THE EFFECT OF pH ON THE EXTRACTION OF MICROGRAM LEVELS OF HAFNIUM AS THE NITROSOPHENYLHYDROXYLAMINE COMPLEX WITH VARIOUS NON-AQUEOUS SOLVENTS

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ABSTRACT

THE EFFECT OF pH ON THE EXTRACTION OF MICROGRAM LEVELS OF HAFNIUM AS THE NITROSOPHENYLHYDROXYLAMINE COMPLEX WITH VARIOUS NON-AQUEOUS SOLVENTS

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The separation and determination of microgram levels of hafnium has historically been a cumbersome, difficult procedure. The nitrosophenylhydroxylamine (cupferron) complex of hafnium can be extracted from an aqueous solution with an immiscible non-aqueous solvent. The pH at which the extraction occurs and the solvent used are both contributing factors which determine the percent of hafnium cupferrate extracted from the aqueous phase. In this study, the hafnium remaining in the aqueous phase, following an organic decomposition, is determined by x-ray fluorescence following precipitation and filtration of hafnium cupferrate on a membrane filter. Other methods of hafnium detection were found to be unsuitable for this application. Graphite furnace atomic absorption was inadequate due to insufficient hafnium atomization, residual hafnium in the graphite tube, and high detection limits. Those factors lead to poor reproducibility of the standard curve. Another x-ray fluorescence technique in which hafnium was collected on a graphite slurry, mixed with bakelite, and pressed into a wafer for x-ray fluorescence determination, proved to be inferior to the membrane filtration technique because of lower total counts of hafnium for the same levels of hafnium and difficulties in reproducing data. The extraction curves of pH versus percent extraction of hafnium cupferrate depend on the hafnium cupferrate equilibria and their relationship with the various characteristics of the solvents over the pH range being researched. The extraction curves obtained exhibited two areas of high extractability in highly acidic solutions and slightly alkaline solutions. The curves also contained two areas of lower extractabilit in weakly acidic solutions and strongly alkaline solutions. Characteristics of the solvents studied that were found to exert major influences on the extraction of the hafnium cupferrate complex include polarity, the dielectric constant, and functional groups present. The use of chloroform as the extraction solvent with an aqueous-phase pH of less than 1.0, provides the most selective, quantitative extraction of hafnium. Depending on the particular application, this proper combination of pH and solvent can provide the desired conditions for either analysis, or removal of hafnium in the organic extract or the aqueous portion after the extraction.

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CHAPTER I

INTRODUCTION

In recent years the use of some formerly relatively unimportant transition elements has increased due to advances in technology, undependable sources of mineral supplies, and numerous other minor reasons. One example of this is in the manufacturing of turbine blades for use in jet aircraft engines. Recently, the need for improved fuel efficiency and quieter engines has required turbine blades to be made of stronger alloys. This has increased the use and importance of certain metals in these alloys, which formerly were of minimal concern. Analytical methods, as well as basic analyical data, are need for these trace metals in a variety of matrices. For example, the determination of less than 50 ppm of hafnium in certain nickel-base superalloys is presently one such analytical problem. The primary intent of this study is the development of an analytical method for the determination of microgram levels of hafnium. The determination of hafnium will occur after the extraction of hafnium cupferrate with a suitable solvent. The effectiveness of the extraction is dependent on the relationship of certain characteristics of the solvent, such as polarity and functional groups present, with the equilibrium of hafnium cupferrate as related to pH. After data have been obtained, it will be used for developing an appropriate model for predicting future applications of hafnium cupferrate extractions depending on the type of solvent and the pH of the solution. Eventually, this technique could be applied towards the determination of low levels of hafnium in some of the new nickel base superalloys.

History of Cupferron Extractions

The nitrosophenylhydroxylamine complex, commonly called cupferron, has long been widely used as an organic precipitating agent for a number of metals.[1-4] It has been shown that metals which precipitate in relatively acidic solutions can be separated, through extraction, from those metals which are precipitated in comparatively less acidic mediums.[5] For this reason, a number of extremely useful separations can be made by extractions of the metal cupferrates which would require otherwise lengthy and tedious manipulations before separations could be achieved. Although work has appeared on metal cupferrate solubilities since early in this century, practical studies did not appear until the 1940's, when such work was spurred on by the need for relatively simpler separation techniques during atomic energy studies of that time. Much of the early work used chloroform as the primary organic extraction solvent, although numerous other solvents, including a variety of ethers, benzene, 4-methyl-2-pentanone, and isoamyl alcohol as the most popular alternatives, had been used with a great deal of success, depending on the particular application.[6-8] One of the first complete works on metal cupferrate extractions was by Furman et. al.[9] who developed some of the relationships between pH and effectiveness of extraction for a number of metals. Later studies by Stary[10] and Fritz[11] have researched the effect of pH further, using it as a means to control the extraction and separation of most of the common elements.

Historically, the use of cupferron as a precipitating agent for hafnium has been used as a means of gravimetric analysis with great success.[12] However, studies dealing with the extractability of the hafnium cupferrate complex have been quite limited. Ruzicka[13] mentions extraction of the complex with chloroform as a means of eliminating hafnium as an interference before a determination of indium. Elwell[14] uses the chloroform extraction of hafnium cupferrate as a means of eliminating hafnium as the matrix when analyses of certain trace metal contaminations in hafnium ores are being sought. The lack of available data dealing with hafnium cupferrate extractions can be attributed, to a large respect, to the close chemical behavior of hafnium and zirconium. Hence, some analysts have incorrectly used certain data interchangeably. Although some techniques, which may be employed for hafnium as well as zirconium, will be referred to, only the extraction of hafnium cupferrate will be dealt with in this study.

Cupferron Extraction Methodology Limitations

Hafnium Detection

As is the case in any multi-step analytical procedure, the final results are only as good as is the least accurate step in the entire method. Therefore, paramount to beginning research dealing with the detection of a species, it becomes a primary necessity to develop a method of detection which will provide the greatest possible accuracy. This is very critical in avoiding confusion over the statistical errancy of such a detection method, and the final changes in data as a result of the controlled variables. Often the analyst is limited by the resources available particularly in the area of instrumental analysis. Hence, in this study, the method of hafnium determination would likewise be limited by the same general parameters discussed above. It was decided that the method of hafnium detection for this study would need to have as low of a detection limit as possible to determine when extraction techniques had, in fact, removed all traces of hafnium. With the resources available for this study, the best sensitivities for hafnium detection would be achieved through atomic absorption or x-ray fluorescence, the final selection coming after obtaining the appropriate analytical data.

Analytical Approach

In order to study the effect of pH on the extraction of hafnium cupferrate, there was a need for an accurate method of hafnium determination. The accuracy and reliability of the method of detection would limit or enhance any such study, and therefore, the selection of an appropriate method would be of extreme importance, as mentioned earlier. The ideal method should be relatively rapid to perform, free of matrix and chemical interferences, and one for which standards could be easily prepared or obtained. In order to make the method applicable to some of the situations discussed earlier, the sensitivity of the method should be accurate at microgram levels. The two analytical methods, which are available and fulfilled these requirements, are atomic absorption spectrophotometry and x-ray fluorescence spectrometry. Other instrumental methods such as visible spectrophotometry and wet chemical methods were disregarded on the basis of being prone to chemical interferences.[15] After determining the accuracy, sensitivity, and limits of detection for different techniques using the two detection methods, the appropriate method will be selected.

The optmization of an extraction procedure will require the control of several variables. Until actually performing the extraction procedure, the effect of the variables will not be entirely known. The basic approach will be to initially prepare a standard hafnium solution, and from this solution, spike known amounts into other solutions of equal volumes, but varying pH values. Then, after adding known amounts of solvent and cupferron, an attempt will be made to extract the hafnium cupferrate complex into the organic phase. The amount of hafnium cupferrate extracted will be determined from either the aqueous or non-aqueous portion, depending on the method of detection selected. An extraction curve plotting pH versus percentage extraction of hafnium cupferrate will then be prepared. This general procedure will be employed for other solvents representative of certain types of solvents until sufficient extraction data are obtained.

CHAPTER II

SELECTION OF METHOD FOR HAFNIUM DETERMINATION

Available Methods

Before discussing the rationale used in selecting the methods of hafnium determination and the conditions for the extraction, a brief descriptive look at the analytical methods available for hafnium determination should provide a basic background of fundamentals involved in the analytical procedure of this element, with respect to the applications involved in this study. Generally speaking, hafnium is chemically similar to zirconium. This relationship has both hindered and enhanced the research involving hafnium. Because the chemical properties are so similar, the difficulty in obtaining either element in its pure form places an initial restriction on any study involving either element. However, because of the similar properties, research for either one of the two elements is usually applicable, to some degree, to the other element. Therefore, as a preliminary screening technique, only methods and techniques which have been used with some success for analyzing zirconium, will be considered as viable methods for hafnium determination.

Flame Atomic Absorption

Although flame atomic absorption has been routinely used to determine relatively volatile metals, some refractory metals can also be determined without great difficulties.

TABLE 1

MELTING AND BOILING POINTS OF ZIRCONIUM AND HAFNIUM COMPOUNDS[a]

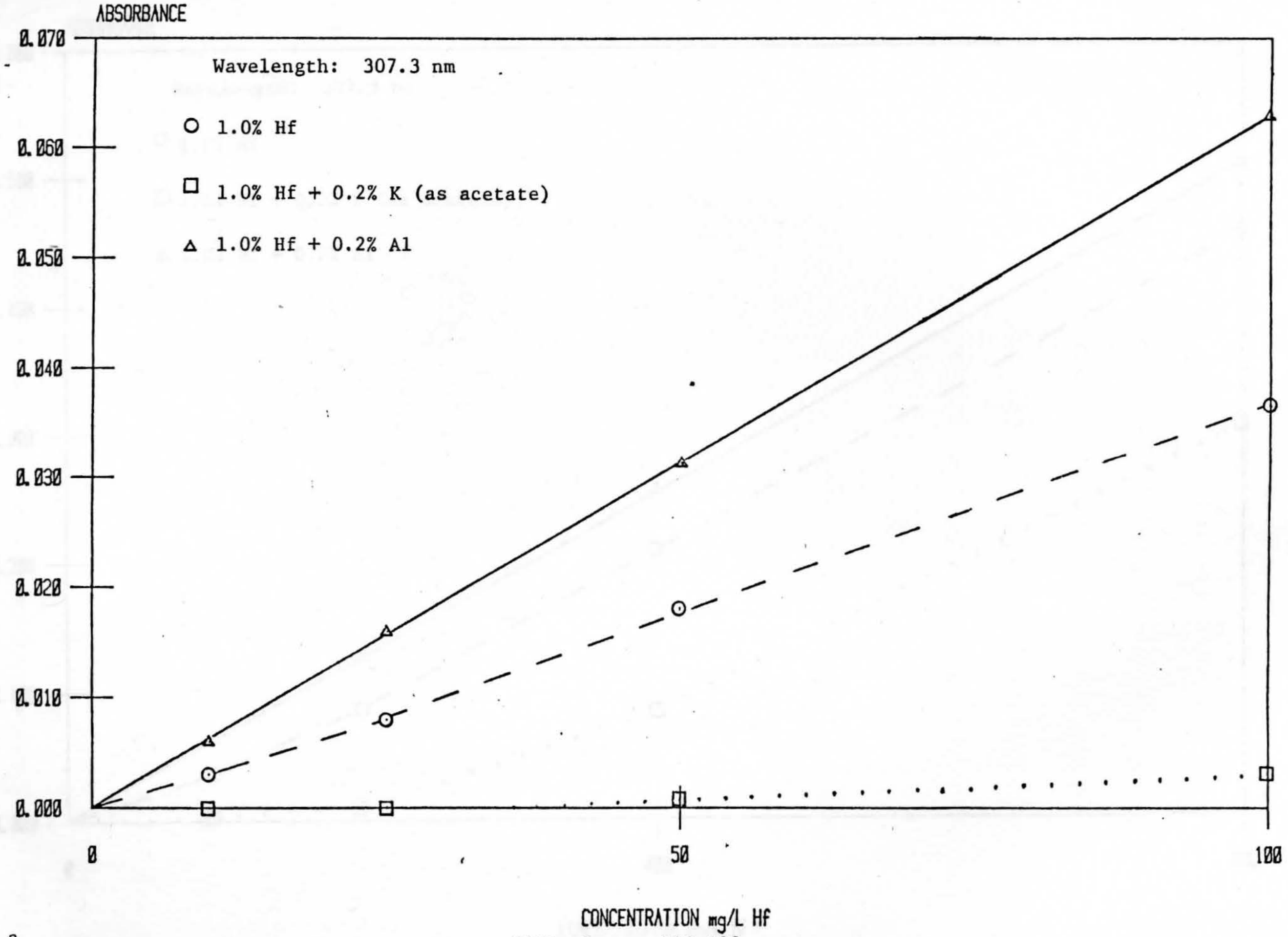
Name	Symbol	Melting Point, °C	Boiling Point, °C
Zirconium	Zr	1852 ±2	3580
Hafnium	Hf	2222	5400
Carbide	HfC	3887[b]	--
Oxide	HfO_2	2810[b]	--

[a] Anil K. Mukherji, Analytical Chemistry of Zirconium and Hafnium, Pergamon Press, New York, 1970, p. xi.

[b] Charles D. Hodgman, Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland, 1956, p. 524.

