

AN ABSTRACT OF THE THESIS OF

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Title: AN INVESTIGATION OF THE ABSORPTION SPECTRA OF
EGTA METAL COMPLEXES AND THE DEVELOPMENT OF
SPECTROPHOTOMETRIC METHODS FOR THE ANALYSES
OF COPPER, ERBIUM, EUROPIUM, HOLMIUM,
NEODYMIUM, AND PRASEODYMIUM

Abstract approved: *Redacted for Privacy*
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The reactions of EGTA, [ethylene bis (oxyethylenitrilo)] tetraacetic acid, with 51 metal ions have been studied spectrophotometrically in aqueous solutions. The absorption spectra of the chelates formed were measured with a recording spectrophotometer between 200 and 700 m μ . The pH of each solution was varied and a spectrum was scanned at different acidity levels.

EGTA stock solutions were prepared by dissolving the acid in two or more equivalents of sodium hydroxide followed by aqueous dilution. The dibasic EGTA ion existed below pH 8 and the tetrabasic ion existed above pH 10. The reagent solutions possessed outstanding stability and with few exceptions retained their stability when complexed with metal ions.

The spectra of 25 metal ions showed measurable differences in the presence of EGTA. The majority of the solutions that formed characteristic spectra were stable. Many of the complexes formed were colorless in the visible region but did have characteristic spectra in the ultraviolet.

The most pronounced spectral changes in the ultraviolet region resulted from EGTA chelation with the following ions: iron (II), copper (II), palladium (II), europium (III), and thallium (I). In the visible region praseodymium (III), neodymium, holmium, erbium, iridium (III), gold (III), and uranyl ions had significant spectral differences resulting from the addition of EGTA.

The variety of spectral changes induced in various rare earth ions by complexation with EGTA made possible a specific qualitative identification of praseodymium in the presence of much greater concentrations of erbium, holmium, and neodymium.

The combining ratio of metal ion to EGTA was determined by a spectrophotometric method of continuous variations for copper (II), neodymium, holmium, and erbium. All ions formed 1:1 chelates. The conformity of the EGTA-metal ion solutions to Beer's Law was determined for copper, neodymium, europium, holmium, and erbium complexes.

A study was made of the quantitative use of the copper (II)-EGTA absorption maximum at 298 m μ and the holmium-EGTA

absorption peak at 450 m μ . Though the spectral absorption sensitivity of the holmium-EGTA complex was not large, the complex did have a molar absorptivity of over twice that of holmium ion. The absorption of the copper (II)-EGTA complex at 298 m μ , with a molar absorptivity of 3065, made possible routine analysis of copper ion in concentrations above one part per million.

The results of a series of analyses of solutions with copper concentrations from 4.00×10^{-5} M to 4.00×10^{-4} M showed good agreement with an average error of 1.4% of the known concentration.

An Investigation of the Absorption Spectra of EGTA Metal
Complexes and the Development of Spectrophotometric
Methods for the Analyses of Copper, Erbium,
Europium, Holmium, Neodymium,
and Praseodymium

by

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I. INTRODUCTION

EGTA

The compound EGTA, [ethylene bis (oxyethylenitrilo)] tetraacetic acid, derived the abbreviated form of its name from the designation under which it is marketed, ethylene glycol bis(beta-aminoethyl ether)-N, N'-tetraacetic acid. The compound can also be identified as 1, 2-bis-[2-di-(carboxymethyl)-aminoethoxy]-ethane and 1, 2-di-(2-aminoethoxy)-ethane-N, N, N'N'-tetraacetic acid.

The acid form of the compound (designated H_4X) has four replaceable protons and is insoluble in water. Like EDTA it is generally used in analysis as the disodium salt. Table I lists various ionization constants which have been reported for the dissociation of H_4X .

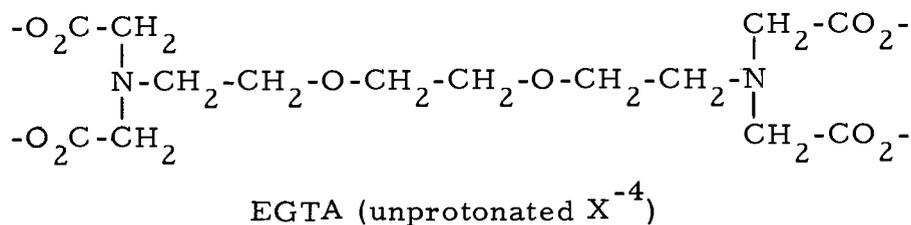


Table I. Dissociation constants for EGTA

$$\begin{aligned} \text{H}_4\text{X} &\rightleftharpoons \text{H}^+ + \text{H}_3\text{X}^{-1} \\ \text{H}_3\text{X}^{-1} &\rightleftharpoons \text{H}^+ + \text{H}_2\text{X}^{-2} \\ \text{H}_2\text{X}^{-2} &\rightleftharpoons \text{H}^+ + \text{HX}^{-3} \\ \text{HX}^{-3} &\rightleftharpoons \text{H}^+ + \text{X}^{-4} \end{aligned}$$

	A(8)	B(6)	C(19)	D(40)	E(31)	F(2)	G(41)
pK ₁	1.85	2.0	2.71	2.0	1.9		
pK ₂	2.86	2.65	3.06	2.65	3.2		
pK ₃	8.73	8.78	9.54	8.85	8.55	8.88	8.78
pK ₄	9.38	9.46	10.23	9.46	9.38	9.53	9.25

The values of A, F, and G in Table I were determined at 25°C, and the values of B, C, and D were determined at 20°C. No temperature conditions were reported for E.

Sudmeir and Reilley (41) have studied the protonation of X⁻⁴ in aqueous solution based upon NMR spectral shifts with the addition of equivalent amounts of H⁺ to the fully unprotonated form. Their results indicate that as the small difference between pK₃ and pK₄ was very close to the statistical minimum for dibasic acids ($\Delta\text{pK} = 0.6$), apparently two sites of equal basicity were protonated simultaneously as the number of equivalents of acid added went from zero to two. The symmetrical arrangement of the EGTA molecule suggested two types of basic sites. There were four acetate positions of equal basicity and two nitrogen positions of equal basicity. The shifts in the

NMR spectra indicated that when two equivalents of protons had been added, the two nitrogen positions were protonated 94 ± 6 percent of the time and the acetate sites 3 ± 3 percent.

The interaction of EGTA with metal ions as a chelon was a function of these properties.

Historical Aspects

The compound was first reported by Holleck and Eckardt (14) in a study of the effects of various complexing compounds on the visible absorption spectra of the neodymium ion in aqueous solution. The paper was submitted for publication on May 30, 1953.

On August 5 of the same year a British patent, number 695,346, was issued to J. R. Geigy, A.-G., of Basel, Switzerland for the preparation of EGTA with the notation that it was suitable for the simultaneous determination of alkaline earth metal ions by titration.

Holleck and Eckardt (12, 13) extended their studies to the term splitting effects of EGTA on the spectra of erbium and thulium. Later Holleck and Liebold (15) investigated the relationship between the decrease in paramagnetism of rare earth complexes and the magnitude of the complex stability constants. EGTA was one of six complexing agents studied. Holleck (11) summarized this work in 1959.

Schmid and Reilley (37) developed a method for titrating calcium in the presence of magnesium with EGTA using a mercury

indicator electrode for detecting the end point potentiometrically.

Ringbom, Pensar, and Wänninen (34) reported a satisfactory method for the visual titration of calcium with EGTA using Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) as an indirect indicator.

Flaschka and Ganchoff (10) developed a titration procedure for the analysis of calcium in the presence of magnesium using EGTA as the titrant and murexide as a photometric indicator. Ishii (17) used 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphtoic acid (N, N) or calcichrome for indicators in the titration of calcium.

Christian, Knoblock, and Purdy (5) titrated calcium with EGTA coulometrically generated from the mercury-EGTA complex at a mercury pool cathode. EGTA was used as a sequestering agent for calcium to permit the analysis of magnesium in blood serum by Lamkin and Williams (21).

In addition to the titration of calcium, EGTA has been used by Flaschka and Ganchoff (9) for the titration of cadmium in the presence of zinc using copper ion as a photometric indicator. Přebil and Veselý (33) also used EGTA for cadmium and zinc analysis. After a known amount of EGTA was added to the solution, the zinc complex was destroyed by the formation of the zincate ion and the excess EGTA (unchelated with cadmium) was titrated with calcium. Cadmium was determined by difference. The stability constants reported in their communication are quite contradictory and without identified origin.

Martínez and Castro (25) described the titration of nickel (II) ion with EGTA using murexide at pH 10 as indicator and reported that cobalt (II) ion also gave a similar color change in solutions sufficiently diluted to prevent the precipitation of Co(OH)_2 .

A number of authors have reported stability constants for various metal ions with EGTA and these are summarized in Table II. Holloway and Reilley (16) conducted a systematic study potentiometrically determining and comparing the stability constants of various metal ions chelated with five different chelons as a function of pH. The copper-EGTA chelate gave an unusual potential change with changing pH.

