1970

Determination of Trace Concentrations of Barium Extracted From Aqueous Systems.

Lucy Edelbeck

Louisiana State University and Agricultural & Mechanical College

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DETERMINATION OF TRACE CONCENTRATIONS OF BARIUM
EXTRACTED FROM AQUEOUS SYSTEMS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Sister Lucy Edelbeck
B.A., Mt. Mary College, 1951
M.S., Creighton University, 1961
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ABSTRACT

Barium is one of those less ubiquitous but potentially harmful contaminants in the environment. Its presence in the environment has been demonstrated. However, securing reliable information about its concentration is hampered by lack of a sensitive, simple, accurate method of analysis. The methods of determination of trace concentrations of barium have been reviewed.

This present work presents a simple, selective, sensitive method for the determination of barium in aqueous systems. The method combines the solvent extraction of the barium hexafluoroacetylacetonate into isoamyl acetate with atomic absorption determination of barium. This combination of methods increases the sensitivity of the barium determination by two orders of magnitude from $0.3 \mu\text{g/ml}/\%$ to $0.005 \mu\text{g/ml}/\%$ as measured from the concentration in the aqueous phase. It also presents a quick method of determining barium at concentrations as low as $0.015 \mu\text{g/ml}$; this is within the range found in natural waters.

Attempts to remove or mask sodium or potassium were unsuccessful. It was found necessary to use a concentration of $1,000 \mu\text{g/ml}$ of potassium in the aqueous phase. The potassium extracted into the organic phase and acted as an ionization buffer in the absorption of barium. Sodium was shown to have no further buffering effect.

The absorption of barium was shown to be a direct function of

the extraction of potassium which is dependent upon pH. The calibration curve showed linearity from 0.015 $\mu\text{g/ml}$ to 1.0 $\mu\text{g/ml}$. This method can tolerate Be^{2+} , Mg^{2+} , Al^{3+} and Co^{2+} at the hundred-fold level. Among the other common ions tested only Cr^{3+} and Mn^{2+} gave significant interference at the thousand-fold level. Tartrate was used to mask the Pb^{2+} interference and Fe^{3+} was masked with diethyldithio carbamate.

PART I INTRODUCTION

CHAPTER 1 BARIUM AS PRESENT IN THE ENVIRONMENT

CHAPTER 2 METHODS FOR THE DETERMINATION OF BARIUM AS A TRACE
ELEMENT

CHAPTER 3 ATOMIC ABSORPTION PARAMETERS OPTIMIZED FOR
BARIUM SENSITIVITY

CHAPTER 1

BARIUM AS PRESENT IN THE ENVIRONMENT

The achievement of any major goal comes about by a progression of steps in that direction, some giant, some meager. The goal challenging the world community today is to restore our damaged environment. A contaminant identified and its degree of contamination made known is one step in a concerted effort.

The National Air Pollution Control Administration recently directed attention to a facet of a healthful environment. "As concern for air quality grows, so does concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere."¹ Barium is one of the thirty such pollutants identified.

Barium exists naturally in the environment only in compounds with other elements. It is too reactive to remain in the elemental form. It is found in the range of 330 - 1600 ppm in upper igneous rock, in shale at concentrations of 580 ppm, but especially in clay at 2300 ppm.²

The main source of our commercial supply of barium is the mineral barite (barium sulfate, BaSO_4). It is found in beds in sedimentary formations, it may remain as a nodule in the weathering process, or appear as gangue with other minerals. Missouri, Arkansas, Georgia and Nevada produce most of the nation's supply of barite. Trace quantities of barium are found also in coal.³

Typical forms of mining barite include open pit mining, either power shoveling or blasting, hydraulic mining or underground mining.

The mineral is then ground and crushed for use; 90 percent is used in oil-well drilling, the remainder for barium chemicals.¹ While insoluble BaSO_4 is administered orally, as an opaque suspension for x-ray examination of the gastro-intestinal tract and no harmful results have been reported, soluble barium compounds, barium chloride and barium carbonate have been reported to be toxic. If ingested the symptoms produced are severe abdominal pain, rapid pulse, and paralysis. If exposed externally, the usual result is irritation of eyes, nose and throat and of the skin.⁴

Workers subject to inhalation of the dust from barium compounds have developed respiratory irritation. Instances of this affliction, referred to as baritosis, have occurred among mine workers in the United States and other countries.⁴

A summary of the toxicity and the uses of the more important barium compounds is presented in Table 1. According to Grabowski and Unice, the presence of barium in nature is widespread. However, analytical data on its abundance is unreliable in many instances in which the concentration of the element approaches the detection limit of the method employed.⁵

Several studies of the barium concentration in the oceans have been completed. Chow and Goldberg⁶ (1960) reported a variation with depth at stations in the Pacific Ocean of $0.012 \mu\text{g/ml}$ - $0.063 \mu\text{g/ml}$. In 1964, Bolter and Turekian reported an average of $0.013 \mu\text{g/ml}$ for six stations in the West Atlantic and Indian Ocean.⁷ Turekian and Johnson⁸ in 1966 reported the most comprehensive study of the presence of barium in the oceans to date. They made over two hundred fifty determinations in all the oceans including the Antarctic and

TABLE 1
TOXICITY AND USES OF SOME BARIUM COMPOUNDS¹

Compound	Toxicity	Uses
Barium carbonate BaCO_3	Poisonous	rat poison in ceramics and enamels in manufacture of paper
Barium chloride	Poisonous	mordant for acid dyes boiler compound for softening water purifying agent in brines flux for magnesium alloys
Barium hexafluoro- silicate BaSiF_6	Highly toxic espe- cially when dissolved in alkali	as pesticide
Barium hydroxide	Poisonous	synthetic rubber vulcanization drilling fluids lubricants pesticides sugar industry
Barium oxide	Poisonous	drying gases and solvents lubricating oil detergents
Barium sulfate	Nontoxic	Photographic paper filler for rubber, linoleum, paper coating X-ray examination

Long Island Sound. They suggest that knowledge of the distribution of barium is important in the elucidation of two major problems of marine geochemistry; (1) the variations of Ra^{226} distribution in ocean water profiles, (2) the barium concentration in sea water as related to the concentration in the tops of the deep sea sediment.

Barium, along with potassium, lithium, strontium and manganese is found dissolved in most oilfield waters. Knowledge of the concentration of the constituents fills several needs enumerated by Collins,⁹ such as: (1) aid in search for petroleum, (2) identification of sources of intrusive brines, (3) increase in geological knowledge of subsurface formations, and (4) aid in identifying and locating valuable mineral reserves. The determination of barium in water to be used for water flooding in oilfield operations is important, because barium will precipitate when mixed with waters containing sulfate and cause severe damage in a waterflood operation.⁹

The presence of Solbar, a barium polysulfide fungicide, on fruit has been reported by Kroller.¹⁰

McLellan¹¹ has found barium present in concentrations ranging from 6 $\mu\text{g/g}$ - 35 $\mu\text{g/g}$ in all of seventy-six samples of alfalfa.

A study of the distribution of barium in the rivers of North America was reported by Livingstone¹² in 1960. He reported from thirty-four samples from major rivers, a mean concentration of 54 ppb. In 1967, Kopp and Krover¹³ reported a distribution of barium in the waters of the United States, based on an analysis of over

fourteen hundred surveillance system samples. The range of barium in solution was from 5 $\mu\text{g/l}$ - 195 $\mu\text{g/l}$. They found two or three times as great a concentration of barium in solution (mean 43 $\mu\text{g/l}$) as in suspension (11 $\mu\text{g/l}$ mean). A ratio of 10/1, solution to suspension, was reported for the Kanawha River in lower West Virginia. This river carries effluent from a chemical complex located in the watershed. The Allegheny River with discharges of oilfield brines and acid mine drainage was found to have a ratio of 7/1.