From the data in Table 1, it is evident that all of the common compounds of hafnium are extremely refractory materials. This will seriously hinder attempts to vaporize hafnium, and limit the use of atomic absorption measuring techniques. However, flame atomic absorption analysis of hafnium had been used with moderate success through the use of hydrofluoric acid, ionization suppressants, and aluminum as solution matrix modifiers as reported by Wallace.[16-18] Additional studies of flame atomic absorption and fluorescence analysis of zirconium show limited promise of analytical applications.[19-22] The low absorbance values, as shown in Figures 1 and 2, even after considerable matrix modification, do not seem to approach the necessary levels required for this study. In order to analyze 50 micrograms of hafnium by this method, it would need to be concentrated to 1.0 mL to achieve the 50-ppm concentration range. This

FIGURE 1



ABSORBANCE VS. CONCENTRATION

FOR 10-100 mg/L HAFNIUM[a]

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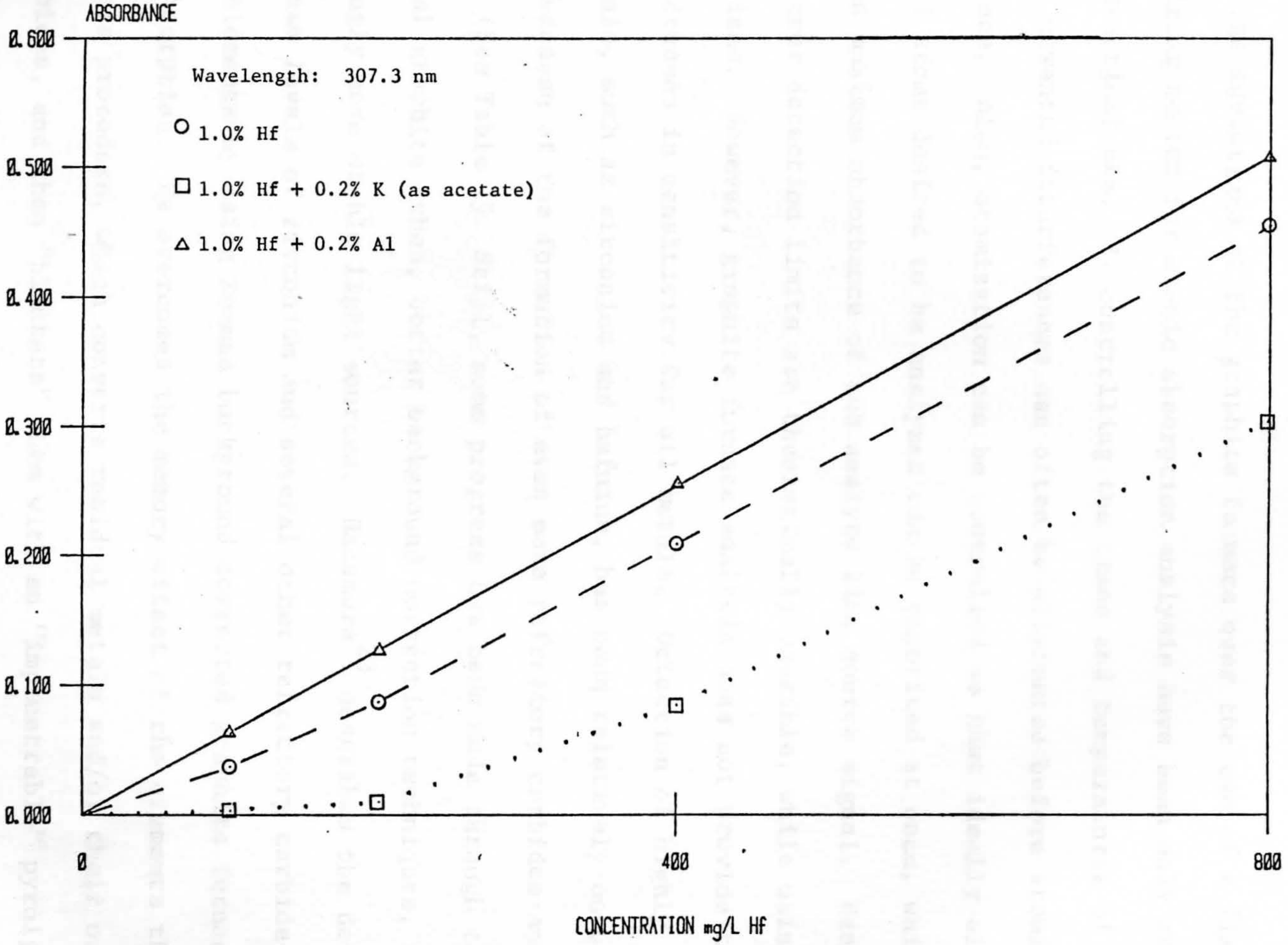
[a] G.F. Wallace, et al., Atomic Spectroscopy, 1981, 2, pp. 130-132.

FIGURE 2

ABSORBANCE VS. CONCENTRATION

FOR 100-800 mg/L HAFNIUM[a]



[a]G.F. Wallace, et al., Atomic Spectroscopy, 1981, 2, pp. 130-132.

small volume would not be practical for flame atomic absorption analysis. Hence, flame atomic absorption would be considered only as a last alternative for this application.

Graphite Furnace Atomic Absorption

The advantages of the graphite furnace over the use of a flame as a vaporizing medium for atomic absorption analysis have been only recently put to practical use. By controlling the times and temperatures of the furnace, unwanted interferences can often be eliminated before atomization takes place. Also, atomization can be controlled so that ideally all of the metal atoms desired to be analyzed can be vaporized at once, which will result in maximum absorbance of the analyte line source signal. Hence, much greater detection limits are theoretically possible, while using micro sample sizes. However, graphite furnace analysis does not provide the large increases in sensitivity for all metals. Detection of highly refractory metals, such as zirconium and hafnium, has been relatively unsuccessful because of the formation of even more refractory carbides and oxides. (See Table 1) Still, some progress has been made through the use of special graphite tubes, better background correction techniques, and increasingly more stable light sources. Hanamura[23] describes the determination of nanogram levels of zirconium and several other refractory carbide-forming elements by using Zeeman background corrected graphite furnace atomic absorption. He overcomes the memory effect of the elements through a pyrolysis procedure, which converts residual metals and/or their oxides into carbides, and then "blankets" them with an "impenetrable" pyrolyzed graphite layer. The memory effect is due to residual metals which remained after atomization, and were present in the graphite furnace prior to the next determination. Therefore, even if a blank were to be run next, the determination would "remember" the residual metals left behind on the previous run, and show that some metal had been detected, when actually the signal would be due to the memory effect. A summary of some of Hanamura's data is presented in Table 2.

After the first determination of zirconium, at least six subsequent analyses were necessary to eliminate the memory effect. However, after the second determination of zirconium, determination 9, pyrolysis treatments after that determination eliminated the memory effect after one additional treatment. Presumably, a similar treatment could be used and applied toward the determination of hafnium by graphite furnace atomic absorption.

TABLE 2

EFFECT OF PYROLYSIS PROCESSING

Determination	Absorption Peak of	Relative Sensitivities
1	127ng Zr	42.0
2	Memory Effect	23.5
3	Memory Effect	19.0
4	Memory Effect	15.5
5	Memory Effect	12.0
6	Memory Effect	13.0
7	Memory Effect	12.0
8	Pyrolysis Processing	5.0
9	127ng Zr	41.0
10	Pyrolysis Processing	12.0
11	Pyrolysis Processing	5.0
12	Blank	12.0
13	Blank	12.0

The memory effect for hafnium was eliminated by this technique in this study as seen in Figure 4 on page 18.

X-ray Fluorescence

As mentioned earlier, because of the close chemical behavior of zirconium and hafnium, analysis of either element in the presence of the other is usually difficult. The use of XRF (x-ray Fluorescence), however, is one method of detection which can be used with a great deal of success, in the simultaneous determination of hafnium and zirconium. In fact, hafnium was first discovered by Coster and Hevesey by its x-ray L spectrum during x-ray analyses of zirconium.[24] In the XRF technique, a sample is exposed to x-rays, elements will absorb some of the primary radiation and will give off secondary or fluorescent radiation. The amount of fluorescent radiation emitted by an element at a specific spectral line, absent of or corrected for interferences, is proportional to the amount of that element present in the sample. Because of the relatively few number of spectral lines produced by each element, interferences and overlapping lines are minimal. To a certain extent, analysis is not dependent on the molecular form of the analyte either. Other advantages of this non-destructive measuring technique include, low detection limits, ease of analysis, and the fact that the sample can be analyzed in a variety of physical forms, i.e. solutions, powders, raw metals, etc. Because of these advantages, the XRF technique appears to be the best technique for hafnium determination of the various techniques mentioned earlier.

Experimental

Graphite Furnace Atomic Absorption

Preparation of Standards

A 1000-ppm hafnium stock solution was prepared by carefully dissolving 0.10000 g of spectrographically pure hafnium in 10 mL hydrofluoric acid and digesting in a Teflon beaker to a low volume, then cooling the solution. After the addition of 10 mL distilled water, the solution was brought to boiling again and cooled. To make the final solution, 5 mL of nitric acid were added, and the solution diluted to 100 mL. The final concentration of this solution may also be expressed as 1000 micrograms hafnium/mL.

Working standards of 50, 10, and 5 ppm were prepared by micropipetting 1 mL, 0.2 mL, and 0.1 mL, respectively, of the stock solution into 10 mL distilled H_2O plus 1 mL each of concentrated hydrofluoric and nitric aicds, and each diluted to 20 mL. A 1.0-ppm solution was prepared in the above manner by micropipetting 0.5 mL of the 50-ppm solution into the appropriate solution and diluting to 25 mL.

Development and Optimization of Standard Instrumental Parameters

The initial instrumental conditions and settings were basically general conditions used as starting points for other refractory metals when developing a method of detection by graphite furnace atomic absorption. These initial settings are listed in Table 3.

TABLE 3

INITIAL CONDITIONS FOR HAFNIUM ANALYSIS BY GRAPHITE FURNACE ATOMIC ABSORPTION

Lamp	Hafnium hollow cathode
Lamp current	30 mA
Wavelength	307.3 nm
Argon pressure	45 psi
Argon flow scale	50 units
Argon interrupt	on
Measuring Mode	Concentration
Chart speed	10 mm/min.
Chart mode	automatic
Sample volume	20 microliters
Scale expansion	4.0
Drying cycle	
total time	60 seconds
ramp time	30 seconds
temperature	105°C
Charring cycle	
total time	50 seconds
ramp time	25 seconds
temperature	500°C
Atomize cycle	
total time	8 seconds
ramp time	--
temperature	2500°C
Automatic high temp. burnout	on
Deuterium background correction	on
Graphite tube	standard

Attempts to produce a standard curve using these conditions were not very promising. Pipetting 20 microliters of the working standard solutions, 1.0-ppm through 50-ppm, did not result in any peak production on the strip chart recorder. However, 1000-ppm solutions would occasionally yield reproducible peaks, but conversely, so would a reagent blank for several analysis afterwards. When the atomization temperature was increased from 2500°C to 2700°C, lower peaks were obtained for both blanks and 1000-ppm solutions. After several burns to eliminate residual hafnium, the atomization temperature was changed back to the initial setting and the scale expansion increased from 4.0 to 10.0. Although small inconsistent peaks for 50-ppm standards could now be detected, memory effects and erratic blanks were still present and appeared to be the major barriers in achieving a satisfactory method.

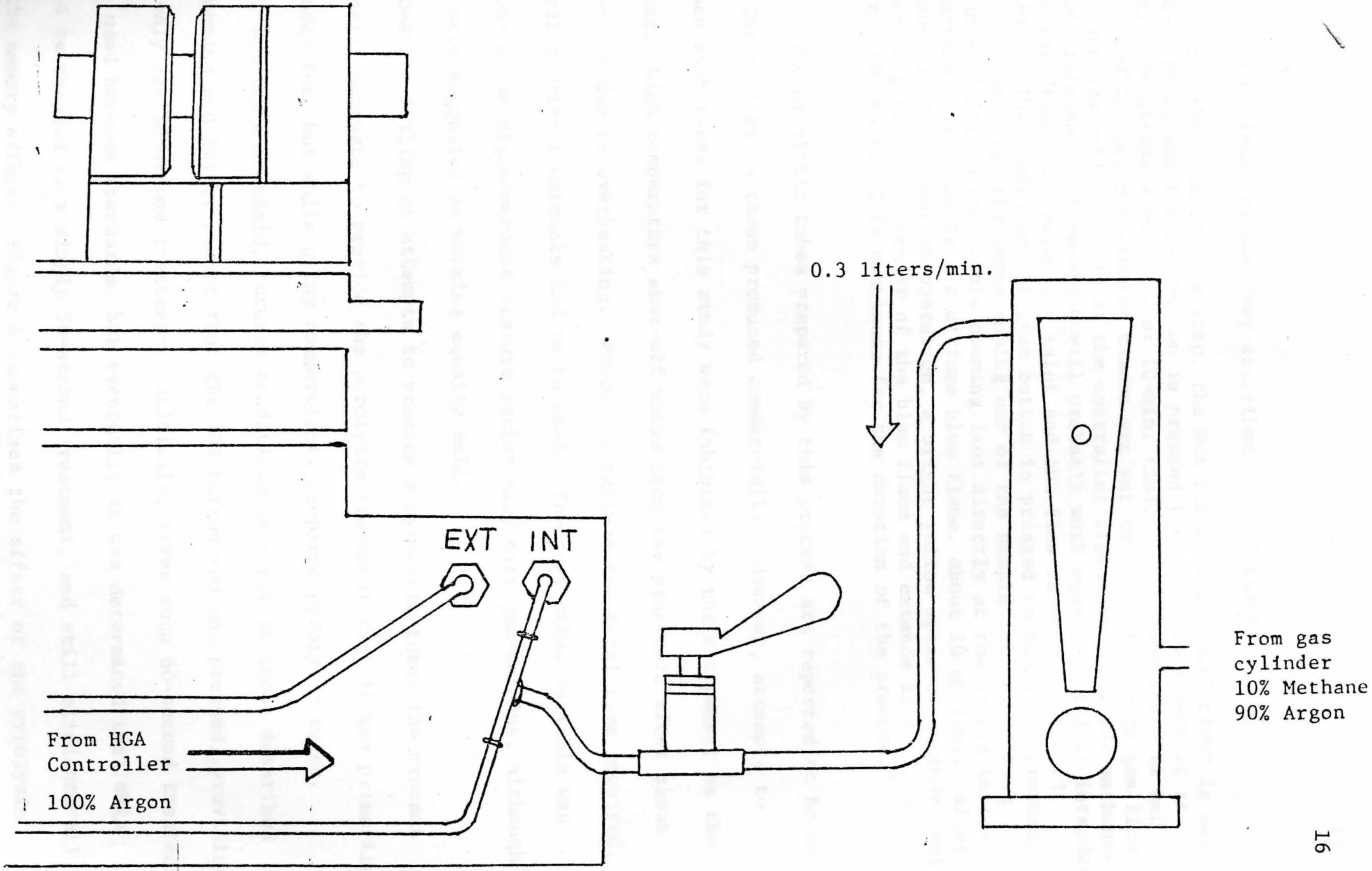
By changing to a commercially prepared pyrolytic graphite tube, increasing atomization time from 8 to 9 seconds, and also increasing the atomization temperature to 2750°C, as high as permitted by the hardware, 10-ppm could be detected occasionally and peak heights increased 2 to 4 times for a 50-ppm standard. Because of the greater sensitivity, the memory effect appears to be even more of a problem. Actually, the full severity of the problem could probably not have been realized at the less sensitive conditions used initially. Because of this, attempts to determine the reproducibility of the peaks were hindered.

