 0.01<br>mg/l samples | <40 | <40 |

*Values in parentheses are time of extraction in hours

## Table 6. Lead Extraction Studies with 0.01 M PIV

| Original Pb Conc., mg/l | Final Benzene Pb Conc., μg/l | Original Pb Conc., mg/l | Final Benzene Pb Conc., μg/l | Final Aqueous Pb Conc., μg/l |
|---|---|---|---|---|
| 100 (1)* | <40 | 25 (6) | 85 | |
| 100 (1) | <40 | 25 (6) | 75 | |
| 100 (2) | <40 | 10 (1) | <40 | |
| 100 (2) | <400 | 10 (1) | <40 | |
| 100 (2) | <400 | 10 (2) | 56 | |
| 100 (2) | <40 | 10 (2) | <40 | |
| 100 (4) | 60 | 10 (4) | <40 | |
| 100 (4) | 45 | 10 (4) | <40 | |
| 100 (6) | <40 | 10 (6) | 56 | |
| 100 (6) | 60 | 10 (6) | <40 | |
| 50 (1) | <40 | 5 (1) | <40 | |
| 50 (1) | <40 | 5 (1) | <40 | |
| 50 (2) | no data | 5 (2) | <40 | |
| 50 (4) | no data | 5 (2) | 63 | |
| 50 (6) | 65 | 5 (4) | <40 | |
| 50 (6) | 45 | 5 (6) | no data | |
| 25 (1) | <40 | 1 (1) | no data | 195 |
| 25 (1) | <40 | 1 (1) | no data | 105 |
| 25 (2) | <40 | 1 (2) | <40 | 133 |
| 25 (2) | <40 | 1 (2) | <40 | 238 |
| 25 (2) | <40 | 1 (4) | 48 | 155 |
| 25 (4) | 57 | 1 (4) | 45 | 175 |
| 25 (4) | 68 | 1 (6) | 47 | 95 |
| | | 1 (6) | 48 | 298 |
| | | .5 (1) | no data | 73, 65 |
| | | .5 (2) | 138 | 155 |
| | | .5 (2) | 182 | 93 |
| | | .5 (2) | 225 | no data |
| | | .5 (4) | 48 | 188 |
| | | .5 (4) | 48 | 105 |
| | | .5 (6) | no data | 183, 55 |

.5 to .05 mg/l samples, all organic values <40 μg/l and no aqueous values above 45 μg/l.

*Values in parentheses is time of extraction in hours.