There are a number of barium-based organometallic fuel additives which have been found effective in reducing the black smoke emissions from diesel engines.¹⁴ The additive reacts to inhibit the dehydrogenation of the hydrocarbon fuel, thus reducing the concentration of carbon in diesel exhaust. The reduction of carbon also reduces carbon deposits and provides wear-protection for injectors and piston rings.¹⁵ Miller's studies also reported no significant difference between the concentrations of oxygen, carbon dioxide or carbon monoxide in the exhaust emissions from fuels containing the barium additive and those from emissions from untreated fuels. Golothan¹⁴ reported no effect on the emission of carbon monoxide or nitrogen oxide from the use of barium-based additives. He also concluded that no significant increase in the emission of polynuclear aromatic hydrocarbons would result from fuels containing a barium-based additive. Golothan reached the following conclusions from his study.¹⁴

(1) Upto 25% of barium compounds consisted of soluble

barium at a sampling point 10 feet from the engine.

- (2) The ratio of fuel sulfur to barium has a noted effect on the ratio of soluble/insoluble barium. Doubling the additive or reducing the fuel sulfur content increased the ratio significantly.
- (3) The maximum amount of soluble barium in exhaust gases, emitted at full load, having an additive concentration of 0.075 percent by weight of barium would be 12,000 $\mu\text{g}/\text{m}^3$.

Figure 1 presents some of the data from tests completed by Golothan on barium in fuel emission.

No standards have been set for ambient air concentrations for barium. The American Conference of Governmental Industrial Hygienists in 1967 recommended an 8-hour threshold limit of 500 $\mu\text{g}/\text{m}^3$ for occupational exposure to the soluble compounds of barium in air.¹

The National Advisory Committee on Water Quality Criteria has accepted a permissible concentration of 1.0 $\mu\text{g}/\text{ml}$ barium in public water supplies.¹⁶

The presence of barium within the environment has been demonstrated by the studies related within this Chapter. No studies have been found to determine its concentration within the atmosphere, although its presence there has been verified.¹

FIGURE 1 SOLUBLE BARIUM EMITTED IN EXHAUST

*
% Concentration normally used

CHAPTER 2

METHODS OF ANALYSIS FOR BARIUM AS A TRACE ELEMENT

Wherever barium is found in the environment, with the exception of its natural occurrence in barium ores and rock sediments, of deep sea sediments and in oil field brines, it is present in trace concentrations at ppm levels. Moreover, as Grabowski and Unice observe, "Analytical data on its abundance is unreliable in many instances where the concentration of the element approaches the detection limit of the method employed."⁵ To make real what analysis at the ppm level entails, the following excerpt is relevant:

1 ppm is equal to 1 inch in 16 miles,

1 ppm is 1 minute in 2 years,

1 ppm is a 1-gram needle in a ton of hay.

1 ppm is one large mouthful of food when
when compared with the food a person
will eat in a lifetime

1 ppm is the theoretical concentration that
one teaspoon of DDT, when spread on five
acres of alfalfa, will impart to hay,

or

1 ppm is 1 drop in 16 gallons, or in 80
"fifths" (a very dry martini indeed!)

Author unknown

All the known analytical methods, adaptable to trace analysis have been used to determine barium. In spectrophotometric methods the sensitivity is dependent upon the proper selection of chemical reagents used in the color producing reactions. The intensity of a colored complex is increased by additional aromatic rings in the structure. We find that all sensitive reagents for barium have one or more aromatic rings, which produce not only greater sensitivity due to color intensity but also increased stability.

Pollard and Martin¹⁷ used o-cresolphthalein complexone to determine barium at concentrations of $.004 \mu\text{g}/\text{cm}^2$. However because all other alkaline earth elements interfered, it was necessary to use a previous separation by paper chromatography. Cameroni and Albasini²³ reported the simultaneous micro determination of barium and calcium using o-cresolphthalein without previous separation. The determination was possible only in the range of $.1 - 2 \mu\text{g}$ of the elements.

Koichi et al.¹⁸ reported that a series of compounds having an o-hydroxy-o-sulphazo grouping were sensitive to magnesium, calcium and barium, yielding sensitivities of $0.5 - 30 \mu\text{g}/\text{ml}$ for barium. Savvin et al.¹⁹ reported a sensitivity of $0.1 \mu\text{g}/\text{ml}$ for barium using a bis-diazo dye based on chromotropic acid. When sulfonic acid groups were used as substituents, specifically in 2,7-bis(o-sulfo-phenylazo) chromotropic acid, called Sulfonazo-III, it became a selective reagent for barium. Only strontium is listed as interfering.

Budesinsky et al,²⁰ using Dimethylsulfonazo-III to increase the absorption reached a sensitivity of $0.01 \mu\text{g}/\text{cm}^2$. Lead, nickel, copper, calcium, and strontium interfered. Using the dianilide of the above, dianilide of 2,7-bis(o-sulfo-p-methylphenylazo) chromotropic acid, Budesinsky and Vrzalova²¹ reported the extraction of the barium complex into butanol followed by photometric determination. The sensitivity range was 5 - 30 $\mu\text{g}/10 \text{ ml}$.

Lukin et al²² studied the diazo compounds of chromotropic acid which contained phosphonic groups. They used Chlorophosphonazo-III for spectrophotometric determination of barium at a concentration of 1 $\mu\text{g}/\text{ml}$.

Emission spectroscopy has been used by several to determine trace concentrations of barium. Wilska²⁴ used the porous cup electrode technique to determine barium in water. He was able to detect at 0.5 $\mu\text{g}/\text{ml}$ concentration by evaporation of the sample from 500 ml to 1 ml. Cardell²⁵ was interested in determining the micro quantities of barium collected on the anode after operation of electron tubes. He dissolved the deposited film and used the open cup graphite electrode. Quantities of barium determined ranged from 20 $\mu\text{g}/\text{ml}$ - 3 $\mu\text{g}/\text{ml}$. Grabowski and Unice⁵ using a rotating disc electrode and spark excitation after sodium carbonate fusion reported concentrations as low as 2 $\mu\text{g}/\text{ml}$ with coefficient of variation of only 4.4%. Goleb et al²⁶ determined impurities in graphite to be used for nuclear reactors. They detected barium at concentrations of 0.1 $\mu\text{g}/\text{ml}$ - 0.5 $\mu\text{g}/\text{ml}$ using the copper spark method on

ashed residue. Kopp and Kroner¹³ using a direct-reading emission spectrograph with rotating disc electrode and high voltage spark excitation detected concentrations from 0.2 $\mu\text{g/ml}$ - 0.001 $\mu\text{g/ml}$ in natural waters.

The methods of analysis to date which have been successfully used to determine barium at the concentrations found in the ocean are neutron activation analysis and isotope dilution mass spectrometry. Relative to this, Turekian² (p. 207) claims, "The low level of barium in most natural waters precludes flame photometric determination without enrichment. High-voltage spark emission spectrography also suffers from this limitation. Hence, for natural waters, isotope dilution mass spectrometry or neutron activation is usually mandatory unless enrichment procedures monitored by radioactive tracers are developed." Bolter et al.⁷ irradiated the sample of barium which had been separated as the chromate and determined concentrations of .013 $\mu\text{g/ml}$. Turekian and Johnson⁸ also used separation prior to irradiation in determining barium with a 25 percent standard deviation. Chow and Goldberg⁶ after precipitation with sulfate and enrichment with standard barium determined concentrations of .012 $\mu\text{g/ml}$.

Flame emission spectrophotometry of barium has been studied extensively. Dean et al.²⁸ determined barium at 1 $\mu\text{g/ml}$, using oxygen-acetylene flames and reported serious interference. Anderson and Hume²⁹ studied the emission of barium in hydrogen flames and the effect of EDTA on the barium emission. Koirttyohann and Pickett³⁰

and McLellan¹¹ successfully used a scanning technique to minimize the calcium interferences while using a nitrous oxide-acetylene flame.

The concentration of barium by ion exchange resin prior to determination by flame emission has been reported by Anderson and Hume.³¹ Koller¹⁰ reports the detection of barium in fungicides. He used paper chromatography and sodium Rhodizonate for development. He reports barium at 0.01 $\mu\text{g/ml}$ concentration.

Three criteria are generally considered when a method for trace analysis is evaluated: sensitivity, accuracy and selectivity.³² Other factors such as the time consumed, the cost of the equipment and the training necessary for success have secondary importance. Of the methods previously reviewed, activation analysis and isotope dilution mass spectrometry have reached the greatest sensitivity. The procedure however is slow and cumbersome and needs expensive equipment.

Emission spectrographic methods for trace analysis suffer from lack of sufficient accuracy and precision especially when arc excitation is used to increase sensitivity.