Pyrolytic Treatment

In an attempt to alleviate the problems associated with the memory effect, due to insufficient hafnium atomization, a system for providing a pyrolysis treatment, as suggested by Hanamura[23], was developed. The actual hardware for the treatment was set up as suggested by Manning and Ediger[25] as they described a treatment for preparing pyrolytic graphite tubes for use in a graphite furnace, as seen in Figure 3.

FIGURE 3

HARDWARE SET-UP FOR PYROLYSIS TREATMENT OF GRAPHITE TUBES



The optimum process they described is as follows:

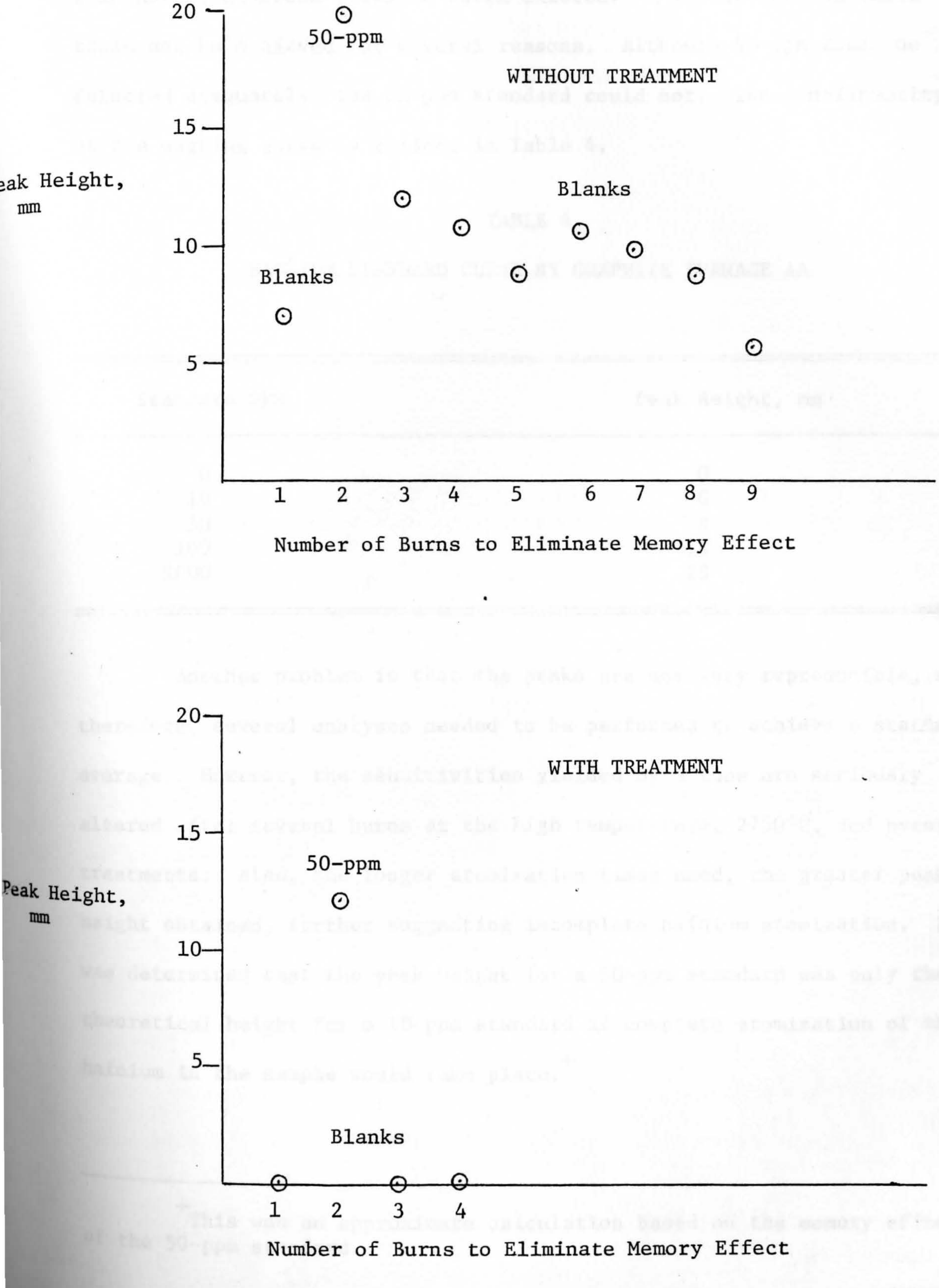
> "For the conditioning step, the HGA controller "char" timer is set to 60 sec., and the 10X button is pressed (button lights when it is on) thus giving a 600 sec. or 10-min. time. Char temperature is set to 2200°C. Dry and atomize timers are set to minimum. Purge gas flow is set nominally to "20" on the controller flowmeter. The 10% methane-90% nitrogen (methane-argon will probably work equally well) is introduced to the "internal" purge gas inlet and the flow is adjusted to 0.3 l/min. The controller program button is pressed to begin the process. If one observes the gases coming out of the sample tube by looking tangentially to the sample opening (not directly at the sample introduction port), one sees a diffuse blue flame, about 10 mm long. After about 15 to 30 sec. of operation, a bright yellow spear of incandescent carbon pierces the center of the blue flame and extends 15 to 25 mm from the hole. This continues for the duration of the process."

The pyrolytic tubes prepared by this process are reported to be of superior quality to those produced commercially. However, attempts to produce such tubes for this study were inhibited by the equipment, as the automatic high temperature shut-off would stop the procedure after about 50 seconds due to overheating. Hence, to achieve the total time required, several shorter treatments had to be used. The only other variable was the use of an argon-methane mixture rather than nitrogen-methane, although both were suggested as working equally well.

Despite failing at attempts to produce a pyrolytic tube, the process was still adequate to provide the pyrolysis treatment that it was primarily intended for, but while using commercially prepared pyrolytic tubes. After running a standard, furnace conditions were set to those described by Manning and Ediger except that the 10X button was not pressed, providing for only one 50-second treatment. Initially, three such 60-second treatments were used between standards, but eventually it was determined that this could be reduced to a single 50-second treatment, and still eliminate all of the memory effect. Figure 4 summarizes the effect of the pyrolysis

FIGURE 4

EFFECT OF PYROLYSIS TREATMENT



treatment. Despite the fact that the memory effect could be entirely eliminated, numerous problems still existed. A linear working curve could not be achieved for several reasons. Although 50-ppm could be detected adequately, the 10-ppm standard could not. The non-linearity of the working curve is evident in Table 4.

TABLE 4

HAFNIUM STANDARD CURVE BY GRAPHITE FURNACE AA

Standard PPM	Peak Height, mm
0	0
10	0
50	8
100	14
1000	29

Another problem is that the peaks are not very reproducible, and therefore, several analyses needed to be performed to achieve a statistical average. However, the sensitivities yielded by a tube are seriously altered after several burns at the high temperature, 2750°C, and pyrolytic treatments. Also, the longer atomization times used, the greater peak height obtained, further suggesting imcomplete hafnium atomization. It was determined that the peak height for a 50-ppm standard was only the theoretical height for a 10-ppm standard if complete atomization of the hafnium in the sample would take place.[+]

[+] This was an approximate calculation based on the memory effect of the 50-ppm standard.

Limitations

The memory effect due to the incomplete removal of hafnium during atomization is the basis of the primary problems with this technique. Because of the high temperatures and relatively long atomization times required to atomize adequate amounts of hafnium for sufficient peak formation, the life of the graphite tube is severly shortened. Also, the pyrolysis treatment required to eliminate the memory effect has the same effect of shortening the useful life of the tube. Hence, the tubes would constantly have to be changed to produce adequate sensitivities, but because of the irreproducibility of the peaks, standard curves could not be obtained before another tube change would be required. Although further modifications of the method could be made to reduce the associated problems, it was decided to look at XRF as an alternate means of hafnium detection for this application, before developing the graphite furnace technique any further.

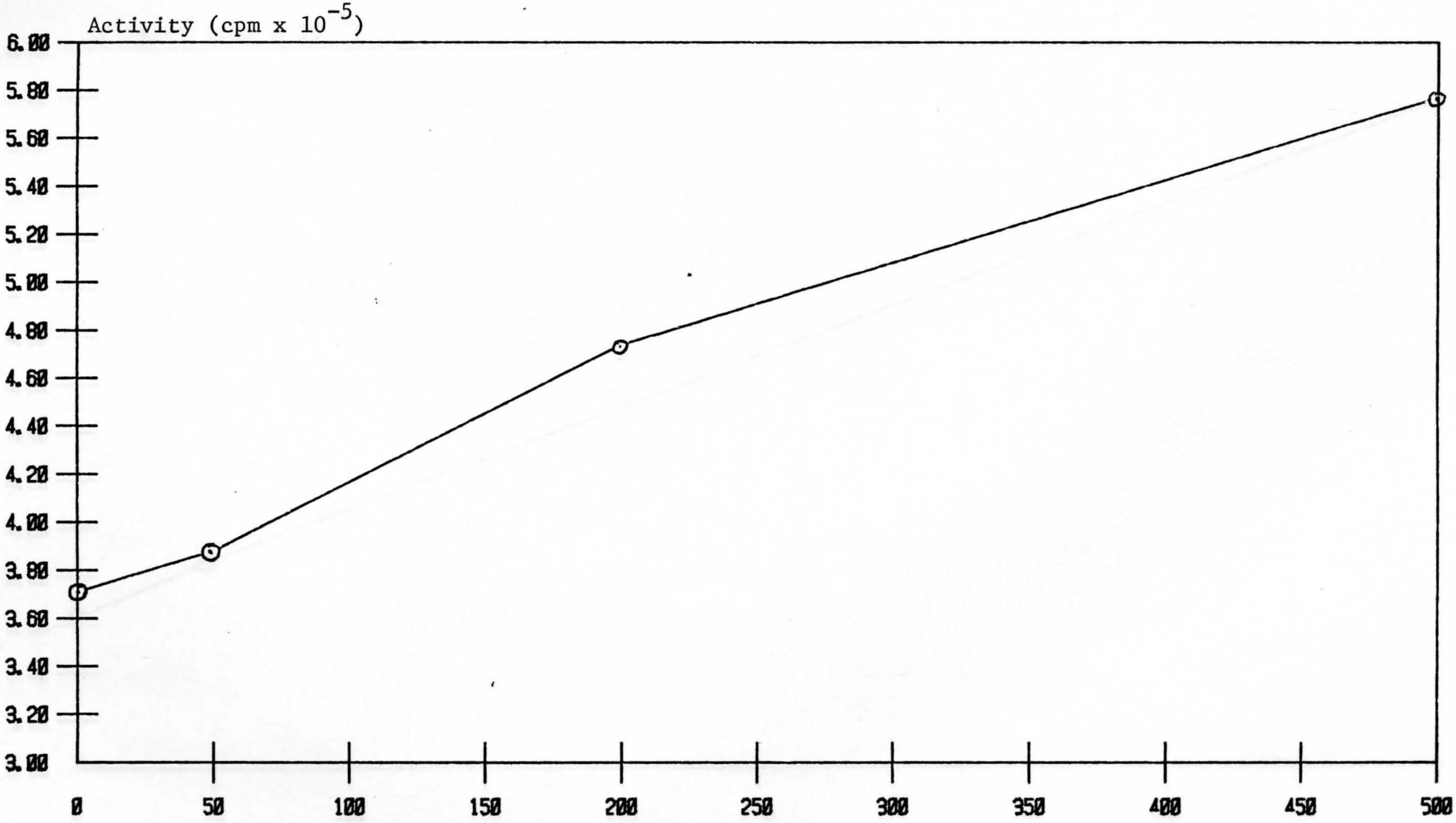
X-ray Fluorescence

Graphite and Bakelite Wafer Technique

The general approach used in this method was to spike known amounts of hafnium into a slurry of graphite, dry the slurry, remove it and mix it with Bakelite, and finally press the mixture into a wafer for use in the XRF determination. The results of the initial curve are given in Figure 5. The XRF technique yielded a much more linear curve than the graphite furnace atomic absorption technique, although the fact that the entire sample would be needed for the determination is somewhat of a disadvantage.