The formation constants listed in Table II were not all determined at the same temperature. References 15, 31, and 34 did not indicate the temperature at which the measurements were made. References 6, 22, and 40 listed measurements at 20°C , whereas references 8, 16, 37, 38, and 39 listed data at 25°C .

Mackey, Hiller, and Powell (22) measured the stability constants for the rare earth ions both potentiometrically and polarographically. Their values included in Table II have been rounded off to three significant figures, due to the reported uncertainty of their measurements.

Schroder (39), by means of a spectrophotometric method involving successive approximations, calculated the tabulated value

Table II. Formation Constants for 1:1 EGTA-metal ion Complexes

Ion	log K		
Mg ⁺²	5.4 (37) ^a	5.21(40) ^a	
Ca ⁺²	10.7 (37) ^a	10.9 (16) ^a	10.97(40) ^d
Mn ⁺²	13.6 (37) ^a	12.3 (16) ^a	
Fe ⁺²	(6) ^{a, f}		
Fe ⁺³	20.5 (39) ^c		
Co ⁺²	12.3 (16) ^a		
Ni ⁺²	13.6 (16) ^a		
Cu ⁺²	17.8 (16) ^a	4.31(38) ^e	
Zn ⁺²	16.3 (37) ^a	12.8 (34) ^a	14.5 (16) ^a
Sr ⁺²	8.1 (37) ^a	8.50(40) ^d	
Y ⁺³	16.8 (22) ^a	17.2 (22) ^b	
Ag ⁺¹	(6) ^{a, f}		
Cd ⁺²	16.2 (37) ^a	16.7 (16) ^a	16.73(40) ^d
Ba ⁺²	8.0 (37) ^a	8.41(40) ^d	
La ⁺³	15.6 (22) ^a	15.8 (22) ^b	
Ce ⁺³	15.7 (22) ^a	16.1 (22) ^b	
Pr ⁺³	16.1 (22) ^a	16.2 (22) ^b	
Nd ⁺³	16.3 (22) ^a	16.6 (22) ^b	14.59(15) ^a
Sm ⁺³	16.9 (22) ^a	17.3 (22) ^b	
Eu ⁺³	17.1 (22) ^a	17.8 (22) ^b	
Gd ⁺³	16.9 (22) ^a	17.5 (22) ^b	
Tb ⁺³	17.3 (22) ^a	17.8 (22) ^b	
Dy ⁺³	17.4 (22) ^a	17.8 (22) ^b	
Ho ⁺³	17.4 (22) ^a	17.9 (22) ^b	
Er ⁺³	17.4 (22) ^a	18.0 (22) ^b	
Tm ⁺³	17.5 (22) ^a	18.0 (22) ^b	
Yb ⁺³	17.8 (22) ^a	18.2 (22) ^b	
Lu ⁺³	17.8 (22) ^a	18.5 (22) ^b	

Table II. (Continued)

Ion	log K		
Hg ⁺²	23.8 (37) ^a	23.8 (16) ^a	23.2 (40) ^d
Tl ⁺¹	5.37(31) ^b	5.63(31) ^d	
Pb ⁺²	14.6 (16) ^a		
UO ₂ ⁺²	9.14(8) ^a	17.7 (8) ^{e, d}	

^aPotentiometrically determined

^bPolarographically determined

^cSpectrophotometrically determined

^dDetermined by pH titration

^e1:2 EGTA-metal ion ratio

^fValues not available

for the iron (III)-EGTA complex. In addition, he titrated EGTA (38) with sodium hydroxide in the presence of two moles of copper nitrate and from the resulting data determined a stability constant for the binuclear Cu₂X chelate.

The complexes formed between the uranyl ion and EGTA were studied using potentiometric titration methods by da Silva and Simoes (8). Pantani (31) polarographically determined the complexation constants for the thallium (I)-EGTA complex.

Wright, Holloway, and Reilley (43) made a comprehensive study of the thermodynamic properties of a number of polyaminocarboxylate ligands, including EGTA, interacting with various divalent metal ions. Almost simultaneously Boyd, Bryson, Nancollas, and Torrance

(2) reported a study of the thermodynamics of divalent ion association with EGTA. Bryson and Nancollas (3) studied the changes in the nuclear magnetic resonance spectra of EGTA-alkaline earth complexes.

Spectrophotometric interest in EGTA, chelated with transition element ions, resulted in a number of papers by Martínez and Castro, published in 1959. Quantitative absorptiometric methods were described for iron (III) (28), copper (II) (27), cobalt (III) (26), and vanadium (IV) (29, 30).

da Silva, Calado, and de Moura (7) included a comparison of the Cu-EGTA visible spectrum with the spectra of other copper polyaminocarboxylic acid complexes. Chiacchierini (4) studied the chromium-EGTA complex in acid solutions both spectrophotometrically and polarographically.

Purpose of This Study

The following statements can be made concerning the experimentation that took place using EGTA prior to the commencement of this study.

1. EGTA did not absorb light in the visible region of the spectrum. It was visually colorless.
2. EGTA did form many stable chelates with positive metal ions as illustrated by the number of significant formation constants

determined potentiometrically and polarographically.

3. The formation of only four colored chelates from EGTA-metal ion interaction had been reported. The greater number of those previously studied had been colorless, though in some instances the investigators had not indicated either the presence or absence of visual color.

4. No studies dealing with the ultraviolet absorption spectra of any EGTA chelates had been reported.

5. A large number of metal ionic forms had not been interacted with EGTA to determine if absorption spectra existed in either the visible or ultraviolet region.

It was proposed in this present study to determine if EGTA had additional value as a colorimetric analysis reagent. This investigator undertook a preliminary examination of the ultraviolet spectra of the nickel (II), copper (II), and iron (III) chelates of EGTA. In the region of 200 to 325 $m\mu$ both copper and iron chelates had characteristic absorption peaks. The copper (II)-EGTA complex had a molar absorptivity over 40 times greater than the absorption of the intense blue-green solution that was formed by the chelate in the visible region. The EGTA itself, had an absorption maxima at approximately 210 $m\mu$ depending upon the pH of the solution. Accordingly, it was proposed to extend this study to the examination, in aqueous solution under various pH conditions, of the spectral interaction of EGTA with

a more extensive selection of water soluble ionic forms. The spectral region to be studied was from approximately 200 to 700 m μ . As a result of this survey, it was also proposed that the possibilities for analytical application of any resulting spectral changes be examined and colorimetric analysis methods developed, if feasible.

II. GENERAL EXPERIMENTAL CONDITIONS

Instrumentation

In the first phase of the study, the examination of the absorption characteristics of EGTA-metal complexes, a Beckman DB-G (grating) spectrophotometer was used. The light source for the visible region was a tungsten lamp. The ultraviolet light source was a deuterium lamp powered by a Beckman transistorized power supply. The output from the spectrophotometer was fed into a model SRL Sargent recorder. The recorder was calibrated to read from zero to one-hundred percent transmittance.

A Cary model 11 spectrophotometer was used for the final portion of the survey of chelate spectra and then was used exclusively for the second phase of the research project, the spectroanalytical applications of EGTA. The Cary-11 was equipped with a tungsten lamp for the visible region and a hydrogen lamp with separate model N power supply for the ultraviolet spectral region. The recorder was an integral part of the instrument and was calibrated in absorbance units with three available ranges, 0-0.1, 0-1.0, and 0-2.4 absorbance.

The variation of pH was measured during the initial phase of the study with a Beckman Zeromatic pH meter. The pH meter was

equipped with a Beckman glass electrode, number 41263, and a saturated calomel reference electrode with a fiber junction.

The preparation of the solutions required a large number of weighings. Without exception, all weighings were made using a Mettler model H monopan balance.

Apparatus

A magnetic stirrer with a teflon coated stirring bar was used in conjunction with the pH meter when the pH of the solutions was changed during a spectral study. Distilled water was further purified by use of a Crystalab Deeminizer which reduced impurities to less than one part per million.

Chemicals with slow dissolving rates were placed in suitable containers on a mechanical shaker to improve solute-solvent contact.

Solutions were prepared in, measured by, or transferred with volumetric Kimax glassware. Teflon stopcock burets were used on occasion for the addition of measured volumes.

The cells used with the spectrophotometers were matched pairs of 1.00 cm Beckman UV silica cells. The Cary spectrophotometer was equipped with an accessory adapter to use this size and type of solution container.

Reagents

The reagent upon which this study focuses, EGTA, was obtained from K and K Laboratories, Incorporated, 121 Express Street Plainview, New York. The supplier reported a minimum assay of 98%. Because the preparative synthesis of EGTA ends with its solution in water as the disodium salt followed by repeated aqueous precipitation at low pH, the compound was quite readily separated from the organic components of its synthesis and was commercially available in high purity. Only two of the investigators (22, 37) who had used EGTA had attempted further purification. Six (5, 7, 34, 38, 39, 41) did not even attempt to verify its purity. The remainder had used various methods to check its purity though none had reported either exact procedures or specific results.