Absorption spectrophotometry or colorimetry lacks selectivity, unless suitable masking processes are used.

Flame emission photometry presents serious interferences when more than one metal is present.

The method which to date seems most promising in achieving the required sensitivity, selectivity and accuracy needed for determining trace amounts of barium as found in the environment is atomic

absorption spectrophotometry. A discussion of the development and refinement of this method as applied to barium determination is presented in Chapter 3.

CHAPTER 3

ATOMIC ABSORPTION PARAMETERS OPTIMIZED FOR BARIUM SENSITIVITY

Since its inception in 1955 with the publications of Walsh³³ and Alkemade and Milatz³⁴ as a sensitive method of elemental analysis, atomic absorption spectroscopy has had a phenomenal growth. Advances followed one after another in all aspects of development. Improved instrumentation modified the optics system from single to double beam, from single pass through a flame to triple pass. Means of atomization were flames, highly developed due to flame emission photometry, sputtering chambers, furnaces with reducing atmospheres, spark discharges, L'vov furnaces, and lasers. Much attention has been directed to the composition of gases producing the flame, the temperature of the flame and the construction of burners to produce optimum atomization. Theoretical studies have been concerned with the flame processes, the nature of the atomization, the absorption process itself, and the 'organic solvent effect'. Applications have been multiple. Methods have now been published for the determination of 66 elements directly or indirectly by atomic absorption.³⁵

This chapter will be devoted to a discussion of the development of those techniques which yield optimum sensitivity for the determination of barium by means of atomic absorption spectroscopy.

The determination of trace concentrations of barium by atomic

absorption methods has been limited by the poor sensitivities which have been currently attained. Sensitivity as referred to in this dissertation is defined as the μg per ml which yield 1% absorption signal. Detection limit is defined as the μg per ml which will yield an absorption signal twice the height of the noise fluctuation signal.

TABLE II
SENSITIVITIES FOR BARIUM BY ATOMIC ABSORPTION ANALYSIS

Reference	Year	Sensitivity $\mu\text{g/ml}/\%$	Detection limit $\mu\text{g/ml}$	Flame
Gatehouse and Willis ³⁶	61	8.0		air-acetylene
Slavin ³⁷	64	5.0	1.0	air-acetylene
Amos and Willis ³⁸	66	0.4 ^a	0.1	nitrous oxide acetylene
Willis et al ³⁹	69	0.3 ^a	0.15	nitrous oxide acetylene

^a Addition of KCl to suppress ionization of barium

Table II presents a record of the sensitivities achieved in determining barium. The two factors which have contributed most to the attainment of ever greater sensitivities are the use of the

higher temperature of the nitrous-oxide acetylene flame and the suppression of ionization with an excess of an easily ionized alkali. These two factors will be discussed in the following pages. A third factor, the use of organic solvents to enhance the sensitivity, to my knowledge has not been applied to barium determinations. A discussion of the principles underlying this enhancement will follow. The experimental work and results make up the greater part of this dissertation.

Nitrous Oxide-Acetylene Flame

The flame provides the essence of atomic absorption spectroscopy in most conventional approaches, that is, it changes the element to the separated, isolated atoms in the ground state, placed in the path of the light of characteristic wavelength. There have been several studies directed to replacing the flame as a means of atomization but to date these methods have not been used for routine analysis.

A flame is characterized by the gases involved, the temperature, the burning velocity, the form in which the gases are mixed, the shape, size, and the regions of reaction.

The air-acetylene flame has been used to the greatest extent for the largest number of metals. It was generally used in a turbulent flow, total consumption burner, and it reached temperatures around 2300°C , with a burning velocity of 160 cm sec^{-1} . With this atomization process, the sensitivity attained for barium reached only $5.0\text{ }\mu\text{g/ml}/\%$. At this temperature, barium, the other alkaline earths and a large number of elements which form refractory oxides were not

totally dissociated. Koirttyohann⁴⁰ estimates that in the air acetylene flame, the fraction of barium existing as a free atom is about 0.0011. In addition, chemical interferences caused by reactions with other substances present in the system formed molecules which remained undissociated. The difficulty of completely atomizing the metal was long recognized as the principal limitation of the atomic absorption technique.

Several studies³⁵ (p. 38) were conducted to investigate the use of the higher temperatures (3060°C) of the oxygen acetylene flames. Due largely to the high burning velocity of this mixture (1130 cm sec^{-1}) the danger of flash back in a premix burner was great.

In 1965 Willis⁴¹ published his work utilizing a nitrous oxide-acetylene flame with a premix laminar flow burner. It was quickly recognized that this flame combined the high temperature (2955°C) of the oxy-acetylene flame with the low burning velocity (180 cm sec^{-1}) of the air-acetylene flame; this flame has been widely used for the determination of the metals forming refractory oxides and the alkaline earths, and virtually all interferences were eliminated. Using the nitrous oxide-acetylene flame, Willis was able to achieve $0.3\text{ }\mu\text{g/ml/1\%}$ sensitivity for barium. The increased sensitivity attained with the nitrous-oxide acetylene flame has been attributed to the high temperature. Kirkbright et al⁴² suggests the enhancement of sensitivity is also due to the existence of more free carbon species in the flame which provide reducing conditions. He was able to detect the existence of CN and NH particles throughout the flame. These are formed in the primary reaction zone and provide a reducing

atmosphere which protects the metal atoms.

The use of the premix laminar flow burner rather than the turbulent total consumption burner is another factor of increased sensitivity. The time the sample remains in the flame is dependent on gas flow rate. In a turbulent burner the flame velocity is high, the gas flow is high, and the residence time in the flame is short. The turbulent flame is circular, approximately 1 cm in diameter and has a very short light path through the sample. The greater instability of the turbulent flame increases the noise fluctuation and gives poorer detection limits.

The premix burner, on the other hand, produces a steady flame with less fluctuation and a more constant concentration of atoms. The flame velocity is lower, consequently the longer residence time in the flame encourages formation of ground state atoms. Chemical interferences are fewer because there is time for more complete vaporization.

The length of the slot varies from 5-10 cm. This allows for a longer light path length. The size of the slot is a compromise between the danger of a flashback when the opening is too large and the tendency to clog with unburned carbon particles when the opening is too small. Clogging sometimes occurs at higher solid contents because of precipitation of the salt at the hot slot from which the flame gases emerge.

A realistic picture of the effectiveness of the premix burner is presented by Allan.⁴³ The sample is sprayed at the rate of

2 ml/min. Only about 0.1 ml is sufficiently finely divided to reach the flame. The remainder is held by the spray chamber and lost. This 0.1 ml is diluted with about 10 liters of air and fuel gas. The volume expands to 80 liters at flame temperature. The procedure is comparable to one in which 95% of the sample is discarded down the drain and the remainder is diluted nearly a million-fold before actual absorption measurements are made.

Suppression of Ionization

When higher temperatures of the nitrous oxide acetylene flame were used a new phenomenon was encountered in atomic absorption spectroscopy of barium. The absorption signal is a function of the number of atoms in the ground state present in the path of the light beam. If the population of ground state atoms were a function only of vaporization and dissociation, then the hottest flame possible would be optimum. However for elements like barium which have an ionization energy of 5.2 eV, one or more electrons can easily be removed and the atom no longer absorbs at the same wavelength. Manning,⁴⁴ using the Saha equation, has calculated the degree of ionization of the barium atoms in the nitrous oxide flame and found it to be 92% ionized. He was able to confirm the ionization experimentally by monitoring the absorption of the ground state barium at $5535\text{\AA}$ and that of the ionized barium at $4554\text{\AA}$. He found 92% ionization.

This ionization can be suppressed by the presence of a more easily ionized metal such as potassium (4.3 eV) or cesium (3.9 eV).

The high concentration of electrons from the reaction

tends to reverse the ionization reaction

Manning has followed the effect of increasing concentrations of potassium on the intensity of signal of both the ground state line (5535Å) and the ion line (4554Å). The results are presented in Figure 2. Manning has studied the effect of the presence of potassium and phosphorus on the absorption of barium in both an air-acetylene flame and a nitrous oxide-acetylene flame. Figure 3 presents graphically these results. The small effect of added potassium in the air acetylene flame indicates very little ionization at that temperature. The increased absorption with increased concentration of potassium in the nitrous oxide acetylene flame is evidence of suppressed ionization. Manning found optimum enhancement of the barium signal at 10,000 ppm potassium concentration.