FIGURE 5

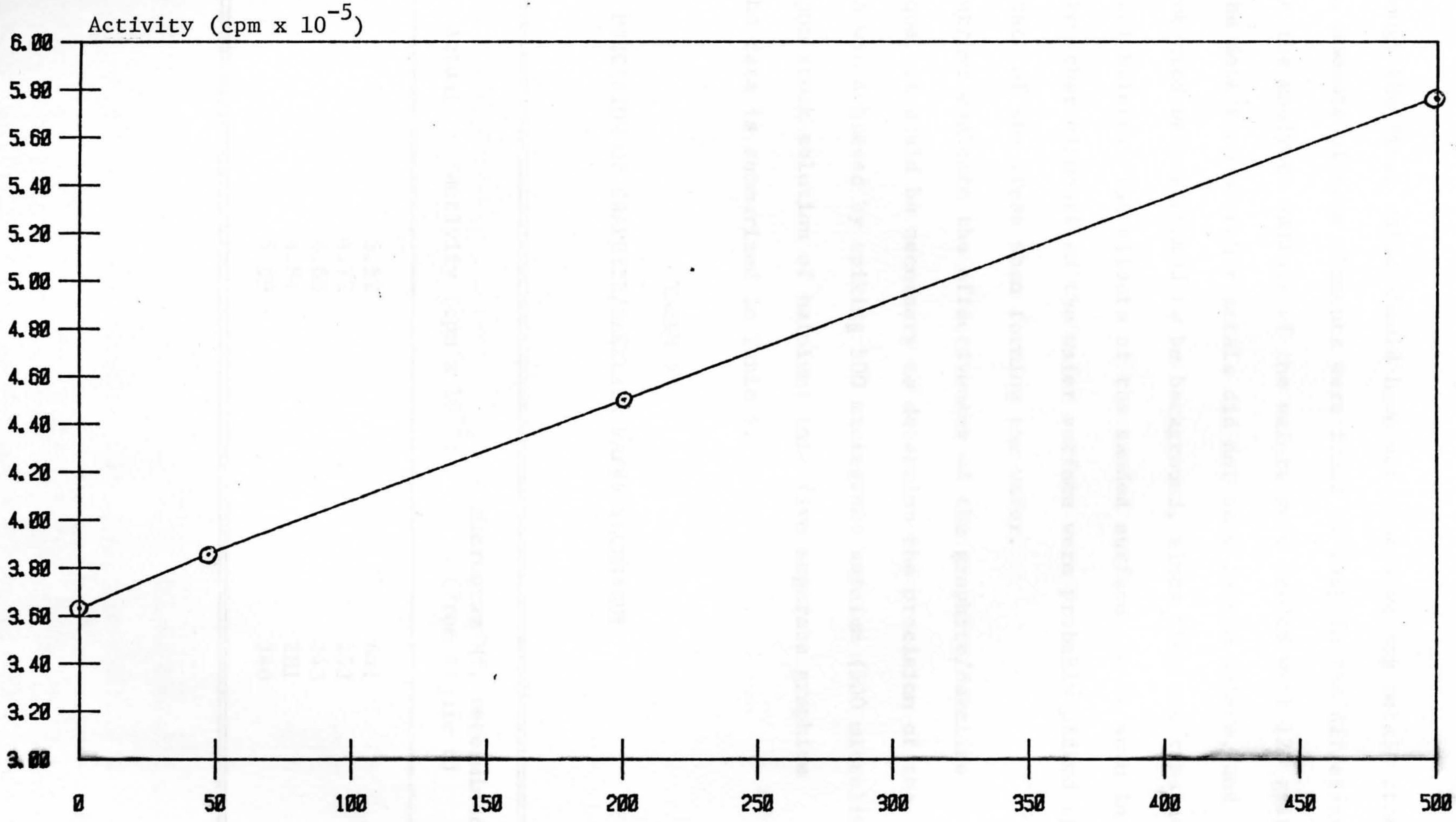
TOTAL COUNTS VS. 0-500 MICROGRAM HAFNIUM



Hafnium, Micrograms

FIGURE 6

TOTAL COUNTS VS. 0-500 MICROGRAM HAFNIUM AFTER SANDING



Hafnium, Microgram

Although the final wafer should have not contained any metals other than hafnium, amounts of some elements were found to vary in the different wafers. When the analyzed surface of the wafers were sanded with 120 grit sandpaper, the detection of other metals did not vary in the wafers, and any counts detected were presumed to be background, since they now remained constant in all wafers. The effects of the sanded surface can be seen in Figure 6. The other elements on the wafer surface were probably picked up from the surface of the press when forming the wafer.

To further evaluate the effectiveness of the graphite/Bakelite wafer technique, it would be necessary to determine the precision of the method. This was achieved by spiking 500 micrograms hafnium (500 microliters of the 1000-ppm stock solution of hafnium) into five separate graphite slurries. The data is summarized in Table 5.

TABLE 5

PRECISION OF GRAPHITE/BAKELITE WAFER TECHNIQUE

Microgram Hf, Actual	Activity (cpm x 10^{-5})	Microgram Hf, Determined (From Figure 6)
500	5.52	441
500	4.72	253
500	4.68	243
500	4.84	281
500	5.09	340

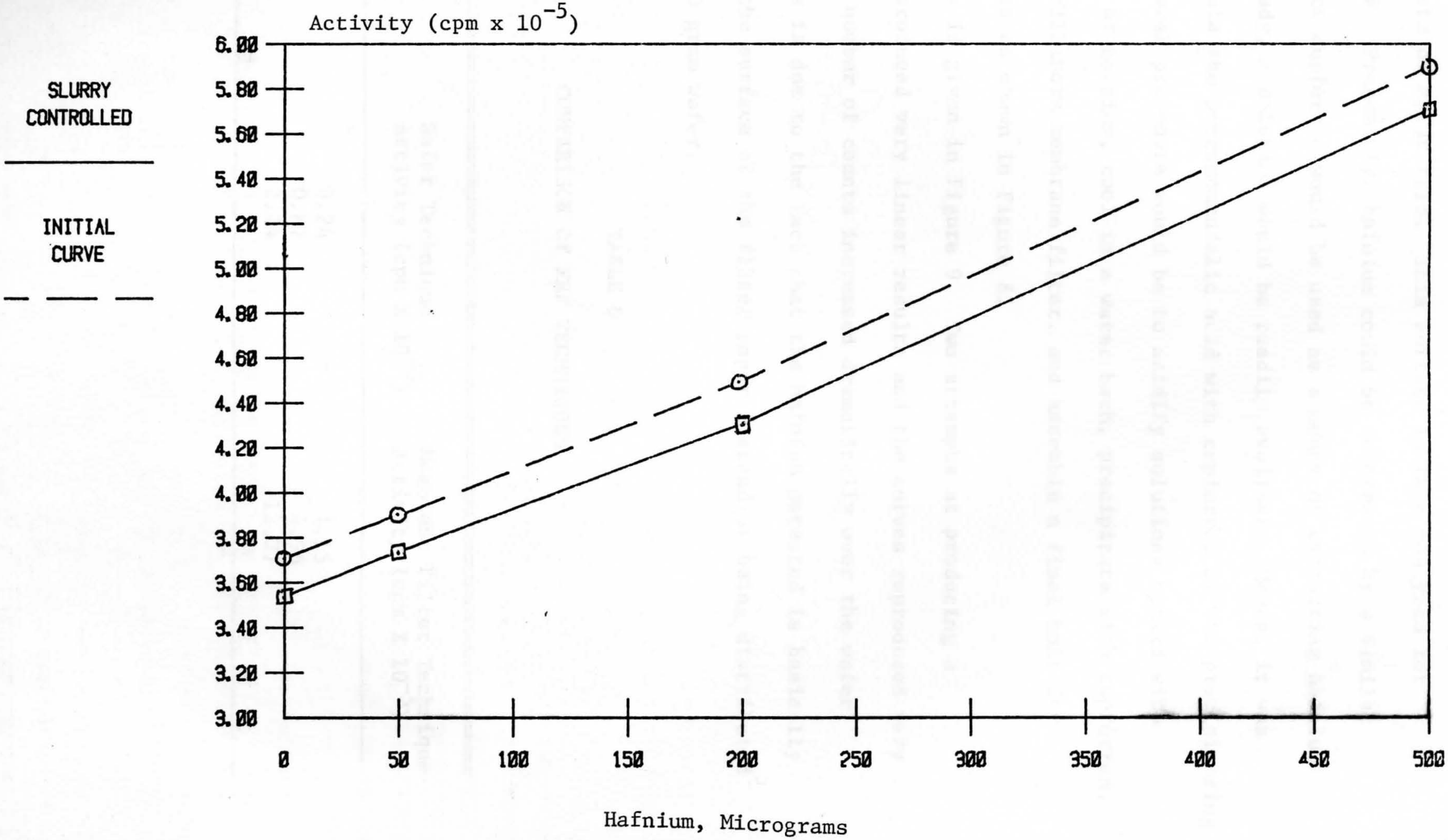
From this data, it was obvious that either the standard curve was incorrect, or that the method was inherently not very reproducible. It could be assumed that because of the high linearity of the curve in Figure 6, that this was not the problem, and that something must have been done slightly different in the procedure to produce the erratic results in Table 5. One possibility was that the amount of water used to create the graphite slurry was increased during the precision study by only a few milliliters to facilitate the production of the slurry. It is thought that when these slurries were evaporated, some of the hafnium became "hung-up" on the sides of the evaporating dish, and was not collected by the graphite. Even though the graphite residue was entirely removed, and the evaporating dish was brushed out as completely as possible, the loss of the hafnium could have occurred here. Hence, another standard curve was prepared while maintaining graphite slurry volumes at a minimum. A comparison of this curve to the initial curve is given in Figure 7. Evidently, controlling the slurry volumes minimizes point scatter. However, the two curves in Figure 7 do not appear to be reproductions of each other, and suggest that less precision exists in this method than originally thought. Still, the use of XRF as a means of hafnium detection appears to be far superior to the use of graphite furnace atomic absorption in this application.

Membrane Filtration Method

To minimize the importance of the analyst's technique in the wafer method, an alternate method of hafnium detection, using XRF as a means of detection, was developed. Kriege and Rudolph[26] describe an XRF method of zirconium determination by precipitating zirconium with p-bromomandelic acid, and filtering on to a Millipore filter sandwiched

FIGURE 7

COMPARISON OF HAFNIUM STANDARD CURVES



between two sheets of Mylar film. This surface is then analyzed for zirconium by XRF. Presumably, hafnium could be determined by a similar technique. Since cupferron would be used as a means of extracting hafnium later in the study, a solution would be readily available. Hence, it was decided to replace the p-bromomandelic acid with cupferron as the precipitating agent. The general procedure would be to acidify solutions spiked with varying amounts of hafnium, cool in a water bath, precipitate with cupferron, filter on to a Millipore membrane filter, and assemble a final unit for XRF determination as shown in Figure 8.

The data is given in Figure 9. Two attempts at producing a standard curve produced very linear results and the curves reproduced very well. Also the number of counts increased dramatically over the wafer technique. This is due to the fact that the hafnium detected is basically all present on the surface of the filter paper instead of being distributed throughout a 2.0 gram wafer.

TABLE 6

COMPARISON OF XRF TECHNIQUES

Micrograms Hafnium	Wafer Technique Activity (cpm X 10^{-5})	Membrane Filter Technique Activity (cpm X 10^{-5})
50	0.24	1.15
200	0.87	4.96
500	2.14	12.77