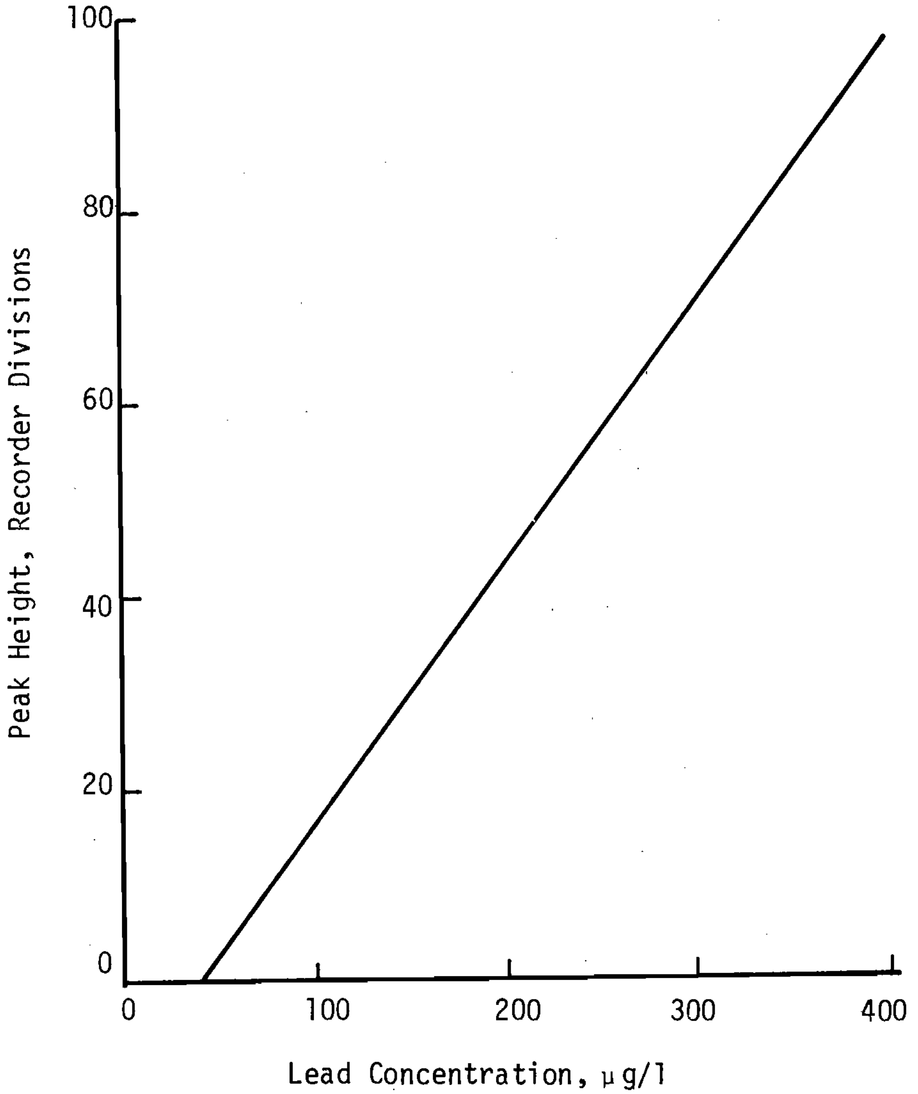


Figure 15. Lead Standard Curve Using MS-63 Carbon Rod

(4) Readings off scale were not repeated upon dilution of the sample.

(5) Where aqueous layers were analyzed, in some cases the lead concentration reported exceeded that originally present.

(6) Where $\Sigma$ was less than original present, loss of lead in carbon rod operation was likely.

Of the 66 vials resealed and sent by mail to The University of Tennessee, 64 were cracked or broken with complete loss of the solutions contained in them. Thus, re-evaluation of the data was not possible.

B. Gas Chromatography: Attempts to gas chromatograph the benzene layers from A above did not yield a peak distinguishable from those of PIV in benzene under conditions reported by Palesh[2]. Evaluation of the chromatographic recordings sent to The University of Tennessee substantiated the student's findings in this regard. Attempts by the student to synthesize $Pb(PIV)_2$ directly from lead metal and 0.1 M PIV in benzene were apparently unsuccessful based upon G.C. analysis. Similar results occurred with direct contact between pure PIV and Pb metal. At this point, the student's involvement in the project terminated and all activities at IIT ceased.

C. $Pb(PIV)_2$ Synthesis Attempt (UT): Outside the formal boundaries of the project support, a re-evaluation of the $Pb(PIV)_2$ synthesis procedure was conducted at The University of Tennessee. The original work of Schweitzer, *et al.*[32] was consulted rather than the procedure used by Palesh[2]. Material and supplies were obtained external to the original project budget and personnel were not funded by the original project. The synthesis procedure, outlined in Table 7, failed to produce a product.

### Table 7. Outline of $Pb(PIV)_2$ Synthesis Procedure

1. Commercial PIV (Pierce Chemical Company, Rockford, Illinois) distilled under vacuum. (Although vacuum maintained at 1.9 mm Hg, liquid boiling temperature at 75° C contrary to literature).
2. Toluene dried 96 hours over $P_4O_{10}$ in desiccator under $N_2$ and distilled from pyrex under $N_2$.
3. 0.1 M PIV solution prepared in purified toluene and 11 grams of atomized lead powder refluxed under $N_2$ for 17 hours.
4. Solution removed and vacuum distilled (1.4-1.8 mm Hg) remove toluene and excess PIV.

Observations - (a) Lead remaining implied low yield
(b) Absence of product upon step of confirmed failure of synthesis.

At this juncture, investigations were terminated because of time and manpower commitments to The University of Tennessee. However, plans have already been made to resurrect the PIV studies via unsponsored research by a graduate student at The University of Tennessee beginning Winter Quarter 1975.

D. Discussion: The failure of a seemingly straight forward extension of previously reported work was, both surprising and disappointing. Rather than question the validity of previous work at this point, the blame more likely resides with some unreported complexity or simple oversight which resulted from the short time scale available to the PIV phase of the project. Continuation of the work as mentioned above will, hopefully, further elucidate the utility of $Pb(PIV)_2$ as a valid analytical method. Looking at the positive side, the negative results obtained to date have demonstrated that the matter is not as straight forward as might have originally been thought.

## V. SIGNIFICANCE OF RESEARCH

The primary significance of this project in light of the improbable succession of difficulties encountered has to be the difficulties themselves. The original premise of the proposed research was (1) the demonstrated behavior of HFAS as both a chelating agent and the successful gas chromatographing of the Nickel, Platinum and Palladium complexes and (2) the commercial availability of HFAS through Pierce Chemical Company. Failure to duplicate published behavior with the HFAS forced a diversion of the project objectives toward investigation of the chelating agent itself. As a result, the product, HFAS, was withdrawn from the commercial market. The end result of these problems has been the stimulation of further investigation into the synthesis, purity and stability of HFAS as an independent effort by a Ph.D. student in the Department of Chemistry at The University of Tennessee (Fred Tungate). If the HFAS is successfully produced, the original objectives of the project will again be pursued and subsequent results will be forwarded to the University of Illinois Water Resources Center as a supplement to this report.