Therefore optimum sensitivity for barium can be achieved by using the nitrous oxide acetylene flame which is hot enough to provide volatilization and dissociation, while adding fixed concentrations of potassium to both standards and sample to suppress the ionization and keep the ground state populated. Willis³⁹ attained a 0.3 µg/ml/% sensitivity by adding 1000 µg/ml of K to the solutions.

Source at High Intensity

The characteristic spectrum of barium consists of an ionic doublet at 4554Å and 4934Å, an atomic resonance line at 5535Å and a

FIGURE 2 EFFECT OF ADDED POTASSIUM ON
 ABSORPTION OF BARIUM

FIGURE 3 EFFECT OF ADDED POTASSIUM AND PHOSPHORUS ON
BARIUM ABSORPTION AT 5535⁰Å

series of emissions from BaOH and BaO within the regions 4500-6100Å. In a hollow cathode source the ion line at 4554Å and the atom line at 5535Å are the most intense, but according to Koirttyohann and Pickett⁴⁵ the ion lines have limited analytical utility because of variable ionization.

Generally the barium hollow cathode lamp is constructed to operate at 20 mA. However, the nitrous oxide-acetylene flame emits intensely and at the given wavelength can exceed the intensity of the source unless the source is capable of intense emission. This high emission from the flame is evident as a strong noise level at the readout. Kahn,⁴⁶ Willis⁴⁷ and Slavin⁴⁸ have each overcome this limitation by operating the barium hollow cathode lamp at a much higher current than 20 mA. All the published methods for the analysis of barium recommend the use of the characteristic wavelength, 5535Å.

Organic Solvent Effect

The sensitivity of an atomic absorption method depends essentially upon the number of ground state atoms in the path of the light through the flame. Any factor which can increase the concentration of atoms of an element will enhance the absorption signal and hence the sensitivity.

A technique which has greatly increased the applications and the range of atomic absorption analysis is the use of organic solvents. These solvents are employed in two ways, either as miscible solvents that are added to the aqueous solutions or as immiscible ones that are sprayed directly into the flame after being used to

extract the metal species from the aqueous phase. The method of extracting a solute from an aqueous solution and spraying it into a flame was first described by Dean and Lady.⁴⁹

When Allan⁵⁰ used organic solvents in atomic absorption analysis, he found that sensitivities were increased 3-7 fold.

The combination of extraction with atomic absorption not only enhances the signal but also gives the added advantage of concentrating a dilute sample or removing an interfering matrix. West et al.⁵¹ attained a hundred-fold enhancement in the sensitivity of silver by extraction into a dithizone-ethyl propionate solution.

When an element is nebulized and enters a flame a sequence of processes takes place. The solvent evaporates or burns to form a solid particle; the particle then vaporizes to form gaseous molecules; thermal dissociation of the molecule occurs and free atoms in the ground state or an excited state are liberated.

How far and how fast these processes proceed depends on the size and dispersion of the droplets and solid particles, on the flame parameters including temperature, velocity of propagation, and composition of flame, on the rate processes and on the thermodynamic stability of the compounds introduced. According to Chakrabarti⁵² the enhancement produced by organic solvents is mostly due to the production of smaller droplets which cause smaller and more volatile droplets to be produced lower in the flame, thus atoms are produced sooner and live longer. This explanation supports the theory first proposed by Robinson⁵³ that enhancement from organic solvents can be attributed mainly to increased atomization efficiency.

The publications of Gibson et al.⁵⁴ and Willis⁵⁵ also propose this explanation. Gibson et al. studied photographically the profile of droplets in the flame. Acetone spray evaporated rapidly, and left no visible droplets more than 1 cm above the burner tip, while water spray was visible throughout the whole volume of the flame and some passed through the flame without being evaporated.

Increased atomization efficiency is considered by most workers in the field to contribute most to the enhancement of the absorption signal; nevertheless, Allan,⁵⁰ Zolotov⁵⁶ and Jaworowski⁵⁷ claim that there is also an increased uptake rate and an increased amount of solution reaching the flame when organic solvents are used. Belcher⁵⁸ has shown that the ratio of the absorbances of silver in methylethyl ketone, water and glycerol is in direct proportion to the ratio of their uptake by the nebulizer.

When water is aspirated into a flame, the vaporization process lowers the flame temperature, but when an organic solvent is introduced the combustion of the solvent causes an increase in temperature. The increased temperature of the flame when organic solvents are used is a contributing factor to the enhancement. Robinson⁵³ has shown that the temperature factor cannot account for the total enhancement. Gibson⁵⁴ has determined a 100°C rise in flame temperature when the solvent is changed from water to acetone; however the temperature increase can account for only a small portion of the overall enhancement.

Other factors that may explain the enhancement produced by organic solvents are the more reducing atmosphere caused by the

presence of a species that contains carbon and the lower energy of dissociation of organic compounds of metals in comparison with the inorganic compounds.

In order to obtain optimal performance an organic solvent that has the following characteristics should be chosen.

The solvent should totally extract the test element,
should burn with a stable flame,
should have a low viscosity,
should have a low surface tension,
should vaporize easily,
should be immiscible with aqueous solution,
should be free from toxic products of combustion,
and should be free from high background and absorption
at the selected wavelength.

Alan⁵⁰ has investigated at length the characteristics of specific solvents to be used in atomic absorption. Chloroform and carbon tetrachloride yield unstable flames which are soon extinguished. The higher alcohols leave an incompletely burned deposit of carbon. Benzene, cyclohexane, petroleum ether and diisopropyl ether aspirate too easily into the flame, and the air supply is insufficient for complete combustion. Benzene produces a large, luminous, smoky flame. Esters and ketones are the only solvents which behave satisfactorily in the flame; they burn completely with a steady flame, and with no absorption of solvent.

PART II EXPERIMENTAL

CHAPTER 4 A CHELATING REAGENT FOR BARIUM

CHAPTER 5 AN EXTRACTION SYSTEM DESIGNED FOR AN OPTIMAL ATOMIC
ABSORPTION SIGNAL

CHAPTER 6 A SENSITIVE, SELECTIVE METHOD FOR DETERMINATION OF
BARIUM IN TRACE CONCENTRATIONS IN AQUEOUS SYSTEMS

CHAPTER 4

A CHELATING REAGENT FOR BARIUM

The barium ion (Ba^{2+}) is a diffuse large ion, (Goldschmidt radius $1.43\text{\AA}$) and is doubly charged. The ease of complexation of an ion increases as the ionic potential of the species increases. This explains why few successful attempts to complex barium are found in the literature. The barium complex of a particular ligand usually exhibits the lowest stability constant relative to the complexes of that ligand with the other alkaline earth elements. A reagent which would not only complex barium but which would form a sufficiently stable molecule to be extracted into an organic solvent had to be found.

Glyoxal bis-(2-hydroxyanil)

Goldstein and Mayer⁵⁹ list barium as an interference in the test for calcium with glyoxal bis-(2-hydroxyanil) (GBHA). The reagent was synthesized and purified according to the method recommended by the above authors. The method recommended by Lindstrom and Milligan⁶⁰ for calcium was used to attempt complexation of barium. A color slightly different from that of the solution of the reagent was observed, but it was not the intense red observed with calcium. The color faded quickly.

Ten ml of each of the following esters, ethyl acetate, ethyl propionate, n-amyl acetate, ethyl formate, were used to attempt extraction. The standard procedure for the determination of

barium by means of Atomic Absorption was followed; a Perkin Elmer 303 Atomic Absorption Spectrophotometer was used. The results were all negative. There was no evidence of barium in the organic phase.

According to Morrison and Freiser³² the alkaline earth metals, being so electropositive, are difficult to complex. Some success has been attained by using an excess of a complexing agent to remove the water of hydration. High concentrations of GBHA were used but no positive results were obtained. Further attempts were made to complex barium by means of the method of Kerr.⁶² He found a pH of 12.2 - 12.6 optimum for calcium extraction. The pH was varied from 10.5 to 13.0. At no time was there evidence that GBHA could successfully complex and extract barium.