FIGURE 8

Membrane Filter Assembly for XRF Determination

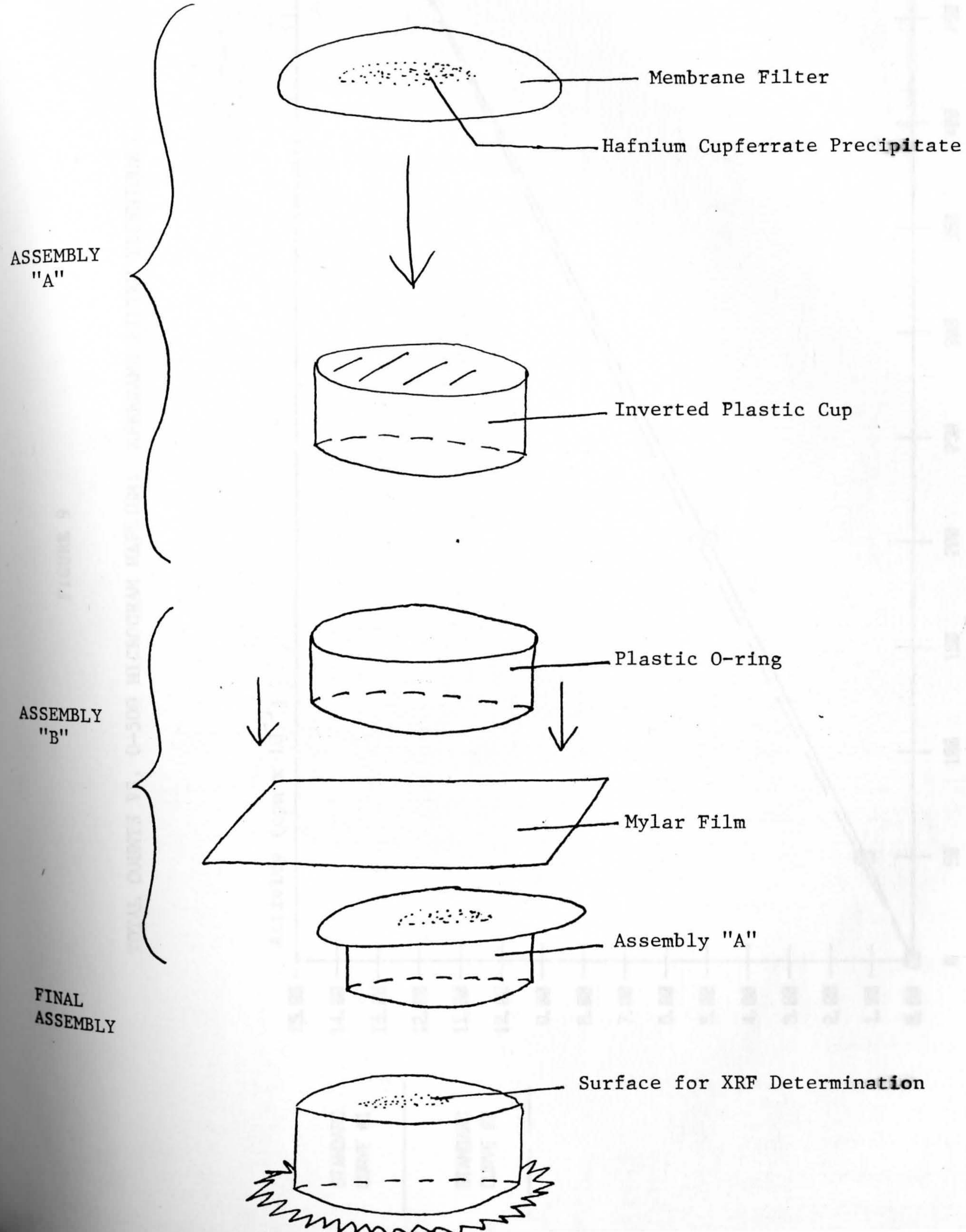
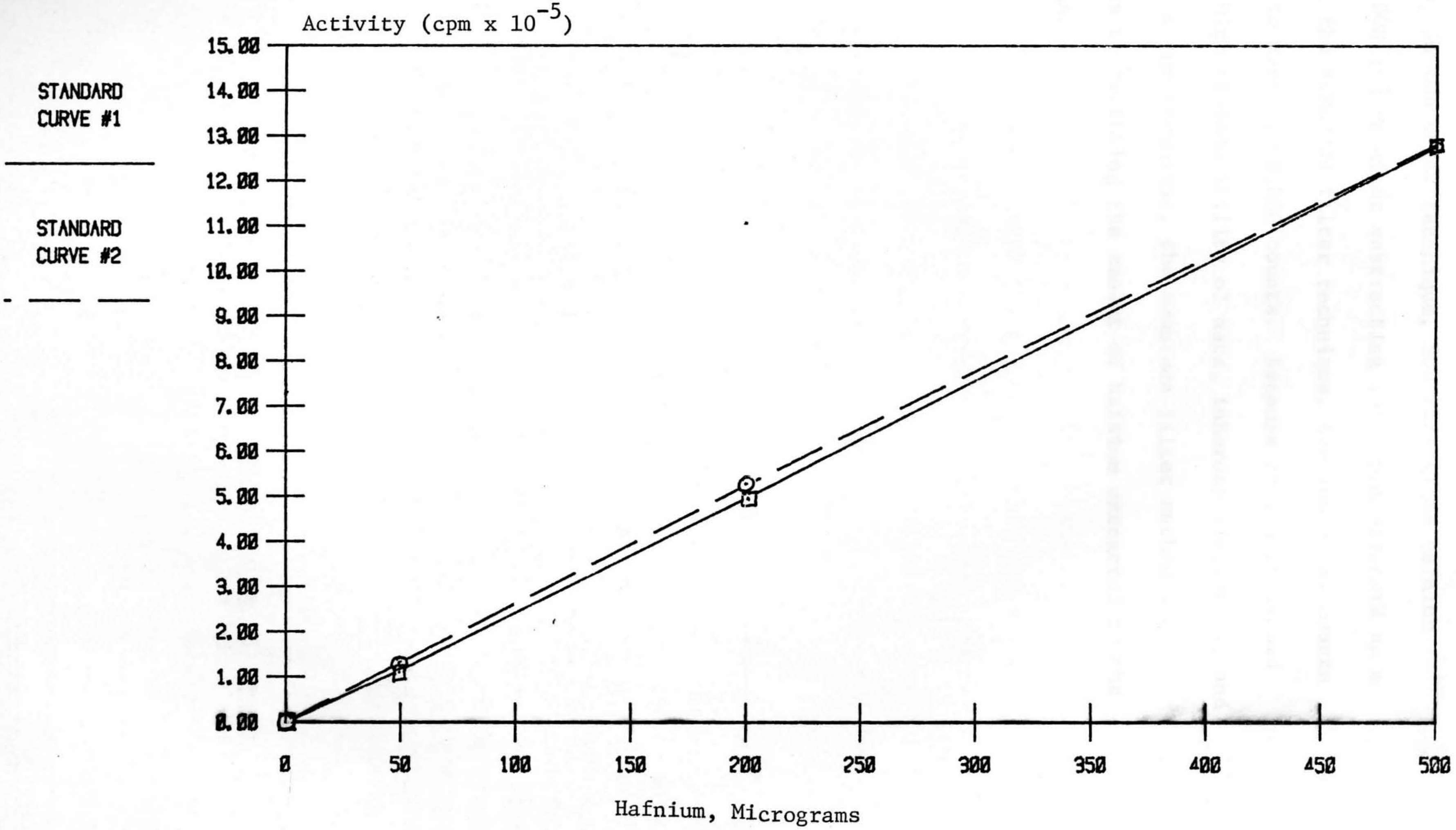


FIGURE 9

TOTAL COUNTS VS. 0-500 MICROGRAM HAFNIUM: MEMBRANE FILTER TECHNIQUE



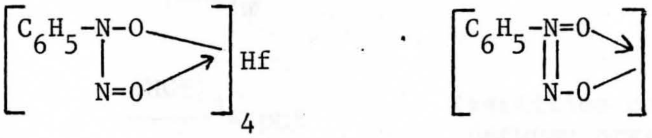
As seen in Table 6, in the wafer technique, 500 micrograms hafnium yielded about 200,000 counts after subtracting the 0 ppm standard as a blank, whereas, in the membrane filter technique, the number of counts increased sixfold to over 1,200,000 counts. Because of the increased number of counts, high reproducibility of data, inherent simplicity, and lack of variables in the technique, the membrane filter method was chosen as the means of detecting the amount of hafnium extracted by the solvent extractions.

CHAPTER III

EXTRACTION OF HAFNIUM CUPFERRATE

Chemistry of Cupferron

Cupferron is used in the analytical form as the ammonium salt of nitrosophenylhydroxylamine. It is thought to form a ligand to metal ratio of 4:1 as the tetracupferrate complex with hafnium under highly acidic conditions, as does zirconium. By varying conditions, the ratio can be changed to anywhere between 4:1 to 1:1 for the hafnium cupferrate complex.[27] On the basis of other cupferrate studies, the complex is thought to exist in the two following forms.[28]



$$\left[\begin{array}{l}C_6H_5-N-O \\ \qquad\;\; | \\ \qquad\; N=O\end{array}\right]_4 Hf \quad \cdot \quad \left[\begin{array}{l}C_6H_5-N=O \\ \qquad\;\; \| \\ \qquad\; N-O\end{array}\right]_4 Hf \qquad (1)$$

Cupferron is used to precipitate almost all the heavy metals in slightly acidic solutions, however, its real value lies in the fact that it becomes more selective at lower pH levels. These characteristics are also related to the extractability of metal cupferrates with organic solvents.

Extraction Equilibria

Sandell and Cummings[29] have proposed the following equilibria in the metal cupferrate extraction system.

$$\text{"HCf} \rightleftharpoons H^{+} + Cf^{-} \quad \text{(aqueous phase)} \qquad (2)$$

$$(HCf)_{w} \rightleftharpoons (HCf)_{o} \qquad (3)$$

Aqueous Phase — Organic Solvent

$$MCf_{m} \rightleftharpoons M^{+m} + m\ Cf^{-} \quad \text{(aqueous phase)} \quad (M^{+m} = \text{metal ion}) \qquad (4)$$

$$(MCf_{m})_{w} \rightleftharpoons (MCf_{m})_{o} \qquad (5)$$

Aqueous Phase — Organic Solvent

The respective equilibrium constants are:

$$\frac{[H^{+}]\ [Cf^{-}]}{[HCf]_{w}} = kCf \qquad (6)$$

$$\frac{[HCf]_{o}}{[HCf]_{w}} = pCf \quad \text{(partition coefficient of cupferron between organic solvent and water)} \qquad (7)$$

$$\frac{[M^{+m}]\ [Cf^{-}]^{m}}{[MCf_{m}]_{w}} = kM \qquad (8)$$

$$\frac{[MCf_{m}]_{o}}{[MCf_{m}]_{w}} = pM \text{"} \qquad (9)$$

The combination of these expressions gives:

$$\frac{[MCf_{m}]_{o}}{[M^{+m}]} = \frac{pM}{kM}\ \frac{kCf^{\ m}}{pCf}\ \frac{[HCf]_{o}^{m}}{[H^{+}]^{m}} = K\ \frac{[HCf]_{o}^{m}}{[H^{+}]^{m}} \qquad (10)$$

The value of kCf has been reported to be approximately $4x10^{-5}$.[30] Also, because the partition coeffcients for cupferron between various organic solvents and water are relatively high, the expectation is that after extraction at a low pH, the amount of cupferron not extracted would be negligible. This relationship will be dealt with further when examining the data obtained in this study.

Experimental

As a starting point for extraction conditions, those suggested by Fritz, Richard, and Bystroff[11] were used with some minor modifications. In order to realize the maximum precision available, 100-mL solutions of distilled water were all spiked with 500 micrograms of hafnium, using a micropipette, representing the limit of the standard curve developed. The pH of this aqueous solution was then adjusted to the desired value using either hydrochloric acid or sodium hydroxide. The volumes were then all adjusted to 150 mL, and transferred to 250-mL glass separatory funnels with Teflon stopcocks. After the addition of 10 mL of the desired solvent and 2.0 mL of a cold 6% cupferron solution*, the solutions were shaken vigorously for 45 seconds. After allowing the layers to separate for 10 minutes, the aqueous layer was drawn off for hafnium determination. The amount of hafnium <u>not</u> extracted was determined in the aqueous layer by the membrane filter XRF technique. The amount of hafnium extracted was calculated by subtracting the amount not extracted from the original amount spiked in. Therefore, a 100% extraction would indicate that no hafnium was detected in the aqueous phase following extraction.

---

*Cupferron solutions must always be refrigerated, as decomposition into nitrobenzene occurs rapidly as solutions become warmer. Fresh solutions were prepared weekly.

Extraction With Chloroform

The chloroform extract exhibited a green tint initially at about a pH of 3, and became increasing darker as pH was lowered during the extractions to 0.5. This apparently is the result of increasingly higher amounts of cupferron being extracted at lower pH levels. Also, when the aqueous portion was being cooled from room temperature to make it cold enough for a cupferron precipitation without decomposition, small droplets of chloroform that had not separated with the original organic extraction were detected at the bottom of the beaker. During filtration on the Millipore filter, it was necessary to pour off all but the last, approximately 10 mL, into the filtration funnel, then rinse the last few milliliters with distilled water.* The remaining chloroform would then be discarded, since it may partially dissolve some of the hafnium cupferrate collected on the filter pad if it was introduced into the filtration unit. The effect of not using the rinse can be seen in the lower amounts of hafnium recovered at a pH of 3.0 as summarized in Table 7.

---

* A 1% cold cupferron would probably be a better choice as too much water could partially redissolve the remaining precipitate. However, if the amount of water used in the rinsings were minimal, the effect would be neglible.

TABLE 7

EFFECT OF RINSE IN CHLOROFORM EXTRACTION

	Microgram Hf Recovered in Aqueous Phase After Extraction with $CHCl_3$ at pH = 3.0
Without Rinse	338
With Rinse	441

Other variables that were present during the extractions, that may have affected results, were the effects due to sodium ions, pH meter accuracy, and ionic strenth of the solutions. It was also decided that immediately after the extraction the aqueous portions be cooled in a water bath, prior to the first additions of acid in the determination sequence, to avoid raising the temperature of the solutions above those at which the extractions took place. At low pH levels, little, if any, amounts of cupferron would be present in the aqueous portion. However, at higher pH levels, the amount of cupferron in the aqueous portion may increase and an increase in temperature could result in increased decomposition of the unextracted cupferron into organic compounds. These compounds might erratically affect the subsequent cupferron precipitation, and/or the final determination of hafnium. To assure that the presence of sodium ions was not reponsible for decreasing the extractibility of hafnium cupferrate, the pH was adjusted to a slightly acidic condition with sodium hydroxide, and then lowered to a pH of 0.5. Also, ammonium and sodium hydroxides were used to adjust the pH to the same values before extraction. In all instances, the amount of hafnium cupferrate extracted was the same regardless of the amount of sodium present. The extractability of the complex into the organic phase is very dependent on the pH in the transition range from high to low percent extraction. The inherent uncertainty of the pH readings in unbuffered solutions with varying ionic strength could lead to large differences in the percent of the complex extracted in this pH range. This is experimentally demonstrated by an enormous change in the extractability of the complex in the presence of a 0.1 molar sodium chloride solution. Under the experimental conditions used in this study, no extraction occurred at a pH of 4.0. However, if the extraction took place in a 0.10 molar sodium chloride solution, extraction was measured at 73%. Other minor variables such as amounts of reagents used, and times during the extraction process were kept constant to eliminate them as variables in the procedure, even though minor variations in these would probably not have an affect on the data.