While the use of EGTA in this investigation was primarily qualitative, and for many quantitative analyses was used in excess, it was still thought desirable to verify the level of purity of the compound.

An infrared analysis by KBr pellet revealed only a trace of H_2O . Attempts to dehydrate the compound further by drying, at temperatures from 60°C to 110°C , were unsuccessful. No loss of weight occurred until the compound began to decompose slowly with a somewhat disagreeable odor at approximately 90°C .

The purity of the compound was checked by titration, with standard calcium chloride solution, in the presence of 2.5×10^{-3} M ammonium oxalate. The calcium solution was prepared from a weighed amount of primary standard calcium carbonate (Mallinckrodt Chemical Works) which had been dried at 300°C for two hours. The calcium carbonate was treated with an excess of dilute hydrochloric acid, boiled gently for 15 minutes to remove the carbon dioxide, cooled, quantitatively transferred to a volumetric flask, and precisely diluted to volume. Aliquots of carefully prepared EGTA solution, titrated until the first cloudy precipitate of calcium oxalate persisted at pH 9, yielded a purity value of $98.8 \pm .5\%$. The compound was used without further purification.

The chemicals interacted with EGTA in this study were obtained from various suppliers. In the appendix is tabulated each chemical, the supplier, and the indicated purity. In certain cases the purity listed is the minimum certified purity. In instances where the supplier listed the analysis of the compound this value is reported. In those cases where the supplier listed the maximum amounts of impurities "permitted," the value listed in the appendix reflects the minimum purity of the compound according to the supplier.

The less common of the chemicals were obtained, principally, from three inorganic suppliers: D. F. Goldsmith Chemical and Metal Corporation, 909 Pitner Avenue, Evanston, Illinois, City

Chemical Corporation, 132 West 22nd Street, New York, New York, and Alfa Inorganics, Incorporated, 8 Congress Street, Beverly, Massachusetts.

The molybdenum metal (processed by Mackay, Incorporated) and the indium perchlorate (processed by G. F. Smith Chemical Company) were marketed by E. H. Sargent and Company. The remainder of the common reagents were obtained from well known chemical supply firms (see appendix).

The inorganic compounds were used without further purification except as noted in Chapter V.

Discussion

The Beckman DB-G spectrophotometer was equipped with a photomultiplier detector tube which had satisfactory sensitivity from 725 $m\mu$ down to about 225 $m\mu$, where the output of the deuterium ultraviolet source began to drop off rather rapidly. In the longer wavelength region the detector's use could be pushed to 825 $m\mu$ for qualitative purposes. In the shorter wavelength region the overall instrument sensitivity was such that the electronic circuitry had difficulty establishing a 100% T (or a null) reading below 225 $m\mu$ if both light paths contained solutions whose individual transmissions versus an air path were less than 50% T. This handicap prevented the measurement of the absorbance difference between EGTA and an EGTA

chelate in this wavelength region where EGTA had its only absorption peak in the visible and near ultraviolet spectral region.

The instrument had two scanning speeds. The slower one was one-fifth the scan rate of the faster. As the greatest number of inorganic absorption "bands," or maxima, in the visible and ultraviolet region are quite broad, it was generally convenient to use the faster scan speed. This reduced the total time for each spectral analysis very significantly without impairing the measurement in any way. However, the absorption spectra of a few ionic forms in aqueous solution were more sharply defined. In order to have the photodetector register the maximum absorbance of a sharp narrow peak it was necessary to operate the spectrophotometer at its slower scan speed. A finite recorder pen response time would also contribute to the need for a slower scan rate. There was no indication that the Sargent recorder was not equal to the response characteristics of the DB-G.

The absorbance range recorded by the Cary spectrophotometer could be varied by the replacement of the recorder's potentiometer slide wire. Of the three slide wires available only the zero to 0.1 absorbance and the zero to 1.0 absorbance ranges were used in this study. The instrument also had a range doubling circuit built in that permitted the measurement of absorbance values to 2.0 units, for example, with the zero to 1.0 slide wire.

In the ultraviolet region the zero to 0.1 absorbance slide wire was of more uncertain usefulness than its use in the visible spectral region. The background noise was high and the instrument base line shifted at irregular intervals by about .006 absorbance units. Efforts to locate and correct this fluctuation were unsuccessful while this study was in progress. The base line uncertainty proved to be the limiting uncertainty of the measurements taken on this instrument.

A number of spectra recorded by these two instruments are shown in the following chapters. The identity of the instrument used to record each spectra can be noted by glancing at the units plotted on the vertical axis. Absorbance units, versus wavelength, were traced by the Cary-11. Percent transmittance, versus wavelength, was traced by the Beckman instrument.

The volumetric glassware was used without further calibration.

In this investigation of each ion and its interaction with EGTA a solution was prepared of known concentration. As a general rule, solutions prepared from colorless metal salts were prepared as either 0.050 M or 0.10 M in concentration. Colored salts were prepared in concentrations of 0.0050 M or 0.010 M. From the initial solution two identical aliquots were added to two volumetric flasks of the same volume. To one flask EGTA solution was added in sufficient volume to equal the metal ion concentration upon dilution to volume. The other volumetric flask was diluted to volume and this

solution's spectra was run as a reference or comparison spectra. The strip chart paper was then rewound in the recorder and the spectra of the EGTA-metal ion solution was run on the same chart paper to make the difference in the spectra more obvious. Changes in pH were effected by the addition of fractional drops of concentrated acid or 6 M base as required. The resulting spectra were run on the same chart paper for the most effective comparison.

The pH range examined was limited to the acidic pH region for those ions that had a greater tendency to form insoluble hydroxides than to chelate with the EGTA. In some instances the chelate formed was apparently very stable and the pH could be varied over a wide range without precipitating EGTA in the acid regions or a metal hydroxide under basic conditions. Some difficulty was experienced in preparing solutions with a pH less than 2, as the EGTA would precipitate if only weakly bonded to a metal ion.

As a general rule, the absorption in the UV region for each ion was greater than in the visible region. Thus, any strongly absorbing solution was volumetrically diluted in an attempt to determine if a characteristic spectra existed in a previously totally absorbing spectral region.

III. SPECTROPHOTOMETRIC STUDY OF EGTA AND CERTAIN ANIONS

EGTA Solutions and Spectra

The light absorption due to EGTA and to the various anions, whose metal salts might be selected for the solutions studied, was determined in order to evaluate better the spectral characteristics of EGTA-metal ion interaction. The first component to be spectrally examined was EGTA.

The stock solutions of EGTA used during this entire study were prepared by dissolving $3.85 \pm .01$ grams in 40.0 ml of 1.00 M sodium hydroxide. This solution was prepared in a 60 ml Pyrex evaporating dish, quantitatively transferred to a 100 ml volumetric flask, cooled to room temperature ($22-24^{\circ}\text{C}$), diluted to volume with freshly boiled and cooled deionized water, and thoroughly mixed. From this 0.100 M solution a 10.0 ml aliquot was transferred to a second 100 ml volumetric flask and diluted to the mark. This 1.00×10^{-2} M solution was used to prepare 1.00×10^{-3} M EGTA in the same manner. These solutions were used as a source of EGTA for complex formation. Portions of the solutions were stored and found stable for at least 1.5 years.

The light transmittance characteristics of the three EGTA concentrations were similar. Figure 1 shows the spectra of the