Eriochrome Black T

Since Eriochrome Black T can be used as an indicator in the titration of calcium and the alkaline earth ions, an attempt was made to complex barium with this reagent. The method of Pollard and Martin¹⁷ was used:

Experimental:

Stock solutions of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} were used at a concentration of 10 mg/ml. Twenty-five ml of a buffer solution (0.75% W/V NH_4Cl /dil NH_4OH) were added to 10 ml of the metal solution. Ten ml of a 0.1% solution of Eriochrome Black T in methanol were added and the final solution was diluted to a volume of 100 ml.

Absorbance readings were taken by means of a Beckman DB Spectrophotometer. The results appear below:

Metal	Color	Absorbance
Mg^{2+}	decided rose	strong peak at 560 mμ

Ca^{2+}	rose	less strong peak 560 m μ
Sr^{2+}	blue	peak at 620 m μ
Ba^{2+}	blue	peak at 620 m μ
blank	blue	peak at 620 m μ

When the concentration of barium was increased, a slight peak was visible at 560 m μ .

The method of Rowley, Stoenner and Gordon⁶³ was attempted; 200 mg, 100 mg, 50 mg, and 10 mg Ba^{2+} samples were used. Evident color changes from blue of the blank to rose of the samples indicated that a complex had formed.

After extraction with isopropyl ketone there was a rose organic phase and a blue aqueous phase. An acetone solution of potassium tetraphenyl boron^{*} was added to the organic phase and atomic absorption readings were taken. The maximum absorption of barium was still in the aqueous phase.

EDTA

EDTA has long been recognized as a complexing agent for barium as well as for many other metal ions. Recently an EDTA-metal complex has been extracted successfully.⁶⁴

Experimental:

A sample of $\text{Ba}(\text{OH})_2$ had been irradiated and the tracer Ba^{131} was used. Ba^{131} was complexed with EDTA following the method of Sijderius.⁶⁵

* Added as a source of potassium necessary to suppress the ionization of barium in atomic absorption. Previous studies indicated this as a suitable method of dissolving potassium in an organic solvent.

Experimental:

Ten ml of an $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ buffer, and 5 ml of 0.01 M EDTA solution were added to 10 ml of a barium solution of 2 mg/ml concentration.

Extraction was attempted using the method of Zolotov.⁶⁴

Five ml of diphenylguanidine (DPG) 0.9 M were added to the above solution. Ten ml of 1:1 nitromethane and isobutanol were used to extract the EDTA-barium complex.

The efficiency of extraction was found by determining Ba^{131} by means of a Geiger-Muller tube. Results are given below:

	15 minute count
Organic phase	98 cpm
Aqueous phase	36 cpm
Background	41 cpm

The activity of the tracer was so low that no significant conclusions could be drawn, except to note that there was evidence of some extraction into the organic phase.

Sulphonazo-III

A reagent, Sulphonazo-III or 3,6-bis(o-sulphophenylazo) chromotropic acid, specific for barium had been synthesized and studied by Savvin.¹⁹ Several features are worthy of note:

- (a) Studies show that the reagent is planar, and is able to coordinate barium, to form a series of 6-membered ring structures.
- (b) There is possibility of modifying the chelate by varying the group which is meta to the diazo coupling.
- (c) The three sulfonic acid groups that are not involved in

chelation cause high solubility in aqueous systems and difficulty in extracting the complex into organic solvents.

Experimental:

The Budesinsky⁶⁶ method of complexing barium was attempted.

Ten ml Ba^{2+} (13.6 $\mu\text{g/ml}$) was added to 5 ml 10^{-4} M Sulphonazo-III. The pH was adjusted to 2.4 by means of a utropine buffer.

Results:

The blank reagent was violet, the barium complex a distinct blue. Spectrum obtained by means of the DB Spectrophotometer at pH 6.0 showed a maximum at 638 m μ for the complex but showed no maximum characteristic of the blank. When utropine was added, the blue color changed to violet. This indicated an unstable complex.

Sulphonazo-III containing 4 sulfonic acid groups tends to be extremely soluble in H_2O and resists extraction into an organic layer. Kuznetsov⁶⁷ had successfully extracted complexes of Arsenazo-III containing 2 sulfonic acid groups by converting the anion groups to simple salts with diphenylguanidine (DPG) and extracting with n-butanol. His method was adapted in an attempt to extract the Ba-Sulphonazo-III complex.

Experimental:

Ten ml of Ba^{2+} (13.6 $\mu\text{g/ml}$) is mixed with 5 ml of Sulphonazo-III (10^{-4} M). Three ml of 20% DPG in HCl were added. Five ml of butanol were used to extract.

Results:

When the DPG is added, the blue color of the complex changes

to the violet color of the reagent. Complete extraction of the color results; the aqueous layer is colorless, the organic layer deep violet. Barium was complexed at pH 6.0, 4.0, 2.4 and 1.0. The barium-complex remained stable at all pH's except those below 2.4. Upon addition of DPG, the complex was unstable.

A number of amines were substituted for diphenylguanidine. In each case the stability of the complex was indicated by the retention of its blue color, but the complex was totally insoluble in an organic solvent.

The stability of the complex is related to the acid character of the sulfonic acid group ortho to the azo coupling. The strength of this acid group is influenced by the inductive nature of the group para to the azo coupling. Dimethylsulphonazo-III and Dibromosulphonazo-III were both used as chelating reagents. Better results were attained but at no time was an extraction efficiency better than 48% achieved.

Budesinsky²¹ has successfully extracted the barium-complex of the methyl derivative of the dianilide of sulphonazo. A sample of the reagent was obtained from him and extractions were attempted. The results obtained were the most promising to date and further investigation is suggested using this method. However the reagent is not available commercially and much better extraction was achieved when the β -diketones were used as ligands.

β -diketones

A study was then begun to compare the efficiency of extraction of a number of β -diketones which were available from a Senior thesis

study.⁶⁸ The method of Eshelman and Dean⁶⁹ was adapted.

Experimental:

Four ml Ba^{133} (5.0×10^{-5} M) was combined with 10 ml NH_4OAc (1 M) to adjust pH to 5-6. Ten ml β -diketone (0.1 M) in methyl isobutyl ketone were used to extract. The phases were separated and 5 ml of each phase was counted for 5 minutes.

The results are presented in Table III

TABLE III
EXTRACTION OF BARIUM- β -DIKETONATES

	Count/ml		% extraction*
	organic	aqueous	
4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione	6036 cpm	5236 cpm	46.1
4,4,4-trifluoro-1-phenyl-1,3-butanedione	3108 cpm	5462 cpm	28.9
2-phenyl-1,3-indandione	water soluble		
1,1,1,5,5,5-hexafluoro-2,4-pentanedione	9242 cpm	199 cpm	97.6

$$* \quad D = \frac{\text{cpm/ml organic}}{\text{cpm/ml aqueous}}$$

$$\% E = \frac{100 D}{D + V_w/V_o}$$

Extractions of the hexafluoroacetylacetonate were repeated with

other solvents.

Results:

<u>Solvent</u>	<u>% E</u>
MIBK	94.5
ethyl propionate	97.06
butyl alcohol	93.65
butyl acetate	97.70

Conclusion:

Of all the complexing reagents used, only hexafluoroacetylacetone formed a sufficiently stable chelate with barium to allow complete extraction of the barium into an organic solvent. All further studies were directed toward determining optimal conditions for extraction and improvement of the sensitivity in atomic absorption determination. The structural formulas for the chelating agents are presented in Figure 4.

FIGURE 4 CHELATING REAGENTS FOR BARIUM

Glyoxal-bis(2-hydroxyanil)

Eriochrome Black T

Hexafluoroacetylacetone

Sulfonazo - III (Y = H)

Dimethylsulfonazo - III (Y = CH₃)

Dimethylsulfonazo - III DAL (Y = CH₃)

CHAPTER 5

AN EXTRACTION SYSTEM DESIGNED FOR AN OPTIMAL ATOMIC ABSORPTION SIGNAL

It was evident that hexafluoroacetyl acetone was efficiently extracting barium. The variables affecting the extraction system were studied in order to maximize the absorption of barium in the organic phase. Factors known to influence this absorption were:

- (a) Selection of either the ground state line at $5535\text{\AA}$ or the excited state line at $4554\text{\AA}$.
- (b) Selection of the solvent that gives optimum sensitivity.
- (c) Presence of sodium or potassium in the organic solvent to suppress ionization.
- (d) pH at which the extraction takes place.
- (e) Concentration of the chelating agent.
- (f) Concentration factor relating the volume of the aqueous phase to that of the organic phase.