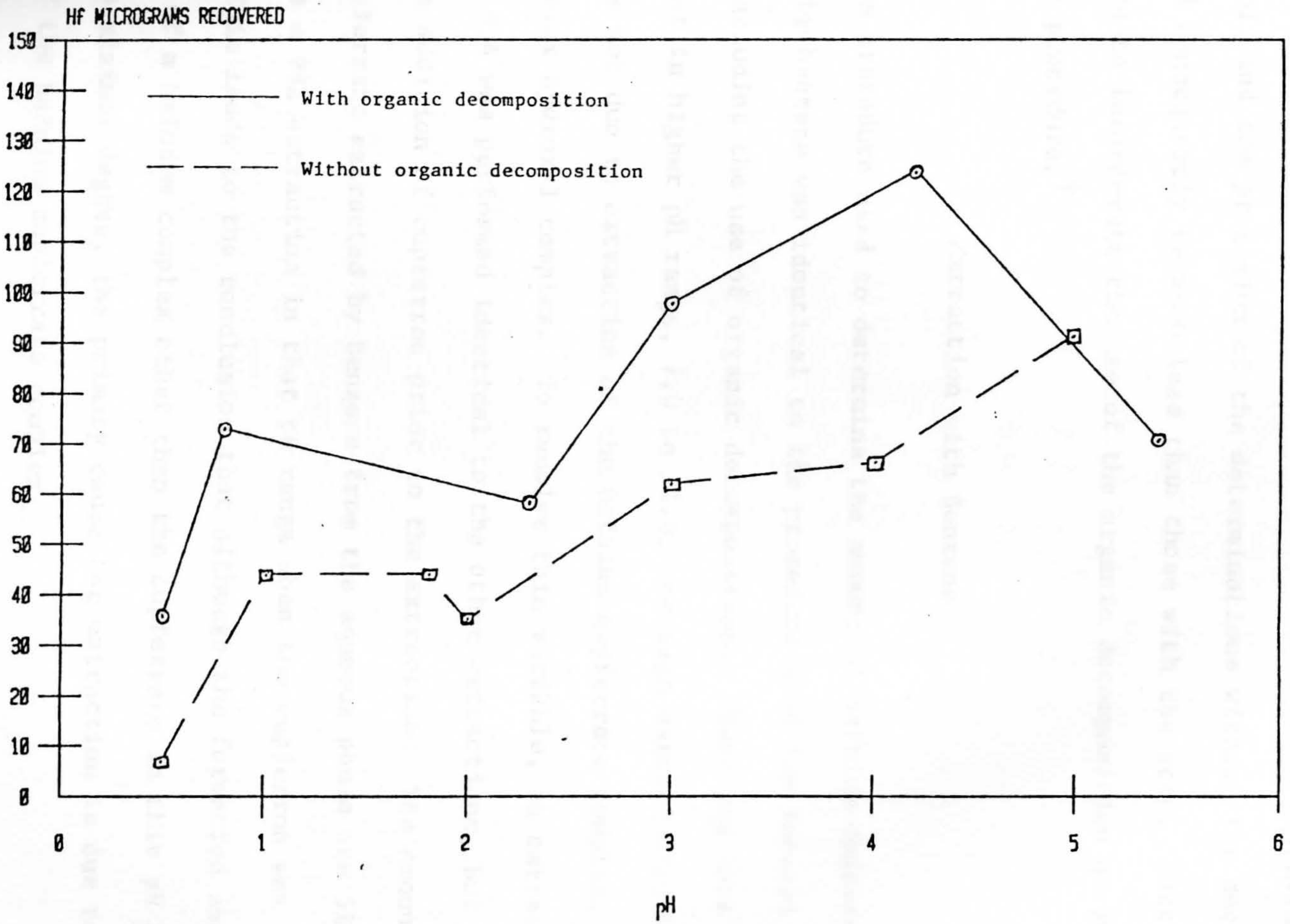
Extraction with Isoamyl Alcohol

Initially, the procedure used for extraction with isoamyl alcohol, 3-methyl-1-butanol, was the same as in the chloroform extraction. However, the pungent aroma of isoamyl alcohol was rather strong in the aqueous portion after extraction, and during the hafnium determination steps. Although the solubility of isoamyl alcohol in an aqueous solution is reported by Riddick and Bunger[31] to be 2.67% by weight at 25°C, this is apparently enough to cause the strong aroma. In addition to the disagreeable odor, the presence of the alcohol may have a tendency to dissolve the hafnium cupferrate precipitate before and/or during filtration. If the alcohol would, for example, dissolve the hafnium cupferrate filtered on the membrane filter, this would result in less hafnium detected in the aqueous phase, and lead to the incorrect result indicating more hafnium cupferrate extracted into the organic phase than actually occurred. It became necessary to determine if this actually were occuring, if so, to what degree, and finally how to eliminate the effect. The destruction of isoamyl alcohol in the aqueous phase was achieved by a decomposition by additions of nitric acid and sulphuric acids, and boiling the solutions to low volumes before the hafnium determination was made. To determine that the decomposition did not affect the detection portion of the analysis, a blank solution at a pH of 0.5 was spiked with 500 micrograms hafnium after the extraction and before the decomposition phase. If the detection method was not altered by the decomposition, theoretically, 100% of the hafnium would be detected. The actual amount detected was 102.9% of the amount spiked, which is within the statistical variance of the detection method. Therefore, it was assumed no variables were created by the use of the organic decomposition. To evaluate the actual affect of the soluble isoamyl alcohol on the determination portion of the method, another set of extractions was run identical to the first, with the exception of including the organic decomposition step. The data is given in Figure 10. The data generally suggests that more hafnium was recovered, if an organic decomposition was used prior to the hafnium determination, and that indeed some of the

FIGURE 10

EFFECT OF ORGANIC DECOMPOSITION

PRIOR TO HAFNIUM DETERMINATION



hafnium cupferrate was dissolved by the soluble alcohol. Although this conclusion is not overwhelmingly evident, some of the erratic data may have been caused by inconsistent dissolution of the hafnium cupferrate by the alcohol, and the precision of the determinations without the decomposition step would consequently be much less than those with the step. Hence, it was decided to incorporate the use of the organic decomposition as part of the entire procedure.[+]

Extraction with Benzene

The procedure used to determine the amount of hafnium cupferrate extracted by benzene was identical to the procedure used for isoamyl alcohol, including the use of organic decomposition. There was some concern that in higher pH range, 7.0 to 11.0, the high extractability of hafnium was not due to extraction of the hafnium cupferrate complex, but of a non-polar hydroxyl complex. To resolve this variable, an extraction at a pH of 9.4 was performed identical to the other extractions, but without the addition of cupferron prior to the extraction. The amount of hafnium cupferrate extracted by benzene from the aqueous phase was 5% compared to a 98% extraction in that pH range when the cupferron was present. This leads to the conclusion that although the formation and extraction of a hafnium complex other than the cupferrate in this pH range occurs to a minimal degree, the primary cause for extraction is due to the presence of the hafnium cupferrate complex.

[+] Because chloroform, being heavier than water, had a much higher density, 1.48 g/L, and relatively low solubility in water, 0.815% by weight, the use of the rinse technique as described in the previous section on the chloroform extraction, eliminated the need for the organic decomposition described here.

Extraction with Cyclohexane and Other Solvents

Extraction studies using cyclohexane were performed according to the method described for isoamyl alcohol and benzene. As most notably in the chloroform extracts, the cyclohexane extracts from highly acidic solutions were tinted a yellowish green, and became less colored at higher pH levels. One purpose in using cyclohexane as a solvent was to help resolve the question of the type of hafnium complex extracted at varying pH levels, by using a completely non-polar solvent such as cyclohexane. These results will be discussed in detail during CHAPTER IV of this study. Other solvents for which some extraction data were obtained were 4-methyl-2-pentanone (MIBK), a mixture of othro-,meta-,and para-xylenes, and ethyl acetate. These extractions were performed prior to the decision to use the organic decomposition and, hence, the data obtained may be inaccurate. However, it was thought unnecessary to repeat these extractions, as the extraction data collected for the other solvents was sufficient to resolve the extraction characteristics of the hafnium cupferrate complex at varying pH levels. The data was also sufficient in developing a theoretical relationship for predicting the extraction curves of hafnium cupferrate with different solvents at varying pH levels.

CHAPTER IV

SUMMARY

Extraction Curves

The final extraction curves were obtained through the use of the procedure detailed in Appendix B. The use of chloroform as an extraction solvent for hafnium cupferrate, Figure 11, is most useful in an extremely acidic solution, pH <2.0. The extraction sharply drops off at a pH just less than 2.0 until no extraction occurs in a slightly acidic solution, pH 4.0 to 5.5. The extraction gradually increases as pH rises, about 90%, then decreases gradually to a pH greater than 10.0. Finally, extraction of hafnium cupferrate drops rapidly as the solution becomes increasingly alkaline. The extraction curve obtained while using benzene as the extraction solvent, Figure 13, closely parallels that of chloroform with a few exceptions. The basic shape of the curve is the same, but initial extraction is not as complete at low pH levels. Some extraction does occur in a weakly acidic solution, and rises to become nearly complete in a weakly alkaline solution. However, similar to the chloroform extraction curve, very little extraction occurred in extremely alkaline solutions. The extraction of hafnium cupferrate with cyclohexane, Figure 14, produced a curve similar to that with benzene, except that extraction in strongly acidic solutions was extremely low. The extraction curve obtained with isoamyl alcohol, Figure 12, differs drastically from the other curves. The large drop in extraction