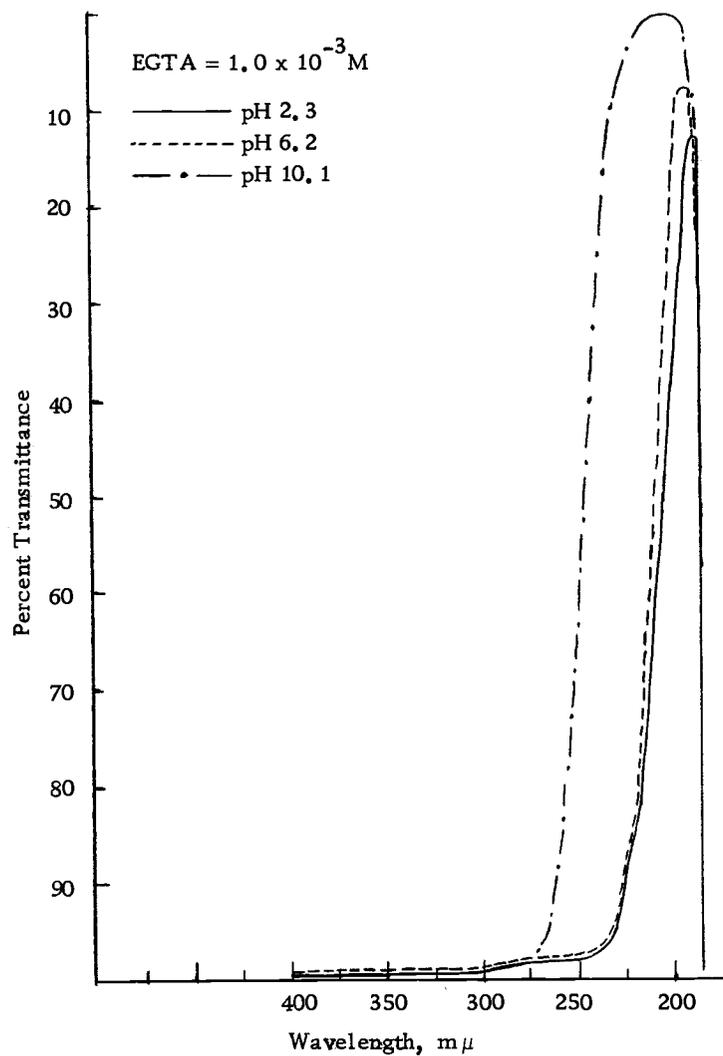


Figure 1. EGTA spectra

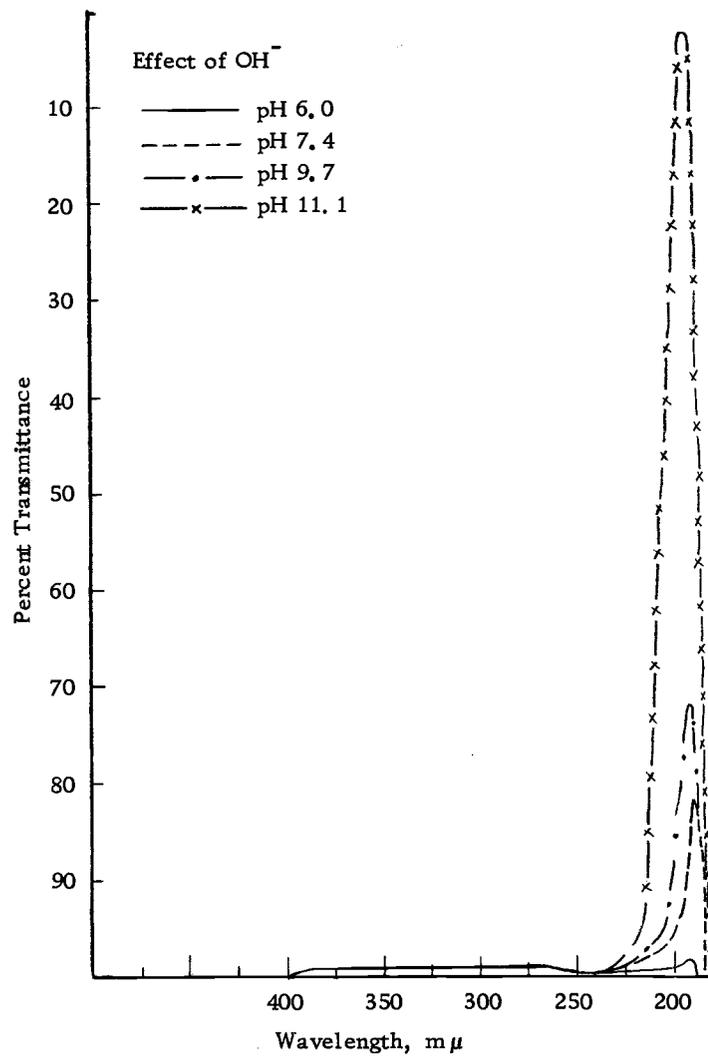


Figure 2. H₂O spectra

1.00×10^{-3} M EGTA solution together with spectral variations caused by changing pH. The higher concentrations of EGTA, while colorless in the visible region, absorbed strongly in the ultraviolet. Table III compares the three concentrations of EGTA and lists the wavelength where EGTA begins to absorb ($T = 99\%$), the wavelength where the linear absorption increase reaches $T = 90\%$, and the wavelength where nearly complete light absorption takes place ($T = 10\%$). While the increased absorption was gradual from $T = 99\%$ to $T = 90\%$, the next part of the spectral curve was a steep rise from $T = 90\%$ to $T = 10\%$.

Table III. Transmittance of EGTA solutions

EGTA Concentration	Wavelength $T = 99\%$	Wavelength $T = 90\%$	Wavelength $T = 10\%$
10^{-1} M	445 m μ	310 m μ	270 m μ
10^{-2} M	375 m μ	275 m μ	255 m μ
10^{-3} M	300 m μ	260 m μ	230 m μ

The effect of pH on the absorption of the EGTA solutions was next determined. The pH was varied by the addition of fractional drops from a micropipet, of either 6 M sodium hydroxide or 18 M sulfuric acid, to 30 ml of 1.00×10^{-3} M EGTA placed in a 50 ml beaker. The pH was measured with a Beckman Zeromatic pH meter calibrated at pH 7.00 with a 10 fold dilution of the Beckman pH 7.00

concentrate. When the pH range under examination was less than pH 4.0, the meter was calibrated in a similar manner with Beckman pH 4.00 solution and the electrodes rinsed with distilled water and wiped dry before immersion in the test solution.

Between each spectral scan, after the pH had been changed, the light absorption sample cell was repeatedly rinsed with the solution to be measured and the rinsings were returned to the 50 ml beaker. Only after the cell had thus been prepared for the sample was a final pH reading recorded. The contents of the beaker were magnetically stirred using a small teflon coated stirring bar. In this way the total volume required was kept at a minimum. The total volume of sulfuric acid and sodium hydroxide solution added was less than one percent of original sample volume.

The absorption spectra were scanned from 800 to 200 $m\mu$ using a reference cell filled with distilled water. Five scans were run on the Beckman DB-G spectrophotometer at pH 11.1, 10.1, 8.0, 6.2, 3.8 and 2.3. In Figure 1 are shown the scans at pH 2.3, 6.2, and 10.1. There was no absorption prior to the wavelength region plotted in Figure 1. The spectra at pH 3.8 and 8.0 are almost identical to the scan at pH 6.2. The pH 11.1 solution transmitted approximately 2-3 percent less light than did the solution at pH 10.1.

This same procedure for pH variance was used throughout the study. In many instances it would have been more convenient to work

with larger quantities of sample solution. However, the limited quantities of many of the ionic forms did not permit the use of large volumes and it was believed best to standardize the procedure. In this way the estimated acid or base additions for pH change were relatively the same.

Spectral Effect of the Hydroxide Ion

The significant changes in the EGTA spectra as the pH was varied above pH 8.0 prompted an investigation of the absorption resulting from the hydroxide ion in water as plotted by the DB-G. The results are shown in Figure 2. While the theoretical limit of this instrument was 185 m μ , it was questionable whether any significance could be attached to the spectral plots below 200 m μ . At 200 m μ the solution at pH 7.4 was absorbing 4.5% of the available radiation, 12% at pH 9.7 and 93% at pH 11.1.

The absorption of the hydroxide ion became increasingly significant at less than 215 m μ . The hydroxide ion absorption did not, however, account for the increased absorbance of EGTA in the vicinity of 225 to 250 m μ as pH 10 was approached from the neutral side. The absorbance in this spectral region must have resulted from the presence of the X^{-4} ion in contrast with a weaker absorbing H_2X^{-2} ion. This was in accordance with the deprotonation of H_2X^{-2} which took place, according to Sudmeir and Reilley (40),

between pH 8 and pH 10. With proper instrumentation it should be possible to measure pK_3 and pK_4 by means of a photometric titration to compare with the various other methods which have been employed.

Spectral Effects of Selected Anions

The presence of two strongly absorbing components (EGTA and OH^-) in the lower wavelength region of the spectrum available for analysis made it important to avoid the use of metal salts with anions that might also reduce the spectral region even further. Individual solutions were prepared, 1.00×10^{-2} M in concentration, from the sodium salts of the acetate, bromide, chlorate, chloride, cyanide, dihydrogen orthophosphate, fluoride, nitrate, perchlorate, and sulfate ions. A comparison of some of the spectra of these ions appears in Figure 3 and Figure 4. The acetate spectra (not shown) was almost identical to the chlorate scan whereas cyanide (not shown), fluoride (not shown), and perchlorate (not shown) had spectra very similar to that of the sulfate ion.

Anion Considerations in the Selection of Metal Salts

The final choice of the anion, to be associated in the solutions under study, was based upon a number of considerations. Some of these aspects were in conflict with one another.