Solvent

Experimental:

Twenty-five ml Ba^{2+} solution $100\text{ }\mu\text{g/ml}$, was buffered to a *pH of 9.0 using a 1/10 ratio of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$. *Ten ml of HFA (0.1 M) in selected solvent was added and the solution was agitated for 5 minutes. The absorption for the aqueous and for the organic phase was determined.

* pH value and reagent concentration had been suggested by Westrich.⁷⁰

The results are presented in Table IV.

TABLE IV
EFFECT OF SOLVENT ON EXTRACTION AND ABSORPTION OF BARIUM

Solvent	% Absorption		pH
	organic	aqueous	after extraction
amyl acetate	82	0	7.0
butyl acetate	78	0	7.3
n-butyl alcohol	47	46	7.3
ethyl propionate	64	0	6.9
methyl isobutylketone	70	0	7.3

All of the solvents used, with the exception of butyl alcohol had given complete extraction. Therefore the choice of solvent depended upon other factors. Amyl acetate had given the greatest enhancement of signal. Its solubility in water is given as 0.2 ml/100 ml. N-amyl acetate was used in the above studies, but it was later found that iso-amyl acetate gave comparable results. Iso-amyl acetate was used in all further studies.

Three factors simultaneously influencing the absorption of barium and interacting with one another had to be isolated for study. The study of the pH at which maximum extraction occurred necessitated the use of a sodium or potassium buffer system to

attain a pH above 10. Sodium and potassium both acted as ionization suppressers and altered drastically the absorption signal. The choice of the characteristic wavelength at which barium absorbed was dependent on whether a system was chosen to enhance ionization by removal of all alkali elements or to suppress ionization with the alkalies. The studies will be presented separately but are totally dependent on one another.

Ionization Suppression

The effect of sodium or potassium on the absorption of barium has been discussed in Chapter 3. The extent of extraction of sodium and potassium into the organic solvent had to be determined. Extractions according to the method previously described were repeated both in the presence and absence of sodium and potassium. Absorption was monitored at both the atom line, ($5535\text{\AA}$), and the ion line ($4554\text{\AA}$). The results are presented in Figure 5. The suppression of the ion line from 78% to 54% in the presence of 1000 $\mu\text{g/ml}$ sodium and potassium gives strong evidence that extraction is occurring. The enhancement of the ground state absorption from 42% to 48% supports this. Since the signal at the ion wavelength was yielding greater sensitivities the decision was made to attempt masking the extraction of both sodium and potassium.

Akaza⁷¹ had successfully extracted sodium and potassium, as polyiodides into a solution of nitrobenzene. When this extraction was performed on a barium solution containing equal quantities of sodium and potassium, all of the potassium was extracted, sodium

FIGURE 5 EFFECT OF SODIUM AND/OR POTASSIUM
ON THE ABSORPTION OF BARIUM

was not extracted quantitatively and barium was also extracted into the nitrobenzene.

The next approach was to mask the sodium and potassium in the aqueous phase. Literature contained the possibilities that are presented in Table V.

TABLE V
MASKING REAGENTS FOR POTASSIUM AND SODIUM

Reference	Potassium	Reference	Sodium
74	dipicrylamine	72	zinc uranyl acetate
72	hexanitrocobaltate		potassium hydrogen arsenate
75	tetraphenyl boron		
73	picric acid		1-amino-8-naphthalene sulfonic acid
74	2-chloro-3-nitro-toluene-5-sulfonic acid		
74	4,6,-dinitrobenzofuroxan		

Since sodium is so universally present in aqueous systems, attempts were made to mask sodium from extracting.

Experimental:

Twenty-five ml of a Ba^{2+} solution, 100 μ g/ml, was buffered to a pH of 9.0 using a 1/10 ratio of NH_4Cl/NH_4OH . The volume of the aqueous solution was made up to 100 ml. Ten ml of HFA 0.1 M in isoamylacetate

was used for the extraction. The extractions were varied as follows:

- extraction #1, nothing was added;
- extraction #2, a sodium solution was added to give a sodium concentration of 100 $\mu\text{g/ml}$ in aqueous phase;
- extraction #3, zinc uranyl acetate was added to a solution identical to #2;
- extraction #4, potassium hydrogen arsenate was added to a solution identical to #2.

Results:

The results of the extractions are presented in Figure 6. There was no significant masking of sodium by either reagent while barium itself was masked by the zinc uranyl acetate.

Since we had to work with systems containing sodium and potassium, the decision was made to use the ground state resonance line ($5535\text{\AA}$) and to add sufficient alkali for maximum suppression of ionization of the barium.

Experimental:

Two ml of a Ba^{2+} solution, 100 $\mu\text{g/ml}$, was buffered with 15 ml of buffer. A potassium nitrate solution was added to give the desired concentration of potassium. The solution was diluted to 50 ml, and extracted with 5 ml HFA (1 M) in isoamyl acetate.

Results:

Figure 7 presents the absorption from the extractants. It is evident that there is no further enhancement of signal at any concentration of potassium above 1000 $\mu\text{g/ml}$ in the aqueous phase. All subsequent extractions were carried out with this concentration of potassium.

Figure 8 presents the results of increasing the sodium concentration in the presence of 1000 $\mu\text{g/ml}$ of potassium. Since there

FIGURE 6

ABSORPTION OF BARIUM AND SODIUM IN PRESENCE
OF MASKING AGENTS FOR SODIUM

FIGURE 7 CONCENTRATION OF POTASSIUM NEEDED FOR
MAXIMUM SUPPRESSION OF IONIZATION

FIGURE 8 EFFECT OF SODIUM ON THE ABSORBANCE OF BARIUM IN
 THE PRESENCE OF 1,000 $\mu\text{g/ml}$ POTASSIUM

(Barium concentration 0.5 $\mu\text{g/ml}$)

was no significant enhancement of signal, the presence of sodium can be ignored in any system containing potassium at 1000 $\mu\text{g/ml}$.

pH Extraction Curve

pH studies were initiated using an $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer and HCl to adjust the pH. Extractions were completed from solutions with a pH of 5-10 with significant results. A pH of 10 was the maximum obtainable by the use of an NH_4OH system. Therefore extended studies required the use of NaOH which extended the range from 7-12. Because there was erratic absorption dependent on the presence of sodium, the ionization suppression studies were completed, and indicated the need of a constant concentration of 1000 $\mu\text{g/ml}$ potassium.

The extraction experiments were repeated on the same buffered systems described above. Further extractions in the presence of KOH to give a pH above 10 were completed. The complexation reaction if not buffered shows a large drop in pH. To prevent this pH drop high concentrations of KOH had to be used. To keep the potassium concentration constant in all extractions 15,000 $\mu\text{g/ml}$ was added to each sample. This resulted in a clogging of the burner by an encrustation of salt.

Two phenomena were interacting in the extraction; the extraction of barium and the extraction of potassium. In order to study the two separately Ba^{133} tracer studies were initiated.

Experimental:

Two ml of a Ba^{2+} solution, 100 $\mu\text{g/ml}$, was added to 3 ml of a potassium acetate solution, 100 mg/ml . The solution was buffered with 25 ml buffer to attain the desired pH. For a pH of 4-6 HOAc/KOAc was used; for a pH of 9-11, $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$; and for a pH of 12-14, KOH was used. The final solution was

diluted to 300 ml and extracted with 5 ml HFA (1 M) in isoamyl acetate.

Results:

Identical extractions were carried out; in one series tracer Ba^{133} was used and counts were taken with a Scintillation Counter; in the other series a stable barium isotope was used and atomic absorption signals were recorded. The results are presented in Figure 9. It was clearly evident that barium was extracting completely at every pH, yet the atomic absorption signal is a function of the pH of extraction. This dependence was suspected to be related to the potassium extraction function. A second series of identical extractions was performed and monitored for potassium absorption (4040Å) and barium absorption 5535Å. The results are presented in Figure 10. The conclusion follows that the absorption signal of barium is closely related to the extraction of potassium.