Failure of the alternative objective, the lead-PIV studies, is also significant in as much as it was unexpected. The original intent of pursuing the PIV work was to verify and extend previous work[2,3] conducted at IIT. Verification was not achieved but equally disturbing was the inability to duplicate the more involved synthesis procedure of Schweitzer, et al.[32] for lead $(PIV)_2$. As with the HFAS work, the negative results are not considered conclusive. Rather, they have stimulated a redefinition of the experimental approach in further studies to be conducted at The University of Tennessee.

# REFERENCES

1. E. Bayer, H. P. Muller and R. E. Sievers, Anal. Chem. 43, 2012, 1971.
2. C. Palesh, M.S. Thesis, Illinois Institute of Technology, Chicago, Illinois, 1973.
3. R. A. Minear and C. M. Palesh, "The Application of Gas Chromatography of Volatile Metal Chelates to Water Analysis," in Chemistry of Water Supply, Treatment and Distribution (A. S. Rubin, Ed.), Ann Arbor Science Publishers, 1974.
4. R. W. Moshier and R. E. Sievers, Gas Chromatography of Metal Chelates, Pergamon, 1965.
5. R. D. Hill and H. Gesser, J. Gas Chrom. 1, 11 (October, 1963).
6. W. D. Ross, L. C. Hansen, W.G. Scribner, ARLP-710285 Wright-Patterson Air Force Base.
7. W. D. Ross and R. E. Sievers, Talanta, 15, 87, 1968.
8. M. L. Taylor and E. L. Arnold, Anal. Chem. 43, 1328, 1971.
9. K. S. Eisentrrant, D. G. Griest and R. E. Sievers, Anal. Chem. 43, 2003, 1971.
10. W. R. Wolf, M. L. Taylor, B. H. Hughes, T. O. Tiernan and R. E. Sievers, Anal. Chem. 44, 616, 1972.
11. M. H. Noweir and J. Cholak, Env. Sci. Technol. 3, 927, 1969.
12. W. P. Ross and R. E. Sievers, Env. Sci. Technol. 6, 155, 1972.
13. J. K. Foreman, T.A. Gough and E. A. Walker, Analyst 95, 979, 1970.
14. L. C. Hansen, W. G. Scribner, T. W. Gilbert and R. E. Sievers, Anal. Chem. 43, 349, 1971.
15. S. Savory, P. Mushak, R. W. Sunderman, Jr., R. H. Ested and N. O. Roszel, Anal. Chem. 42, 294, 1970.
16. G. H. Booth, Jr. and W. J. Darby, Anal. Chem. 43, 831 , 1971.
17. R. W. Moshier and J. E. Schwarberg, Talanta 13, 445, 1966.
18. G. Guiochon and C. Pommier, Gas Chromatography in Inorganics and Organometallics, Ann Arbor Science Publishers, 1973.

19. R. Belcher, J. R. Majer, R. Perry and W. I. Stephan, Anal. Chim. Acta <u>45</u>, 305, 1969.

20. J. E. Schwarberg, R. E. Sievers and R. W. Moshier, Anal. Chem. <u>42</u>, 1878, 1970.

21. H. Koshimura and T. Okubo, Anal. Chim. Acta, <u>49</u>, 67, 1970.

22. B. G. Shultz and E. M. Larsen, JACS <u>72</u>, 1949.

23. C. A. Burgett, "Gas Chromatographic Studies of Mixed-Ligand Complexes of Transition and Related Metals," Paper No. 87, Presented at the 24th Pittsburg Conference, March 6, 1973.

24. J. W. Mitchell and C. V. Banks, Anal. Chim. Acta, <u>57</u>, 415, 1971.

25. P. C. Uden, D. E. Henderson and A. Kamalizad, J. Chromatogr. Sci., <u>12</u>, 591, 1974.

26. G. P. Morie and T. R. Sweet, Anal. Chem. <u>37</u>, 1552, 1965.

27. W. D. Ross, R. E. Sievers and C. Wheeler, Jr., Anal. Chem. <u>37</u>, 598, 1965.

28. R. K. Y. Ho, S. E. Livingstone and T. N. Lockyer, Aust. J. Chem., <u>19</u>, 1179, 1966.

29. S. H. H. Chaston, S. E. Livingstone and T. N. Lockyer, Aust. J. Chem., <u>19</u>, 1401, 1966.

30. S. H. H. Chaston and S. E. Livingstone, Aust. J. Chem., <u>19</u>, 2035, 1966.

31. C. G. Barraclough, R. L. Martin and I. M. Stewart, Aust. J. Chem., <u>22</u>, 891, 1969.

32. G. K. Schweitzer, P. B. Pullen and Y-H. Fang, Anal. Chim. Acta, <u>43</u>, 334, 1968.