Spectral considerations were of more obvious importance;

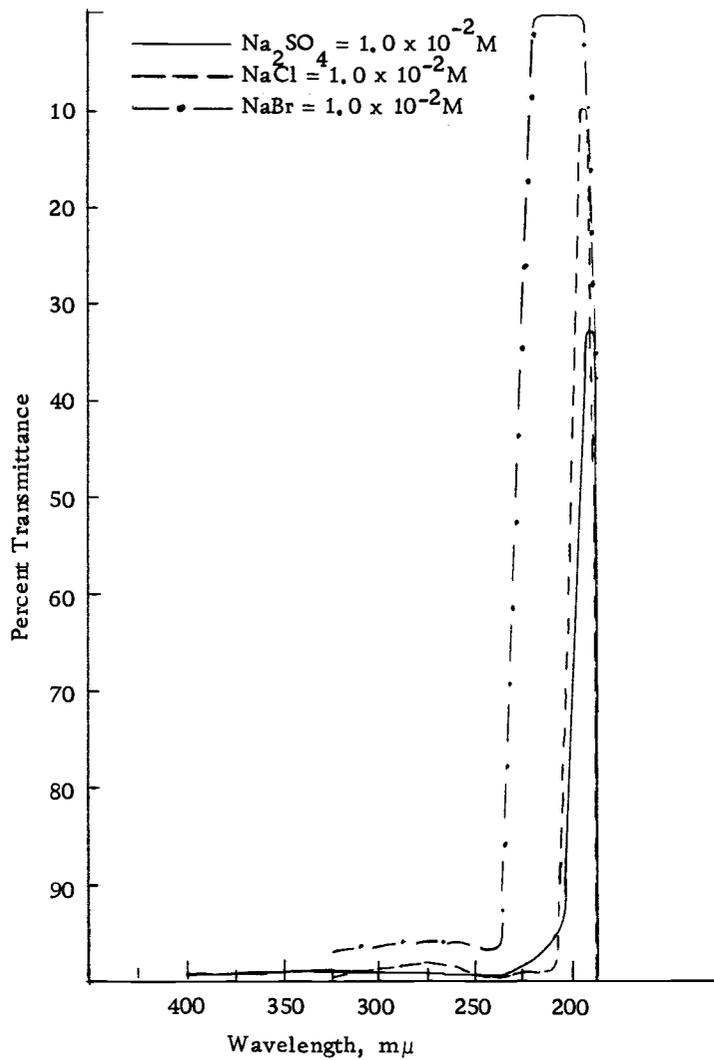


Figure 3. Anion spectra

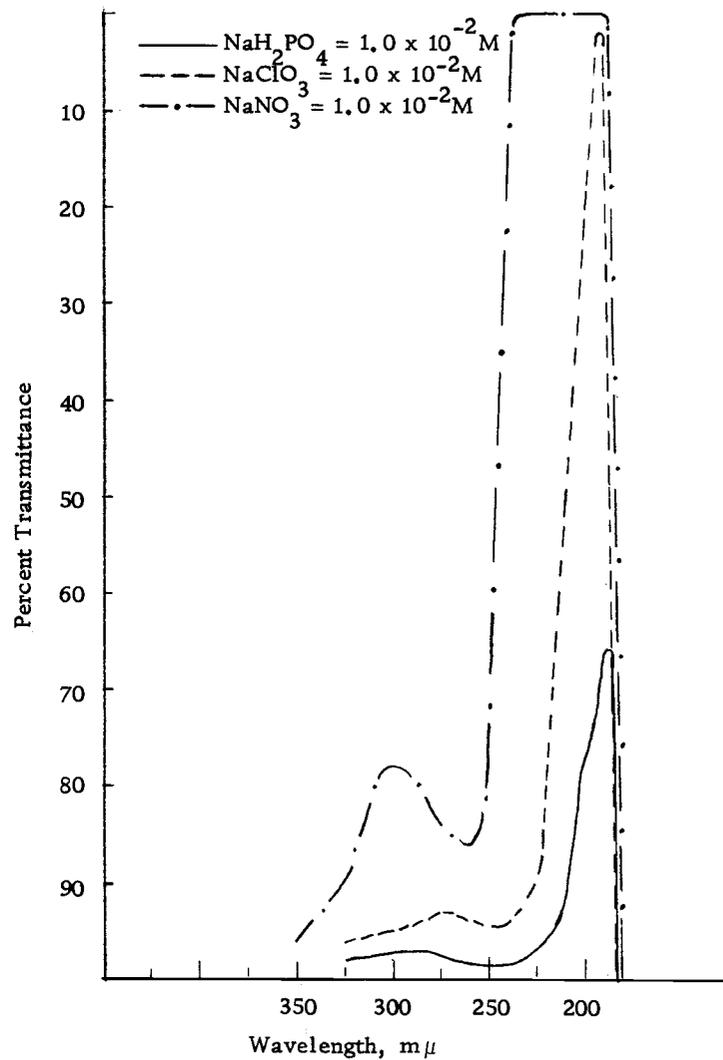


Figure 4. Anion spectra

yet it was equally necessary that the anion should not be a strong complexing agent and thus in competition with the EGTA. It was necessary that the metal salts have sufficient solubility to prepare solutions with concentrations approximately 10^{-2} to 10^{-3} molar. The extensive nature of the study of EGTA interaction with metal ions made it necessary to obtain chemicals of high purity rather than to undertake their preparation. Availability was therefore an important factor.

The soluble nitrates were the first to be avoided due to the strong absorption of the nitrate ion in the ultraviolet region. With few exceptions, the otherwise desirable perchlorates were simply not available. The soluble acetates and chlorides were good complexing agents and could seldom be used in spite of their good solubility, availability, and spectral characteristics. The cyanide and fluoride anions were completely avoided because of complexation. The phosphates were rarely available in high purity. The bromide ion had rather high spectral interference, though it could have been used more extensively if it had been necessary. Thus, by a process of elimination the salts most frequently selected for study were sulfates in spite of the generally low solubility of the sulfate salts.

IV. SPECTROPHOTOMETRIC STUDY OF EGTA-METAL ION COMPLEXES

The discussion of the experimental results for each of the metals listed in Figure 5 will follow the order of increasing atomic number. Certain of the metals were spectrally examined for interaction with EGTA in more than one valence form. Many of the spectra that resulted are graphically presented in the figures included in this chapter. All spectra were measured versus distilled water. Each spectrum was scanned from longer to shorter wavelengths.

Magnesium

A stock solution of 0.10 M magnesium sulfate was prepared by dissolving the required amount of the anhydrous salt in approximately 75 ml of distilled deionized water. The solution was quantitatively transferred to a 100 ml volumetric flask and diluted to volume. From this initial solution two solutions were prepared. One solution contained only 0.050 M magnesium sulfate and the other contained 0.050 M magnesium sulfate plus 0.050 M EGTA. A reference spectrum was scanned using the first solution versus distilled water. Spectra of the second solution, versus distilled water, were scanned at pH 3.0, 5.5, and 8.9. The spectra at pH 3.0 and 5.5 were identical and had the appearance of

the characteristic spectra of EGTA alone at that concentration and pH. The spectral scan taken at 8.9 showed the characteristic increase in absorption that EGTA demonstrates above pH 8.

An attempt was made to measure the absorption of the EGTA-magnesium ion solution versus the reference magnesium sulfate solution, instead of versus distilled water, in an attempt to determine if there were any slight changes from the EGTA spectra alone that could be detected by the instrument. All such attempts of this kind proved unsuccessful for reasons mentioned in Chapter II.

Magnesium ion chelated with EGTA, though the formation constant was not large (see Table II) and the exchange rate of the magnesium ions with the EGTA ions was high according to the NMR data collected by Bryson and Nancollas (3).

Aluminum

A solution of aluminum ion was volumetrically prepared by dissolving the calculated amount of aluminum potassium sulfate dodecahydrate in sufficient distilled deionized water to yield a 0.10 molar solution. From this stock solution two solutions were prepared. One solution was 0.010 molar of the aluminum salt, the other had in addition a 0.010 molar concentration of EGTA.

A reference spectrum, scanned from 700 to 200 $m\mu$, of the first solution showed only the absorption expected from the existing

concentration of sulfate ion. The solution containing EGTA was scanned over the same spectral region at pH 1.9 and 4.0.

While the spectra showed no characteristic difference from EGTA spectra under those conditions of pH and at that concentration, the lack of a precipitate down to pH 1.8 suggests that an EGTA-aluminum complex was formed. EGTA alone will begin to precipitate as the pH is lowered to 2. Above pH 4.2 a cloudy precipitate was formed. The precipitate was believed to be aluminum hydroxide.

Calcium

A 0.10 molar stock solution containing calcium ion was prepared from calcium chloride dihydrate because of the limited solubility of calcium sulfate. Two solutions were prepared, one containing 0.010 M calcium chloride, the other in addition containing 0.010 M EGTA. A reference spectrum was scanned showing only the characteristic chloride absorption. The chelate solution was scanned at pH 3.2, 5.3, 7.2, and 10.5.

The spectra at pH 5.3 and 7.2 are identical. All of the spectra showed only the absorption expected from EGTA without any characteristic changes due to the presence of the calcium ion. Calcium formed a stable chelate with EGTA (see Table II).

Scandium

Scandium sulfate solution was prepared in a 0.05 molar concentration. From this stock solution two solutions were prepared containing 0.025 M scandium sulfate with the second solution of the two also containing 0.050 M EGTA. The reference spectrum of scandium sulfate without EGTA showed only the absorption due to the high sulfate ion concentration (.075 M with respect to sulfate). The EGTA-scandium solution had a spectrum characteristic of EGTA at pH 3.1 and 7.0.