Buffer Capacity

During the studies, a decided drop in pH during the complexation reaction was noted. Therefore it became necessary to control the concentration of the buffer to stabilize the pH. The following extractions determined the quantity of buffer needed.

Experimental:

Solutions of 2 ml of 100 $\mu\text{g Ba}^{2+}$ /ml and 10 ml of 10 mg K^+ /ml were buffered with varying amounts of a buffer of NH_4OAc (2 M)/ NH_4OH (2 M) in the ratio of 1/9. The solutions were diluted to 100 ml and extracted with 5 ml HFA (1 M).

The results are presented in Table VI.

FIGURE 9 EXTRACTION AND ABSORBANCE OF BARIUM AS
A FUNCTION OF pH

FIGURE 10 ABSORPTION OF BARIUM AND POTASSIUM AS A
FUNCTION OF pH

TABLE VI
BUFFER CONCENTRATION NEEDED FOR CONSTANT pH

Vol. of buffer (ml)	pH before extraction	pH after extraction
10	10.6	9.6
20	10.6	10.0
40	10.6	10.2
60	10.6	10.3
80	10.6	10.4

To maintain a pH of 10, it is necessary to use a ratio of 1 to 5, buffer to total volume of solution.

Concentration of HFA needed

Experimental:

One ml of a solution of 10 $\mu\text{g Ba}^{2+}$ /ml was combined with 30 ml of a solution of 10 mg K^+ /ml and 60 ml of the buffer solution described previously. The total solution was diluted to 300 ml and extracted with 5 ml portions of HFA in isoamylacetate of varying concentrations.

The results are presented in Table VII.

TABLE VII
CONCENTRATION OF HFA

Concentration of HFA	Absorption
.05 M	0

TABLE VII (continued)

Concentration of HFA	Absorption
.10 M	0
.30 M	2%
.50 M	5%
1.0 M	9%

The concentration of HFA should be maintained at 1.0 M.

Concentration Factor

One aspect of the method remained to be determined; the dilution from which the system was able to extract efficiently. The efficiency of extraction would be dependent especially upon two factors, the concentration factor or the ratio of the volume of the organic phase to the aqueous phase and secondly the minimum concentration from which barium can be extracted.

Experimental:

Two ml of a solution of 12.5 $\mu\text{g Ba}^{2+}$ /ml was diluted to 25 ml, 50 ml, 100 ml, 200 ml and 1,000 ml. Each sample was made 1,000 $\mu\text{g/ml}$ in potassium. Sufficient buffer was included to attain a ratio of 1:5, buffer to total volume. Extraction was done with HFA in isoamyl acetate. If total extraction took place the absorption signal would be constant since the weight of barium used had been constant.

Three sets of extractions were completed with the results as presented in Table VIII and Figure 11.

TABLE VIII
EXTRACTION FROM MINIMUM CONCENTRATION
AND MAXIMUM DILUTION

Total Volume (ml)	Ba^{2+} Conc. $\mu\text{g/ml}$	Concentration factor	HFA		% Absorption
			Volume (ml)	Conc. (M)	
A Using 2 ml of 12.5 $\mu\text{g } Ba^{2+}/\text{ml}$					
25	1.00	5:1	5	0.3	7.5
50	0.50	10:1	5	0.3	7.5
100	0.25	20:1	5	0.3	8.0
200	0.125	40:1	5	0.3	6.0
1,000	0.025	200:1	5	0.3	0.0
B Using 2 ml of 12.5 $\mu\text{g } Ba^{2+}/\text{ml}$					
100	0.25	20:1	5	1.0	15.5
200	0.125	40:1	5	1.0	16.0
300	0.083	60:1	5	1.0	16.0
400	0.062	80:1	5	1.0	14.0
500	0.050	100:1	5	1.0	11.0
C Using 1 ml 10 $\mu\text{g } Ba^{2+}/\text{ml}$					
20	0.5	4:1	5	1.0	3.0
30	0.33	6:1	5	1.0	4.0
50	0.20	10:1	5	1.0	4.0
100	0.10	20:1	5	1.0	4.0
200	0.05	40:1	5	1.0	4.0
300	0.03	60:1	5	1.0	4.0

Conclusion

These studies showed that extraction was complete down to a concentration of 0.03 $\mu\text{g/ml}$, when a concentration factor of 60:1 was used and the complexing reagent had a 1 M concentration.

CHAPTER 6

A SENSITIVE, SELECTIVE METHOD FOR DETERMINATION OF BARIUM IN TRACE CONCENTRATIONS IN AQUEOUS SYSTEMS

Solutions:

Hexafluoroacetylacetone (1 M)

34.9 ml (52.0 g) were diluted to 250 ml with isoamyl acetate. The reagent was obtained from Columbia Organic Chemicals, Inc. and used without purification. It is highly volatile and irritating to the respiratory tract if inhaled. Adequate ventilation is necessary when it is used.

Buffer solution (pH of 10.4)

55 ml of NH_4OAc (2 M) was added to 500 ml of NH_4OH (2 M).

Potassium

25.0 g potassium acetate was dissolved in 1 liter of solution for a stock solution of 10 mg/ml.

Barium standard solution

1.90 g of reagent grade barium nitrate was diluted to 1 liter to give a stock solution of 1 mg barium/ml.

Interference Cations and Anions

Stock solutions of 10 mg/ml concentration were used as recommended by West.⁷⁶

Apparatus:

Perkin Elmer 303 - Atomic Absorption Spectrophotometer
equipped with a Perkin Elmer Recorder Readout, and Texas

Instruments - Servoriter II. Tri-Flame Laminar-flow Burner from Jarell-Ash. Hoke Fuel Flow Meter.

Procedure: Extraction

Transfer an accurately measured volume of standard or sample barium solution to a 500 ml separatory funnel. Add 50 ml of $\text{NH}_4\text{OAc}/\text{NH}_4\text{OH}$ buffer solution. Add 30 ml of potassium stock solution. Dilute to 300 ml.

Add 5 ml HFA (1 M) solution* and agitate for 1 minute. Allow the phases to separate. Read the absorbance of the organic phase.

Atomic Absorption

The hollow cathode lamp for barium was operated at 30 mA[‡]. A slit width setting of 3(4⁰) and a noise suppression of 3 were used. Readings were taken at 5535⁰Å, the position of the barium resonance line.

A nitrous oxide-acetylene flame was used and while a solution was aspirated into the flame, the acetylene flow was adjusted to yield the maximum signal. On the Hoke flow meter, this flow was usually about 18 units for acetylene flow and 9 units for nitrous oxide flow, and resulted in a red feather zone approximately 1.5 mm high. The height of the burner was adjusted so the

* When the HFA solution is added to the buffered solution, a white smoke results due to the reaction between the fluorine of the HFA and the ammonia vapor. This white vapor is dissolved upon agitation and was not found to interfere with the extraction.

‡ It was originally operated at 20 mA resulting in an excessively noisy signal. When the current was increased the noise diminished.

beam passed through the flame about 1.4 cm above the burner.

A five minute warm up period was allowed after lighting the burner since it was found that the signal increased progressively during that time.

Calibration Curve

When the above procedure was used on standard solutions of barium ranging from 0.015 $\mu\text{g/ml}$ - 1.0 $\mu\text{g/ml}$ the calibration curve presented in Figure 12 and Figure 13 was obtained.

The sensitivity measured from the concentration in the aqueous phase is 0.005 $\mu\text{g/ml/1\%}$ absorption. The detection limit, with a 0.5% noise level, is 0.005 $\mu\text{g/ml}$ to give a signal twice the noise level.

Five separate extractions of barium were performed at 0.1 $\mu\text{g/ml}$ concentration. Results are presented in Table IX.