FIGURE 11

EXTRACTION OF HAFNIUM CUPFERRATE WITH CHLOROFORM AT VARYING pH

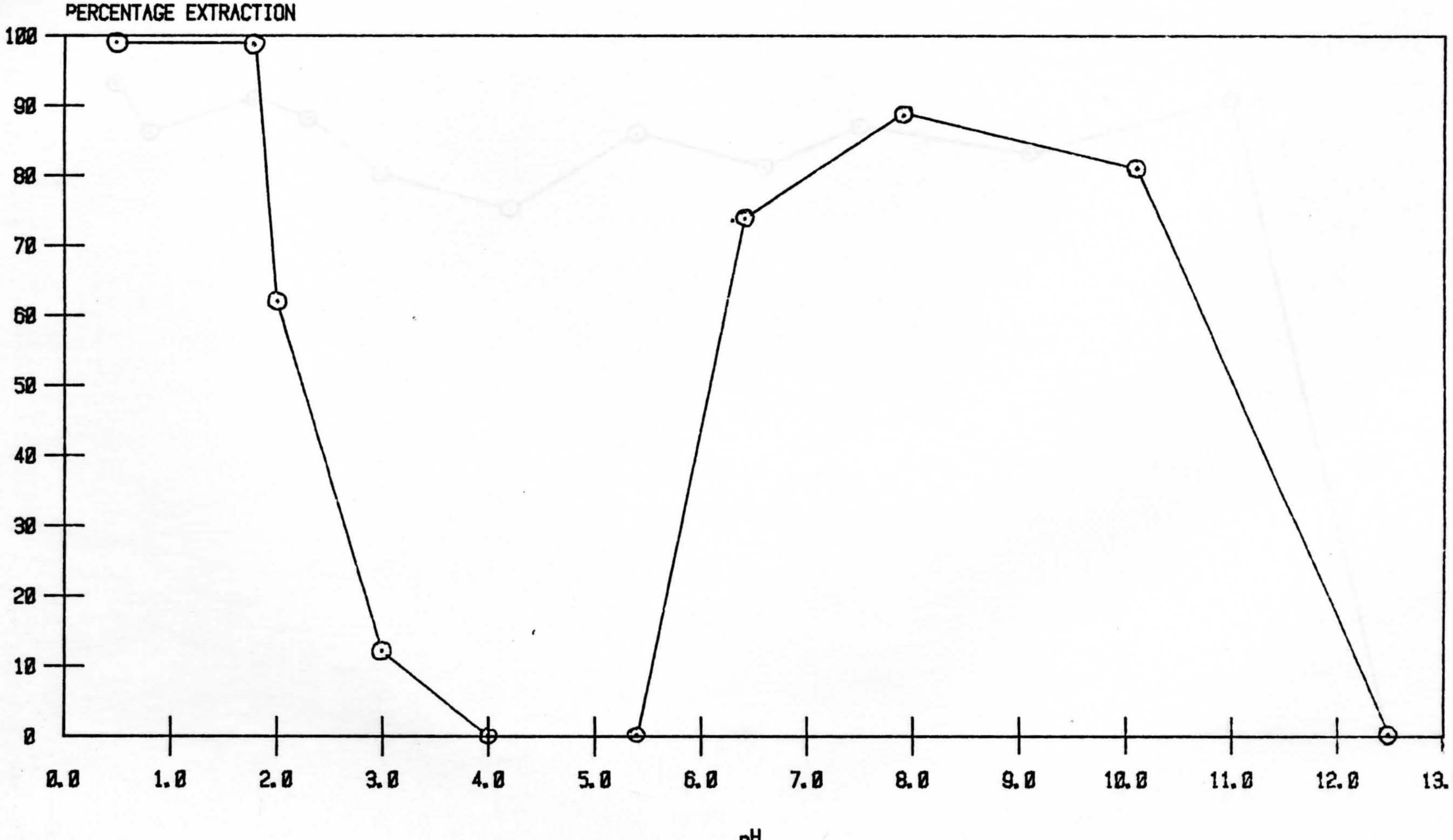


FIGURE 12

EXTRACTON OF HAFNIUM CUPFERRATE WITH ISOAMYL ALCOHOL AT VARYING pH

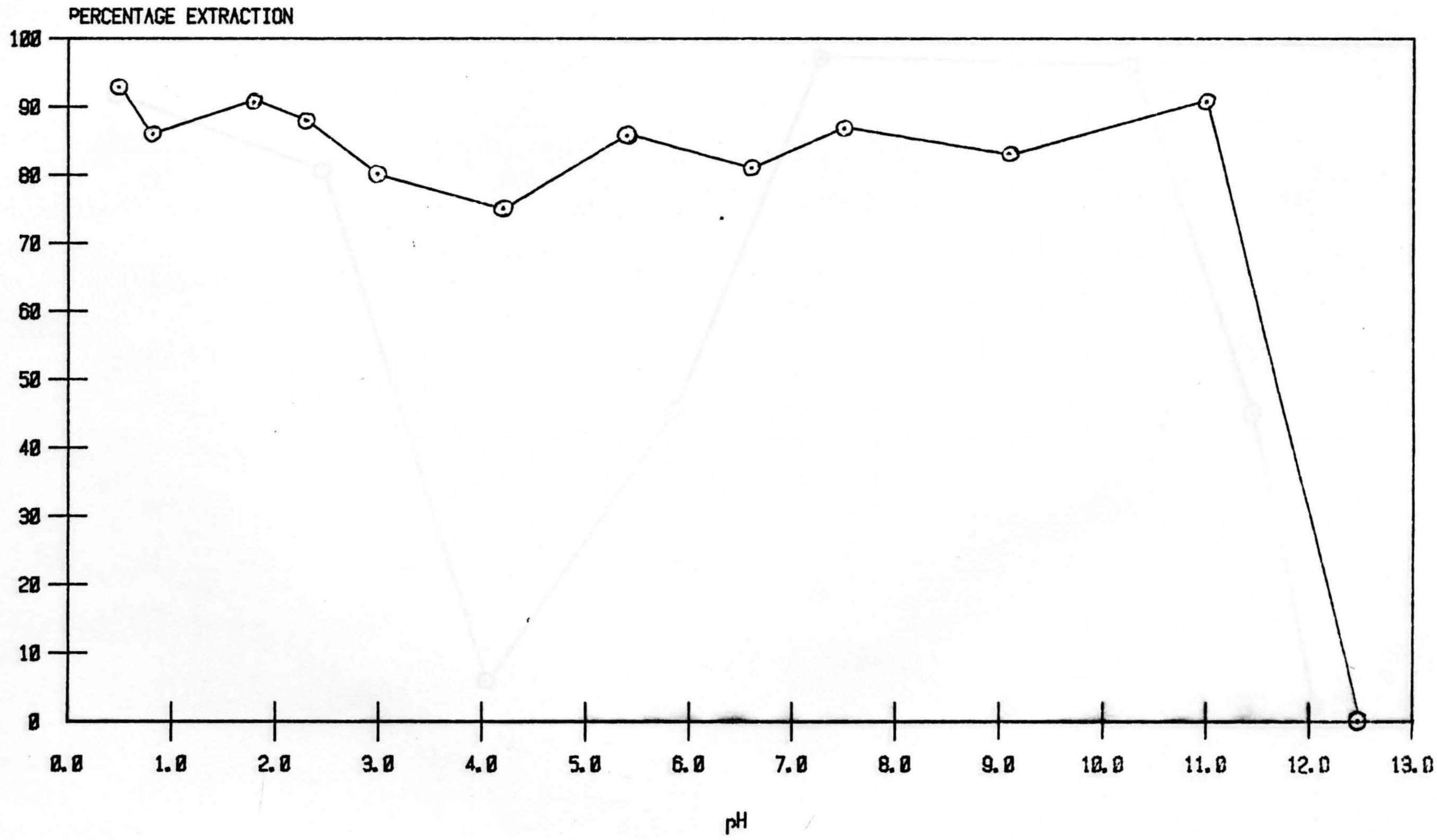


FIGURE 13

EXTRACTION OF HAFNIUM CUPFERRATE WITH BENZENE AT VARYING pH

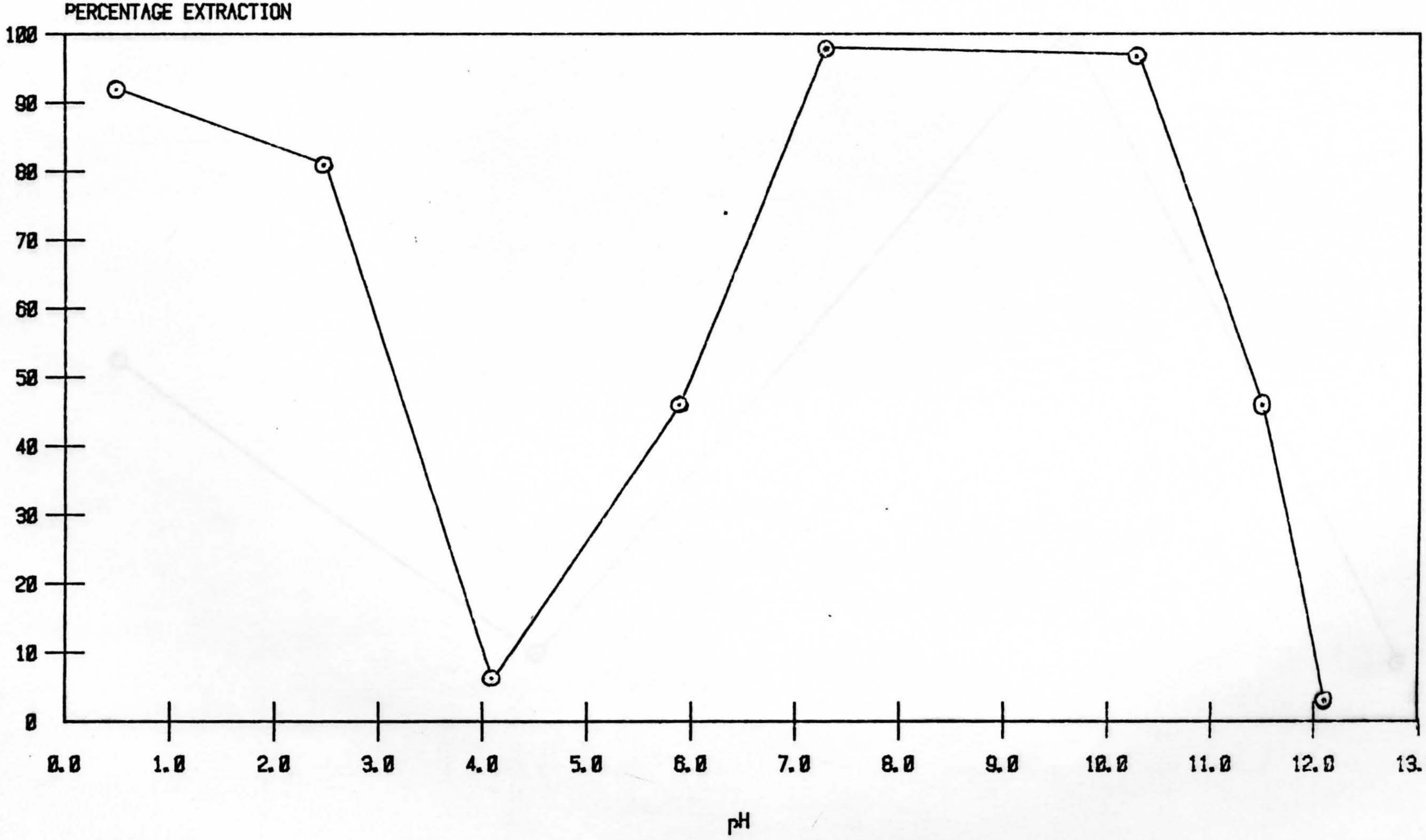


FIGURE 14

EXTRACTION OF HAFNIUM CUPFERRATE WITH CYCLOHEXANE AT VARYING pH

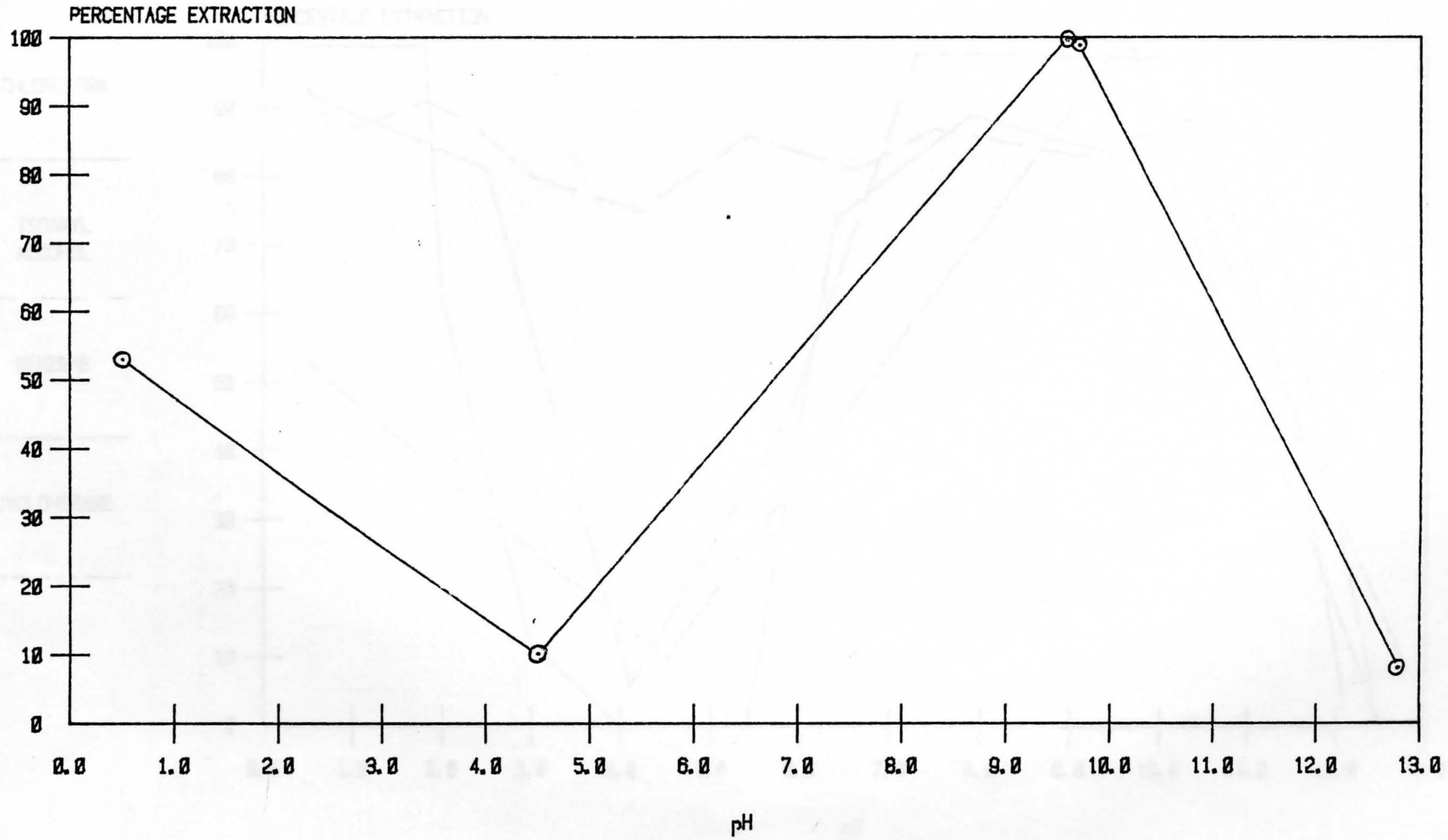
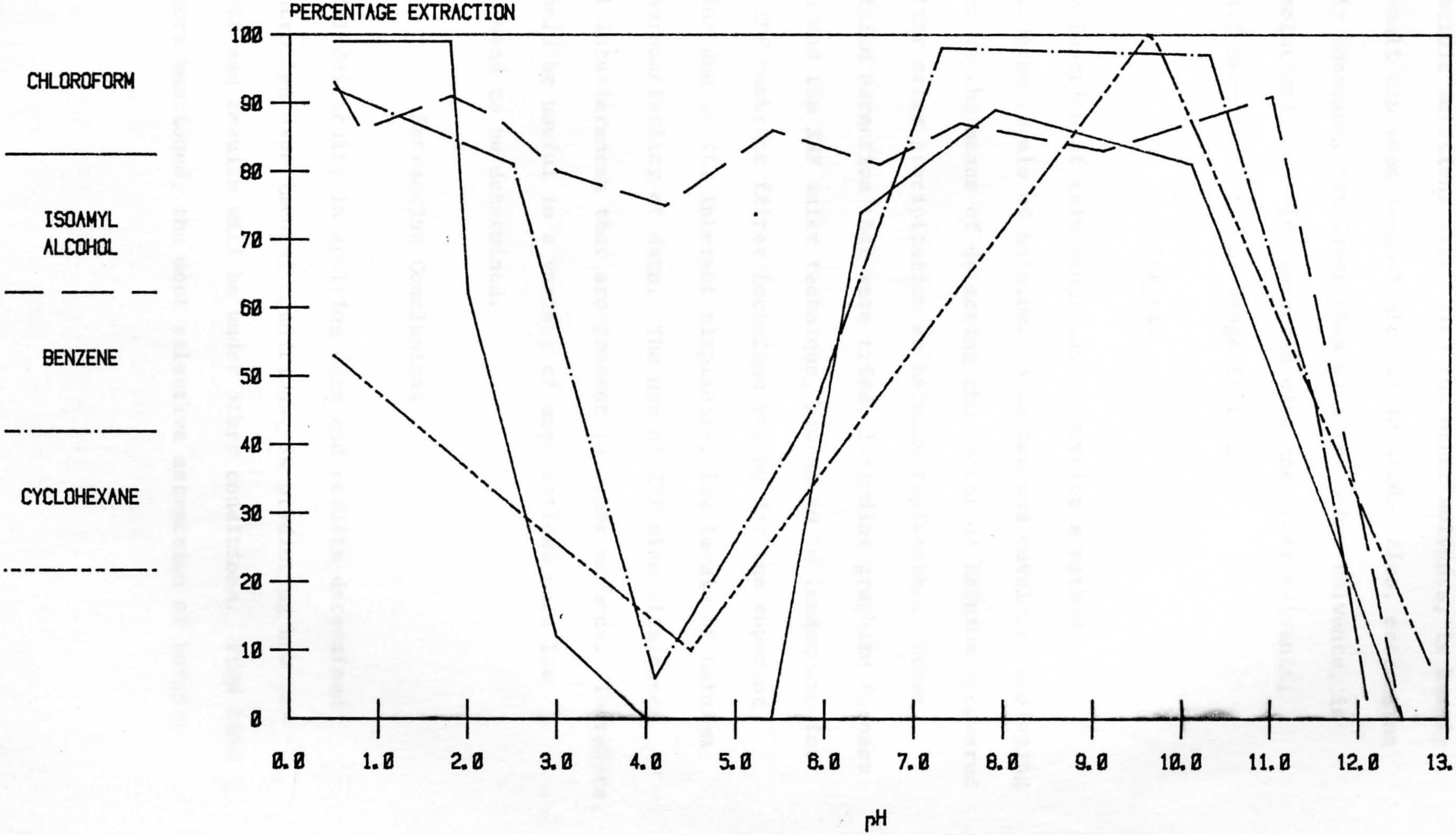


FIGURE 15

COMPOSITE EXTRACTION CURVES OF HAFNIUM CUPFERRATE WITH VARIOUS SOLVENTS



in the slightly acidic solutions noted with the other solvents, is barely detectable as a small dip when isoamyl alcohol is used. Also, extraction remains relatively constant, but lower than with the other solvents, in weakly alkaline solutions. As also detected with the other solvents, extraction fell off sharply in the pH range 11 to 12.