Titanium

Titanium (III) solution was prepared by the volumetric dilution of a MCB solution of buffered 20% titanium trichloride. Concentrations of 1.0×10^{-2} M titanium trichloride were prepared in separate volumetric flasks, with EGTA added to one in equal concentration. Figure 6 shows the resulting spectral scans. The purple-colored titanium solution appeared slightly darker with the EGTA. Attempts to vary the pH of these solutions were markedly unsuccessful. Upon dilution, the pH of the titanium trichloride was still 1.2. The addition of the EGTA solution (pH 10, approximately) was able to shift the combined solution pH to 1.4. If dilute sodium hydroxide was added to make the solution more basic, a blue-black gelatinous

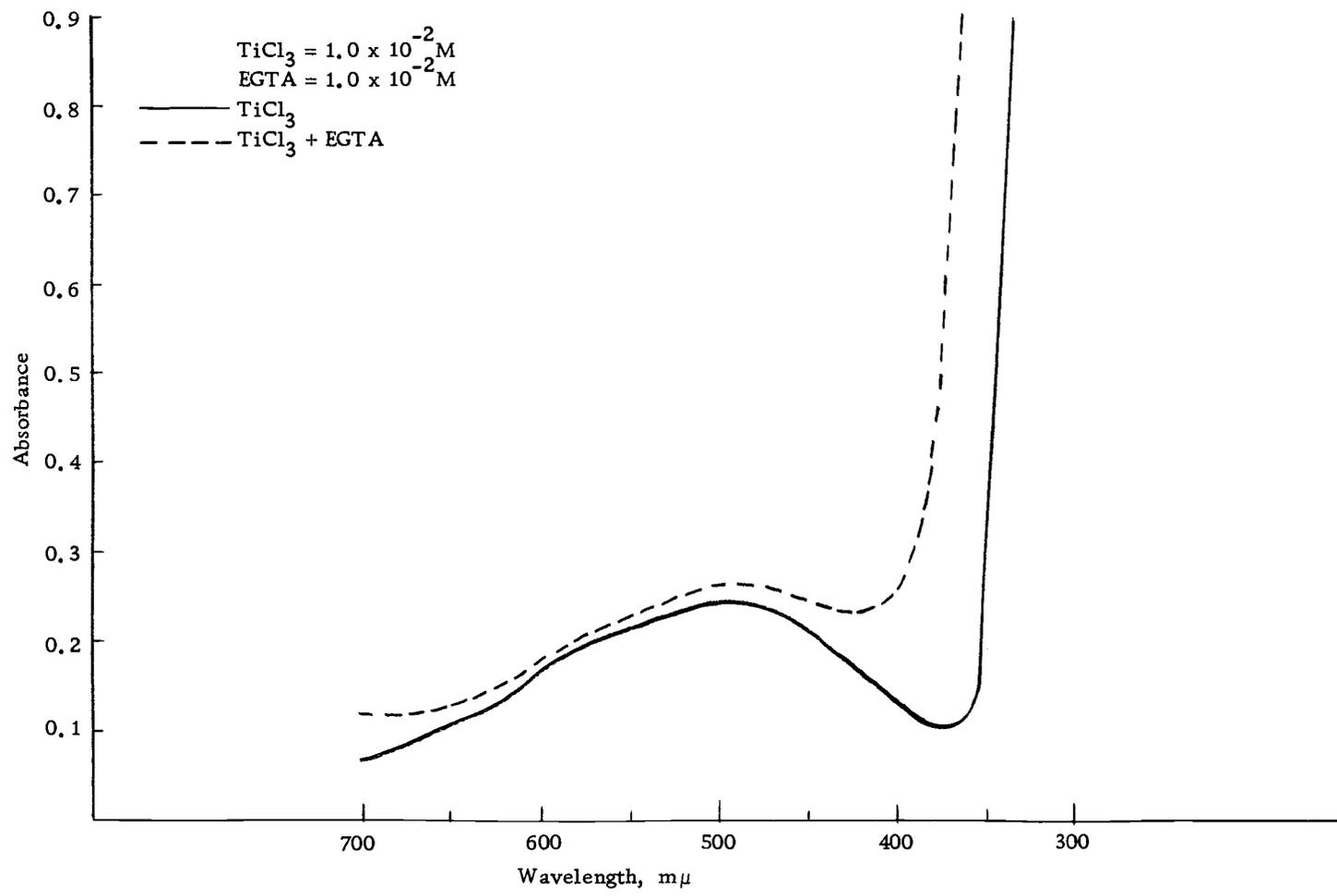


Figure 6. Titanium (III) - EGTA spectra

precipitate formed instantaneously. If the pH was lowered, a fine white precipitate (presumably EGTA) was formed. The EGTA, however, did form a complex with titanium (III); otherwise a precipitate of EGTA would have formed at pH 2 or slightly higher. A dilution of the solution showed no characteristic absorbance maxima in the ultraviolet region.

A solution of titanium (IV) oxysulfate gave no evidence of chelate formation with EGTA. The solution was pH sensitive from the standpoint of precipitate formation and hydrolyzed upon standing.

Vanadium

Vanadium (II) solutions showed no spectral changes in a preliminary study with EGTA and were not further investigated. Vanadium (IV) sulfate, as obtained from City Chemical Company, appeared to undergo disproportionation upon contact with water to yield vanadium (II), vanadium (III), and vanadium (V). Addition of EGTA accelerated this process with a continually changing spectra. Attempts to stabilize the solution were unsuccessful, except for partial success in duplicating the EGTA-hydrogen peroxide effect reported by Martínez and Castro (30). There was no evidence of any characteristic spectra, resulting from EGTA addition, in the ultraviolet region.

Chromium

Chromium (III) solutions, one containing EGTA, were prepared in 1.0×10^{-2} M concentration. The addition of EGTA solution to chromium (III) ions initially formed a precipitate that appeared to be chromic hydroxide. However, as the pH was lowered the precipitate dissolved slowly with constant stirring until at pH 1 the solution was clear again with an intensification of the violet coloration of the chromium solution. The spectrum of the resulting solution showed two differences from the reference solution (see Figure 7). The intensity of the two absorption maxima was increased (transmittance decreased 24% for the 581 m μ peak and 20% T for the 414 m μ maximum). The 581 m μ peak was shifted to a maximum at 574 m μ . The wavelength of the 414 m μ maximum was unchanged. From pH 1 to pH 4 the spectral trace was not significantly changed. Above pH 4 there was a slight increase in absorption with increasing pH. In part, this was due to a trace precipitate formation which slowly formed at higher pH values.

The formation of the chromium (III)-EGTA complex appeared to be rather slow. The complex, once formed, was very stable at lower pH values. A recent study by Chiacchierini (4) indicated that a binuclear complex existed as well as a 1:1 chromium (III)-EGTA complex between pH 2 and 4.