TABLE IX
PRECISION OF METHOD

Ba taken	Ba found
0.100 $\mu\text{g/ml}$	0.100 $\mu\text{g/ml}$
0.100 $\mu\text{g/ml}$	0.100 $\mu\text{g/ml}$
0.100 $\mu\text{g/ml}$	0.099 $\mu\text{g/ml}$
0.100 $\mu\text{g/ml}$	0.100 $\mu\text{g/ml}$
0.100 $\mu\text{g/ml}$	0.101 $\mu\text{g/ml}$
Relative Standard Deviation 0.7%	

FIGURE 12 CALIBRATION CURVE (0.015 - 1.0 $\mu\text{g/ml}$)

FIGURE 13 CALIBRATION CURVE (.015 - 0.10 $\mu\text{g/ml}$)

Interference Studies

Extractions were carried out by means of the procedure described previously from solutions containing 0.1 $\mu\text{g/ml}$ barium and the interfering ion at 100 $\mu\text{g/ml}$. The results are presented in Table X.

TABLE X
INTERFERENCES AT BARIUM CONCENTRATION OF 0.1 $\mu\text{g/ml}$

Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Ba ²⁺ found $\mu\text{g/ml}$	Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Ba ²⁺ found $\mu\text{g/ml}$
Group I			Group II (continued)		
Li ⁺	100	0.102	Ca ²⁺	10	0.104
Na ⁺	100	0.102	Zn ²⁺	100	0.100
K ⁺	100	0.102	Sr ²⁺	100	0.101
Cu ²⁺	100	0.102	Cd ²⁺	100	0.100
Rb ⁺	100	0.102	Hg ⁺	100	0.100
Ag ⁺	100	0.102	Hg ²⁺	100	0.101
Cs ⁺	100	0.102	Group III		
Group II			BO ₂ ⁻	100	0.100
Be ²⁺	100	--	B ₄ O ₇ ²⁻	100	0.101
Be ²⁺	10	0.090	Al ³⁺	100	--
Mg ²⁺	100	0.067	Al ³⁺	10	0.097
Mg ²⁺	10	0.089	Ce ³⁺	100	0.100
Ca ²⁺	100	0.093			

TABLE X (continued)

Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Ba^{2+} found $\mu\text{g/ml}$	Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Ba^{2+} found $\mu\text{g/ml}$
Group IV			Group VI (continued)		
CO_3^{2-}	100	0.096	SO_4^{2-}	100	0.100
SiO_3^{2-}	100	0.096	Cr^{3+}	100	0.078
GeO_3^{2-}	100	0.096	CrO_4^{2-}	100	0.102
Sn^{4+}	100	0.100	SeO_3^{2-}	100	0.104
Pb^{2+}	100	0.064	SeO_4^{2-}	100	0.100
Group V			MoO_4^{2-}	100	0.101
NH_4^+	100	0.100	TeO_3^{2-}	100	0.104
NO_2^-	100	0.106	WO_4^{2-}	100	0.104
NO_3^-	100	0.100	WO_2^{2+}	100	0.032
HPO_4^{2-}	100	0.091	Group VII		
VO_3^-	100	0.106	F^-	100	0.101
HAsO_4^{2-}	100	0.106	Cl^-	100	0.101
$\text{P}_2\text{O}_7^{4-}$	100	0.085	ClO_3^-	100	0.101
Sb^{5+}	100	0.098	ClO_4^-	100	0.101
Bi^{3+}	100	0.097	Mn^{2+}	10	0.042
Group VI			Br^-	100	0.101
S^{2-}	100	0.104	BrO_3^-	100	0.101
$\text{S}_2\text{O}_3^{2-}$	100	0.102	I^-	100	0.101
SO_3^{2-}	100	0.104	IO_3^-	100	0.101

TABLE X (continued)

Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Ba^{2+} found $\mu\text{g/ml}$	Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Ba^{2+} found $\mu\text{g/ml}$
Group VIII			Miscellaneous (continued)		
Fe^{3+}	10	0.028	malonate	100	0.098
Co^{2+}	10	0.093	EDTA	100	0.000
Ni^{2+}	10	0.093	tartrate	100	0.096
Miscellaneous			citrate	100	0.095
CNS^-	100	0.092	gluconate	100	0.101
oxalate	100	0.097	CN^-	100	0.098

Masking was attempted with those ions which gave significant interference in the above tests. These results are presented in Table XI.

TABLE XI

INTERFERENCE IN PRESENCE OF MASKING AGENTS AT
BARIUM CONCENTRATION OF $0.100 \mu\text{g/ml}$

Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Masking Agent	Conc. Masking Agent $\mu\text{g/ml}$	Ba^{2+} found $\mu\text{g/ml}$
Be^{2+}	100	fluoride	500	0.045
Be^{2+}	100	tartrate	100	0.068

TABLE XI (continued)

Interfer- ing Ion	Conc. of Interfer- ing Ion $\mu\text{g/ml}$	Masking Agent	Conc. Masking Agent $\mu\text{g/ml}$	Ba^{2+} found $\mu\text{g/ml}$
Al^{3+}	100	tartrate	100	--
Al^{3+}	100	fluoride	500	0.059
Al^{3+}	100	gluconate	300	0.080
Pb^{2+}	100	tartrate	100	0.104
Fe^{3+}	100	cyanide	100	0.011
Fe^{3+}	100	cyanide	700	0.017
Fe^{3+}	100	gluconic acid	300	0.014
Fe^{3+}	100	citrate	100	0.007
Fe^{3+}	100	tartrate	100	0.033
Fe^{3+}	10	cupferron	100	0.031
Fe^{3+}	10	gluconic acid + hydroxylamine hydrochloride	200 1000	0.031 0.066
Fe^{3+}	10	sodium diethyl- dithio carbamate	0.03M	0.093
Fe^{3+}	50	"	0.03M	0.096
Fe^{3+}	100	"	0.03M	0.073
Co^{3+}	100	tartrate	100	0.082
Ni^{2+}	100	cyanide	100	0.074
Ni^{2+}	100	tartrate	100	0.057

This method can tolerate Be^{2+} , Mg^{2+} , Al^{3+} and Co^{2+} at the hundred-fold level. Among the other common ions tested only Cr^{3+} and Mn^{2+} gave significant interference at the thousand-fold level. Tartrate was used to mask the Pb^{2+} interference and Fe^{3+} was masked with diethyldithio carbamate.

Summary

A sensitive, selective, simple method for the determination of barium in aqueous systems has been developed. The combination of the solvent extraction of the barium-hexafluoroacetylacetonate into isoamyl acetate with the determination by atomic absorption has increased the sensitivity previously attained by atomic absorption by a factor of two orders of magnitude from $0.3 \mu\text{g/ml}/\%$ to $0.005 \mu\text{g/ml}/\%$. Furthermore this method presents a simple quick method of determining barium at concentrations as low as $0.015 \mu\text{g/ml}$. This is within the range often found in natural waters.

It has been shown that the use of a high concentration of potassium in the aqueous system improves the sensitivity. The potassium is coextracted with the barium; it acts to suppress the ionization and enhance the absorption of barium.

At present there are few acceptable methods of adding potassium to an organic solvent for use in atomic absorption. Further study is necessary to determine whether potassium can be added to any solvent by means of its hexafluoroacetylacetonate form.

Further studies are proposed to determine the feasibility of the simultaneous extraction of a group of metals in the form of

their hexafluoroacetylacetonate complexes. The data obtained thus far indicates that other metals are coextracting.

Sulphonazo-III has been shown to act as a selective reagent for the spectrophotometric determination of barium. Further studies are suggested to determine the adaptability of this reagent to the spot test and the ring oven method of analysis.

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VITA

Sister Lucy Edelbeck is a native of Wausaukee, Wisconsin where she completed her elementary and secondary education. In 1948 she made profession and a life commitment to the Community of the Dominican Sisters in Racine, Wisconsin. She taught in the secondary schools in Michigan and Wisconsin. She graduated with a B.A. Degree from Mt. Mary College in Milwaukee, Wisconsin in 1951, and completed studies for an M.S. Degree at Creighton University in Omaha, Nebraska in 1961. She joined the faculty of Dominican College in Racine, Wisconsin in 1962, where she is presently an Associate Professor and Chairman of the Department of Natural Sciences.

She was awarded a Shell Fellowship at Cornell University in 1960, an NSF Faculty Fellowship at Louisiana State University in 1969 and membership in the Honor Society of Phi Kappa Phi in 1969. During the summer of 1965, under the auspices of the NSF College Teachers Institute she began studies at Louisiana State University where she is presently a Candidate for the Degree of Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: Determination of Trace Concentrations of Barium Extracted from Aqueous Systems

Approved:

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July 14, 1970