Conclusions

A primary function of this study was to develop a method of detection for microgram levels of hafnium. A method was developed employing x-ray fluorescence as the means of detecting the amount of hafnium recovered on a membrane filter after precipitation as hafnium cupferrate. Other techniques of hafnium detection that were tried, including graphite furnace atomic absorption and the XRF wafer technique, proved to be inadequate for this study. The XRF membrane filter technique was by far the superior method of detection due to its inherent simplicity, low levels of hafnium detection, and reproducibility of data. The use of XRF also eliminates numerous chemical interferences that are present in other methods. Therefore, this technique could be useful in a variety of applications when low levels of hafnium need to be determined.

Extraction Conclusions

The initial difficulty in applying data and results determined under closely controlled experimental conditions, is predicting how reproducible the data and results will be under other conditions. From this study and the others mentioned, the most selective extraction of hafnium cupferrate would occur from the most acidic solutions. Although nearly complete extraction occurs in weakly alkaline solutions, the extraction would not be as specific for hafnium, and would only be applicable to situations where extraction of other metals would not create additional analytical problems. This could also be to the analyst's benefit, if the extraction of another element with hafnium were desired as a means of eliminating those elements from interfering, in some other respect, in the aqueous portion. In the highly acidic solutions, the recommended extraction solvent was chloroform, which extracted nearly 100% of the hafnium under the experimental conditions. The poorest extraction of hafnium cupferrate at this pH level was with cyclohexane. This is not suprising as non-aromatic hydrocarbons have generally been considered to be poor extraction solvents for metal cupferrates from a practical standpoint. The use of cyclohexane in this study was primarily intended to help determine the type of hafnium complexes being extracted. If an analysis for hafnium in the chloroform extract is desired, a method of recovery for metal cupferrates in the chloroform extract has been used by Pekola[9] with good success. The method is similar to the organic decomposition described in Appendix B of this study. With minor modifications, the method developed in this study might be useful in the analysis of hafnium in nickel base superalloys. Through the proper combination of solvent and pH in eliminating interferences, the method could also be useful in other applications.

Theoretical Extraction Model

It is evident from Figure 15, that there are four major sections to the extraction curves. Two areas of high extraction and two areas of low extraction are present to some degree in each curve. As pH rises, less cupferron is available for extraction, and increasing amounts ionize in the aqueous phase, the amount of hafnium cupferrate extracted is affected. The formation of intermediate ionic hafnium complexes, as seen in Equations 11-14, partially explain the areas of low and high hafnium cupferrate extraction in the pH range of 2.0 to 9.0.

$$\mathrm{Hf(Cf)_4} \rightleftharpoons \mathrm{Hf(Cf)_3^{+}} + \mathrm{Cf^{-}} \qquad (11)$$

$$\mathrm{Hf(Cf)_3^{+}} \rightleftharpoons \mathrm{Hf(Cf)_2^{2+}} + \mathrm{2Cf^{-}} \qquad (12)$$

$$\mathrm{Hf(Cf)_2^{2+}} \rightleftharpoons \mathrm{Hf(Cf)^{3+}} + \mathrm{3Cf^{-}} \qquad (13)$$

$$\mathrm{Hf(Cf)^{3+}} \rightleftharpoons \mathrm{Hf(Cf)^{4+}} + \mathrm{4Cf^{-}} \qquad (14)$$

As less cupferron is available for hafnium to form the non-ionic tetracupferrate, the likelihood of intermediate ionic hafnium cupferrates increases. As this happens, the propensity for extraction into a non-ionic organic solvent would decrease. This does occur as seen in Figure 15 over the pH range of 2.0 to 5.0. The decreased extraction is not as dramatic with the cyclohexane curve, since original extraction is relatively low. As pH rises, the partial ionization of isoamyl alcohol occurs as the functional group begins to dissociate. Hence, extraction into a partially ionized solvent compensates for the loss of extraction due to the presence of an ionic cupferrate species. The fact that the isoamyl alcohol extraction curve varies up and down slightly is attributed to the constant formation of a different hafnium cupferrate complex, which is more or less soluble, than the original complex. The relationships of these complexes with the partial ionization of the alcohol cause the variations. This does not explain the increase of extractability reflected in the other solvents. The explanation for this can be found by examining the nature of the solvents, themselves. The most non-polar solvent used was cyclohexane, then benzene, chloroform, with isoamyl alcohol being the most polar of the solvents. The value of the dielectric constant also follows this pattern for these solvents, as seen in Table 8.

TABLE 8

DIELECTRIC CONSTANTS OF SOLVENTS USED

Solvent	Dielectric Constant[a]
Cyclohexane	2.023
Benzene	2.275
Chloroform	4.806
Isoamyl Alcohol	14.7

[a] Riddick and Bunger, Organic Solvents, pp. 77, 108, 162, and 350.

These patterns are also reflected in the percentage of hafnium cupferrate extracted in the weakly basic solutions. Cyclohexane and benzene yield nearly 100% extractions, isoamyl alcohol extracts approximately 80%, and the extraction with chloroform is basically between 80% and 90%. Although some of the extraction with isoamyl alcohol may be due to the solubility problem mentioned earlier, this extraction pattern suggests that an extremely non-polar hafnium complex is formed, which is extracted most effectively with the most non-polar solvents. The complex is probably one of two types. The first type would be a result of some non-polar geometric orientation of one of the intermediate cupferron species to which one or more hydroxyl groups have become attached, consequently forming an uncharged non-polar species. As discussed earlier, extraction of hafnium in this pH range does not occur without the presence of cupferron, suggesting further evidence of hafnium being extracted as a cupferrate. The second type of species formed that could result in the high extraction at this higher pH level could be due to a reversing of the ionization of hafnium cupferrate, and formation of the tetracupferrate again. This reversal may be encouraged by increasing ionic strength of the solutions as increasing amounts of sodium hydroxide are added to raise pH levels. Hence, the high extraction of hafnium cupferrate in the weakly basic solution may have been a result of increased ionic strength of the solution, formation of a non-ionic uncharged species, or a dynamic combination of both. The area of high extractability at low pH ranges may best be explained by the existence of either ion-pairs, polynuclear complexes or a combination of these and/or some other polar complex that would be easily extracted into the organic phase. Since the protonated cupferron would not be available for these combinations in extremely alkaline solutions, this may partially account for the lack of extraction in this area. Although a definitive extraction model cannot be developed from the data obtained in this study, the data are sufficient to permit a reasonable speculation on the shape of an extraction curve that would be obtained using a particular solvent over a given pH range.

APPENDIX A

Apparatus and Reagents

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Reagents 53

APPARATUS

The following apparatus was employed either in an experimental phase, or in the final procedure used in the determination of the extraction curves.

Buehler Ltd. press, equipped with 1-1/4" mold.

Eppendorf micropipettes, 5 microliters through 100 microliters.

Fisher Accumet Model 230 pH meter.

General laboratory equipment and glassware.

Lindberg muffle furnace, range to 2000°F.

Millipore filtration system, with GSWP04700 Milliporte membrane filters, 0.22 microns pore size, 47 mm diameter, made of mixed esters of cellulose.

Mylar film for plastic mounting ring and cup.

Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer equipped with HGA 2100 graphite furnace and controller, Model 56 recorder, and deuterium background correction.

Perkin-Elmer 260-1633 standard and pyrolytic tubes.

Sartorius analytical balance, sensitivity 0.01 mg.

Siemens MRS 400 Multichannel X-ray fluorescence spectrometer controlled by Digital Equipment Corporation PDP-1103 computer.

Spex Mixer/Mill, Cat. No. 8000.

Reagents

The following reagents were employed either in an experimental phase, or in the final procedure used in the determination of the extraction curves.

Reagent	Manufacture	Grade
Ammonium Hyrdoxide	MCB	Reagent, A.C.S.
90% Argon/10% Methane	Linde	P-10
Benzene	Mallinckrodt	Reagent, A.C.S.
Chloroform	Baker	Reagent, A.C.S.
Cupferron	MCB	Reagent, A.C.S.
Cyclohexane	Eastman	Reagent, A.C.S.
Distilled Water	Laboratory distilled	0.25 megaohms
Ethyl Acetate	Fisher	Reagent, Certified
Graphite	Union Carbide	SP-1C
Hafnium Metal	Teledyne Wah Chang Albany	0.999 Hf, Zr free
Hydrochloric Acid	Ashland	Reagent, A.C.S.
Hydrofluoric Acid	MCB	Reagent, A.C.S.
Isoamyl Alcohol	Mallinkrodt	Reagent, A.C.S.
MIBK	Fisher	Reagent, A.C.S.
Nitric Acid	Baker	Reagent, A.C.S.
pH Buffers	Fisher	Reagent, Certified
Phenolic Resin (Bakelite)	Buehler	Hf free
Sodium Chloride	Fisher	Reagent, Certified
Sodium Hydroxide	MCB	Reagent, A.C.S.
Sulphuric Acid	Baker	Reagent, A.C.S.
Xylenes	Baker	Reagent, A.C.S.

APPENDIX B

Methods

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Hafnium XRF Determination 58

Graphite/Bakelite Wafer Technique

1. Weigh 0.500 g SP-1C graphite into 150 mL teflon dish.
2. Moisten with minimal amounts of distilled water to from a graphite slurry.
3. Add solution to be analyzed. (Use minimal solution volume.)
4. Evaporate to dryness at low heat to avoid splattering.
5. Dry in muffle furnace at 400°F for 5 minutes.
6. Carefully brush out graphite into plastic vial containing 1.5000 g. Bakelite. Remove as much residue from the teflon walls as possible without scratching the teflon surface.
7. Shake vial for 15 minutes in mixer.
8. Press into wafer for 4 minutes, at 350°F, and at 4 psi.
9. Sand surface to be analyzed by XRF with 120 grit paper.
10. Analyze prepared surface for hafnium by XRF. (For a complete description of the XRF parameters used, see Step 9 of the "Hafnium XRF Determination" section in Appendix B.)

Extraction Conditions and Procedures

1. Spike 500 micrograms hafnium into 100 mL distilled water in a 250 mL beaker.

2. Adjust pH to desired level with NaOH or HCl, then rinse pH probes with distilled water back into beakers.

3. Adjust volume to 150 mL with distilled water.

4. Transfer solutions quantatively, using minimal amounts of distilled water, into 250-mL separatory funnels.

5. Add 10 mL extraction solvent.

6. Add 2.0 mL 6% cupferron solution.

7. Immediately shake for 45 seconds, then let settle for 10 minutes.

8. Extract aqueous portion into 400-mL beaker with glass stirring rod and watch glass.

9. If the extraction solvent used is chloroform, dilute to 200 mL, add 15 mL 1:1 H_2SO_4 and procede to Step 1 of the "Hafnium XRF Determination" section of Appendix B.

Organic Decomposition

1. To the aqueous extract from Step 8 of the "Extraction Conditions and Procedures" section add 5 mL concentrated HCl, 50 mL concentrated HNO_3, and 20 mL of 1:1 H_2SO_4.

2. Heat gently to first bubble, to evolve NO_2 fumes on electric hot plate, then remove immediately, and let reaction continue autonomously. It is important to remove the solutions immediately after the first bubble is detected, otherwise solutions may erupt, boiling vigorously even after solutions have been removed from heat. This condition is especially prevelant when isoamyl alcohol has been used as the extraction solvent.

3. Once the reaction has diminished, reheat to gentle boiling with occasional vigorous stirring.

4. After boiling has become even, move beaker to a more intense heat source, e.g. gas hot plate.

5. Evaporate to low volume (approximately 50 mL) remove from heat, let boiling subside, remove the stirring rod, and carefully rinse it with minimal distilled water back into the beaker.

6. Reheat solution to boiling and evaporate to fuming H_2SO_4.

7. <u>Carefully</u> add one drop (or more if needed) of concentrated HNO_3 down the inside of beaker to assure complete oxidation of organic material.

8. After all NO_2 fumes have disappeared, fume an additional 5 minutes, then remove from heat and let cool thoroughly.

9. Rinse watch glass and insides of beaker with distilled water and dilute to 200 mL.

Hafnium XRF Determination

1. Cool solution in cold water bath approximately 20 minutes with occasional stirring.

2. Add 35 mL concentrated HCl.

3. Re-cool as in Step 1.

4. Add 10 mL 6% cupferron solution while stirring.

5. Let stand for 15 minutes in cold water bath.

6. Stir solution mildly before filtering in a Millipore filtration system with 0.22 microns pore size membrane filter of mixed esters of cellulose under medium vacuum.

7. Pour all of the solution into unit at once. Swirl solution slightly when about 20 mL of solution remains. Do not rinse once filter is dry as this may result in an uneven distribution of the hafnium cupferrate precipitate. If chloroform was used as the extraction solvent use the following technique to filter the precipitate. Pour all the solution except the last 10 mL into the filtration unit. Rinse the remaining 10 mL with an equal volume of distilled water, and pour it into the filtration being careful not to allow any chloroform to enter the filtration system. Discard the remaining chloroform.

8. Once the solution is entirely filtered, remove the filter carefully, and place it on an inverted plastic cup. Cover with a Mylar film and seal unit with a plastic O-ring.

9. Analyze prepared filter for hafnium by XRF with the Siemens MRS 400 spectrometer under the conditions that follow:

   The prepared surface is placed in a specimen cup with a high purity gold surface diaphragm with a 27 mm aperature. The sample is brought into the test position with a pneumatic swing arm and the chamber is pumped out to a vacuum. The sample is then bombarded with x-rays from an x-ray tube with a rhodium anode. The fluorescent radiation of hafnium is measured simultaneously by the hafnium channel for 60 seconds, while the specimen cup is rotated once every 10 seconds. The L-alpha 1 line of hafnium is selected by the channel pre-set at a 45.88° 2 theta angle using a logarithmically bent LiF(100) crystal. The emerging radiation from the exit slit of the channel is determined by a scintillation counter as total counts/60 seconds.

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