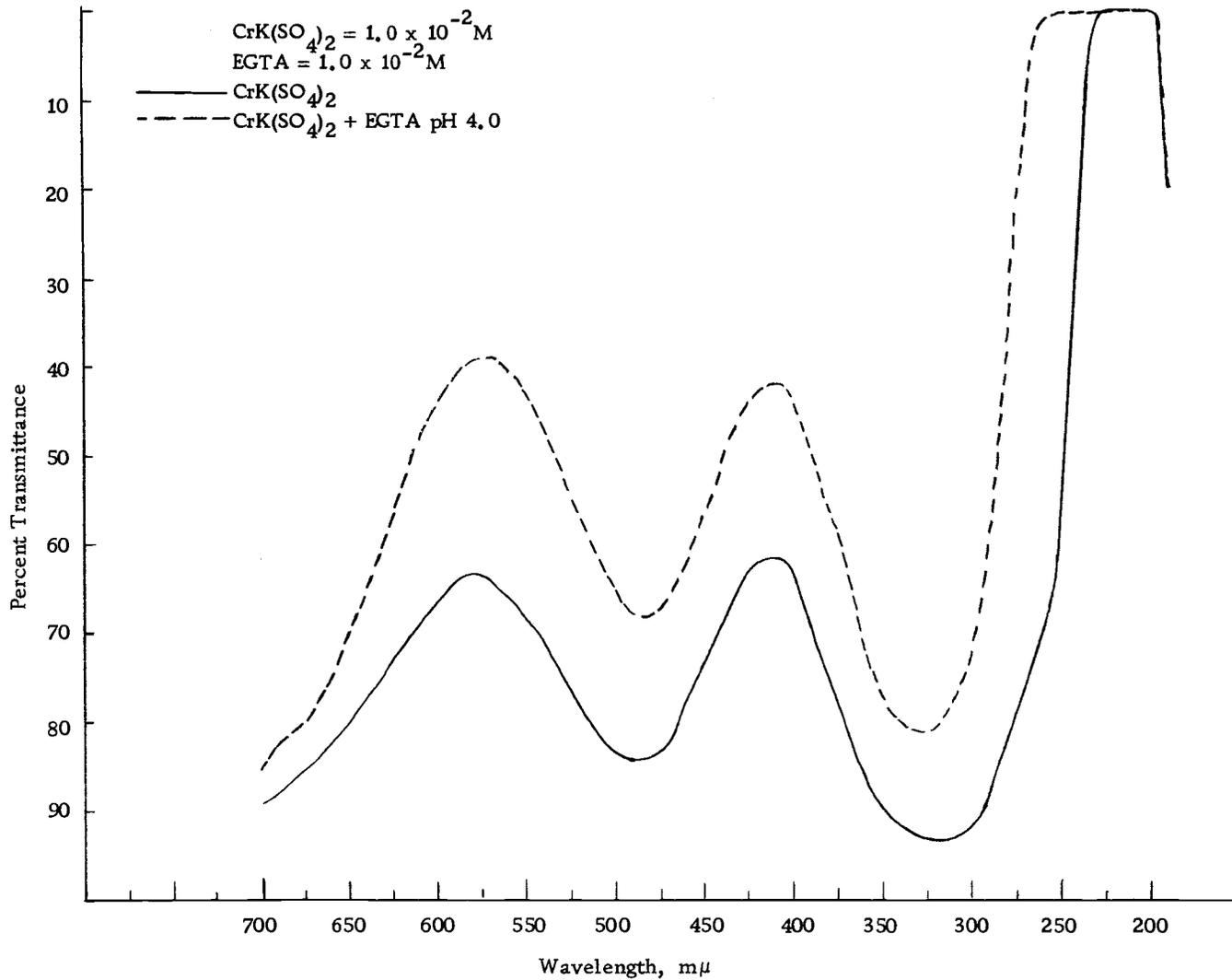


Figure 7. Chromium (III) - EGTA spectra

A solution of chromium (III)-EGTA was set aside for several months. After about 90 days the characteristic blue-green component of chromium (III) solutions was completely gone and the solution was a violet color. The spectra of the solution had the identical configuration of the spectra in Figure 7, except that the absorption maxima were now located at 560 m μ and 395 m μ .

Manganese

Solutions of manganese (II) sulfate were prepared in concentration of 1.0×10^{-2} M. During preparation, EGTA was added in an equal amount to one solution. At a pH 5.1 the only difference between the manganese (II) sulfate reference solution and the one containing EGTA was the increased absorption due to EGTA from 260 m μ to 200 m μ . At pH 1.4 no EGTA precipitated and the solution linearly (with a slope of 1.0) absorbed more light from 350 m μ to 250 m μ , where the solution became strongly absorbing. At pH 8.0 the solution had a light yellow appearance with an overall uniform increase in absorption compared with manganese sulfate solution (and the pH 5.1 chelate solution). At pH 10.4 the yellow color was slightly increased and the absorption of the solution increased with a slope of 0.5 from 550 m μ to 275 m μ where it became strongly absorbing. At pH 11.0 the solution slowly precipitated manganese (II) hydroxide.

The manganese-EGTA chelate appeared to be stable over a wide

pH range. At high pH values manganese would interfere with the analytical use of EGTA over a wide spectral region.

Iron

The spectra of iron (II) sulfate showed limited absorption, even at a concentration of 1.0×10^{-2} M from 700 m μ to 275 m μ . The increasing absorption from 275 m μ to 200 m μ had a shoulder at 245 m μ . With the addition of EGTA the solution became totally absorbing at 400 m μ (pH 6.0) or 360 m μ (pH 0.8). Only a very small trace of EGTA precipitate (perhaps due to a slightly inexact stoichiometric ratio) formed at that low pH, which indicated a rather stable complex.

The spectra of iron (II) solutions at 1.0×10^{-4} M concentration was resolved in the ultraviolet region, as is shown in Figure 9. The iron (II) sulfate transmitted nearly all of the incident radiation to 200 m μ . The iron (II) with EGTA added had a pH of 2.7 when mixed, due to the sulfuric acid stabilized iron (II) stock solution. The solution showed only a slightly increased absorption at 260 m μ . If the pH was raised to 11.0 there was a linear increase in absorption (slope 1.0) by the solution from 475 m μ to 250 m μ . This type of absorption was often found characteristic of solutions where a very fine precipitate (of more nearly colloidal proportions) existed. If, however, the pH was again lowered to very acid conditions, the spectra shown in Figure 9 at pH 0.85 resulted.

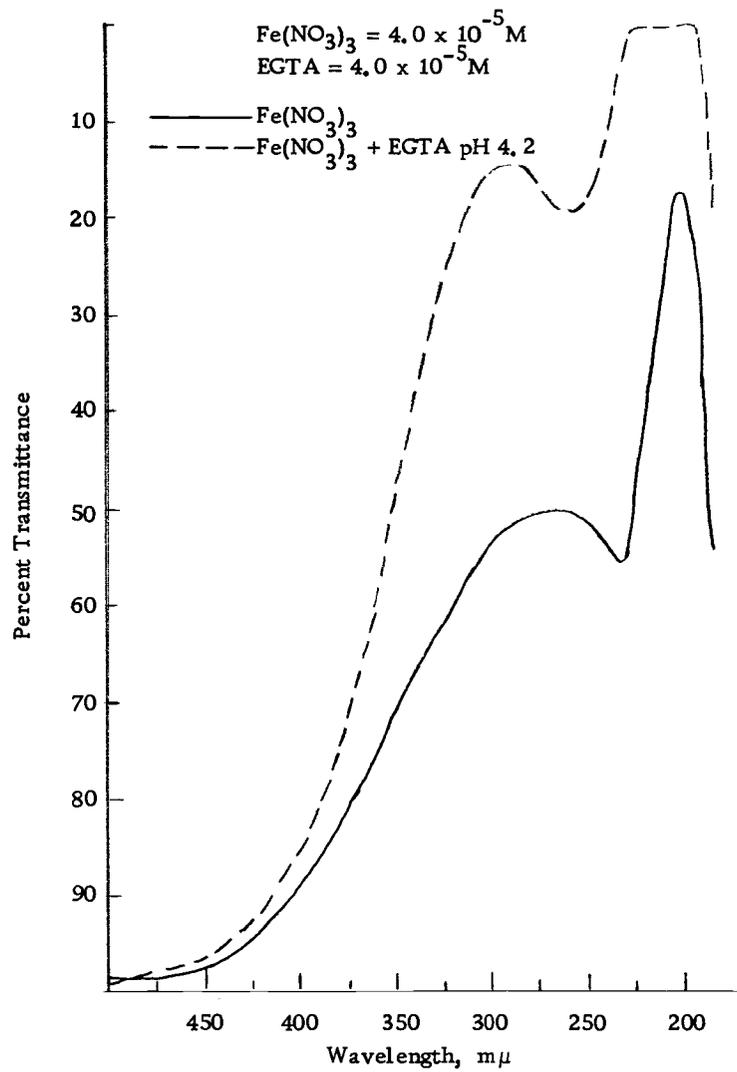


Figure 8. Iron (III) - EGTA spectra

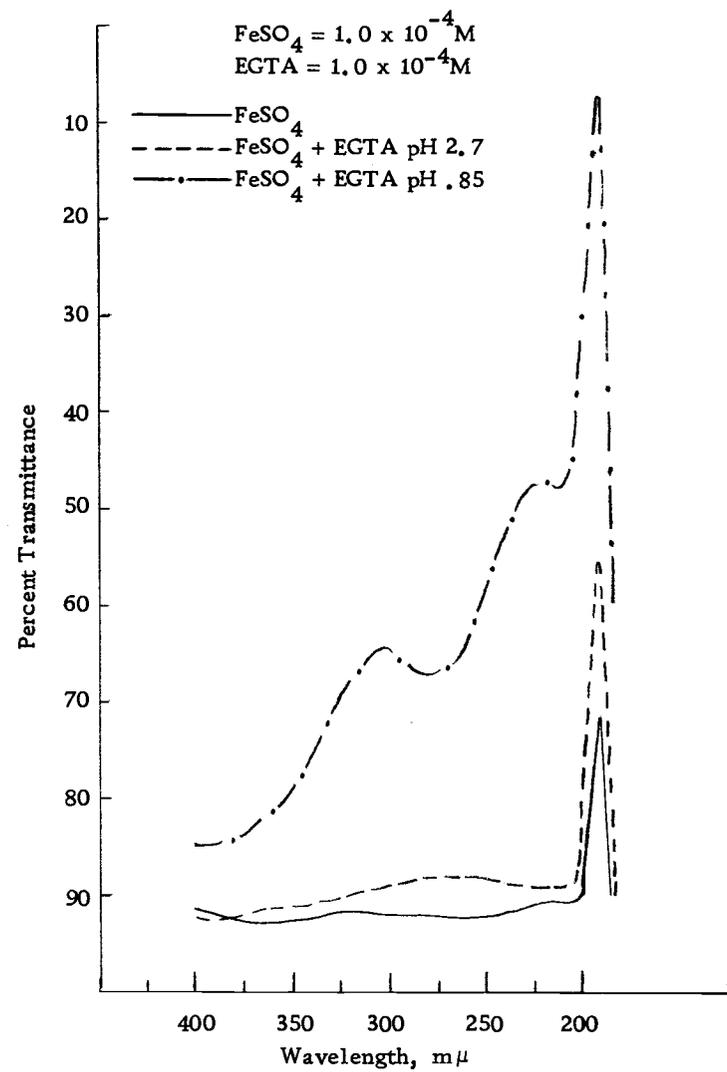


Figure 9. Iron (II) - EGTA spectra

The phenomena was interpreted to suggest that at low pH values, where the EGTA form H_2X^{-2} exists, either a very unstable complex was formed with iron (II) or else the rate of complex formation was very slow. When the pH was increased to 10 or 11, the form X^{-4} existed and chelation took place more readily. Above pH 11, upon standing, a brown precipitate was formed. The formation of the chelate may have been base catalyzed.

Attempts to establish a quantitative system were not successful. There may have been a competition existing between two or more chelate forms such as $FeX^{-2} \rightleftharpoons Fe_2X$, which slowly shifted toward equilibrium. The solutions were not stable and were subject to air oxidation.

The intense yellow color formed by iron (III) and EGTA had been used quantitatively by Martínez and Castro (28) at pH 4-5 in a spectrophotometric method at 430 m μ . Solutions of iron (III) nitrate, concentration 4.0×10^{-5} M, showed a characteristic absorption peak in the ultraviolet region at 289 m μ (see Figure 8). At this concentration the interference of nitrate ion was almost negligible. With the addition of EGTA this absorption was increased and the peak was shifted to 289 m μ . Attempts to develop a quantitative spectrophotometric relationship gave unsatisfactory results. The various equilibria examined by Schröder (39) may have been a factor, or at these concentrations interaction with water molecules may have

introduced additional competing reactions.

Cobalt

Cobalt (II) interaction with EGTA is shown in Figure 10. The solutions were prepared from cobalt (II) sulfate. The visible spectra were pH dependent, whereas the ultraviolet spectra showed only the changes characteristic of EGTA under varying pH conditions.

Cobalt (III) solutions were not examined. Martínez and Castro (26) developed an analysis method for cobalt (III) with EGTA, using a filter photometer.

Nickel

The spectra in Figure 11 resulted from 1.0×10^{-2} M nickel (II) sulfate solutions with an equal amount of EGTA added to the sample solution. The slight increased absorption appeared to be stable up to pH 11.0. The ultraviolet spectra showed only the EGTA characteristics.

Copper

The interaction of EGTA with copper (II) ion in the visible region was well known. Martínez and Castro (27) developed an analytical spectrophotometric method which they used to analyze solutions containing 20-500 milligrams per milliliter of copper (II).

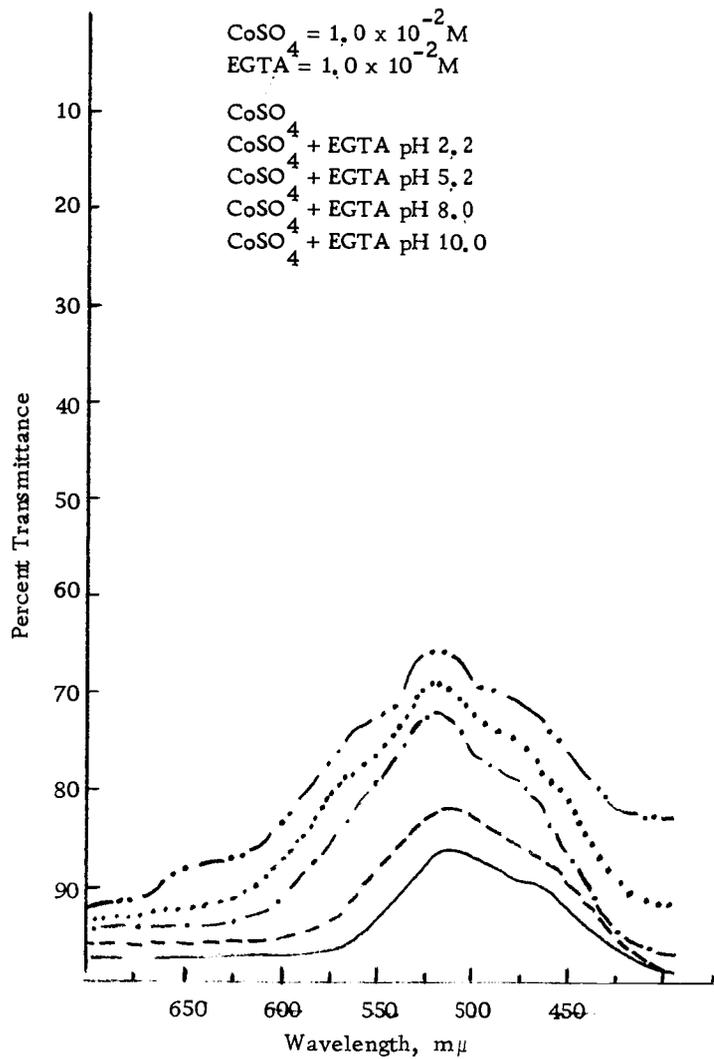


Figure 10. Cobalt (II) - EGTA spectra

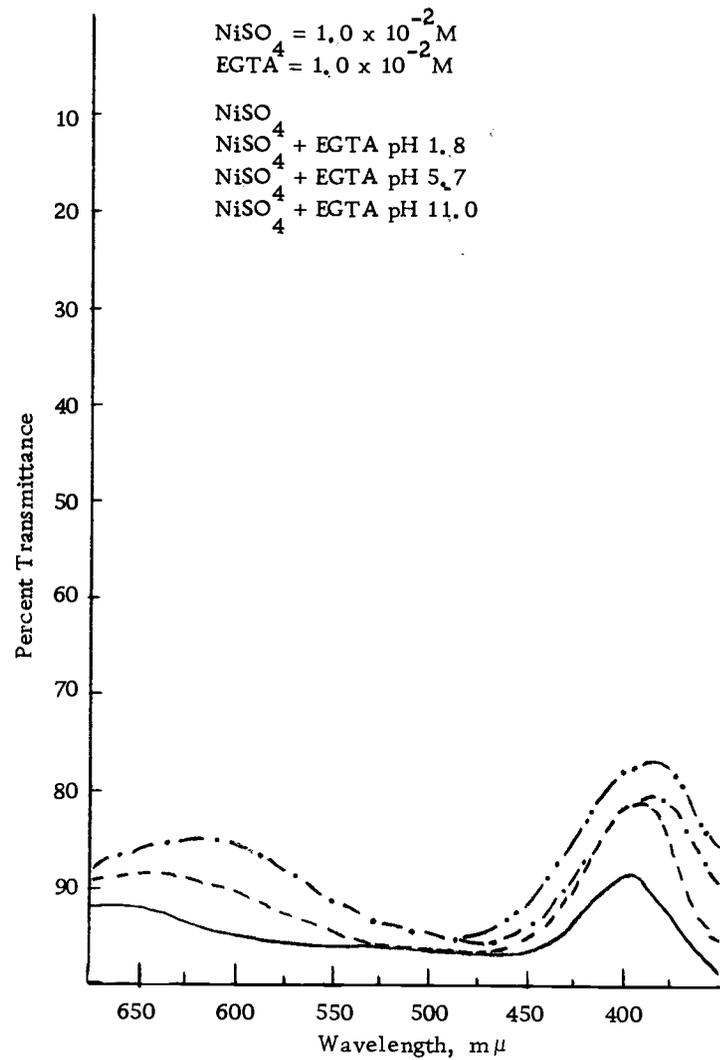


Figure 11. Nickel (II) - EGTA spectra

They stated that the color intensity was constant over a wide pH range. Figure 12 shows the contrast between 1.0×10^{-2} M copper (II) solution before and after the addition of EGTA. The scan at pH 4.8 was typical from pH 4 to pH 8. The spectral shifts at pH 2.0 and pH 11.0 were likely to be the result of the pH sensitive equilibria reported by Schröder (38) from the study of the titration of EGTA with sodium hydroxide in the presence of copper (II) ions. That study indicated the formation of CuHX^- , CuX^{-2} , Cu_2X , and $\text{Cu}_2\text{X}(\text{OH})_2^{-2}$ depending upon the pH and the concentration of copper (II).

In the ultraviolet the 1.0×10^{-2} M copper (II) solution was totally absorbing. The ultraviolet spectra of 1.0×10^{-4} M copper (II) solution with and without EGTA are shown in Figure 13. A similar trace, plotted by the more sensitive Cary instrument with the reference cell filled with copper (II) solution and the sample cell with equal copper (II) plus EGTA concentrations, showed the two peaks to be the same height. The additional height of the peak at 243 m μ must have been due to the absorbance of copper ion as it interacted with water.

Increased acidity at pH 3.00 removed the absorption maxima at 298 m μ . This peak was also removed in an identical fashion when the copper-EGTA concentrations were 2:1. These two observations suggested that both excess copper (II) ions and large quantities of protons did something similar to the 1:1 copper (II)-EGTA chelate.

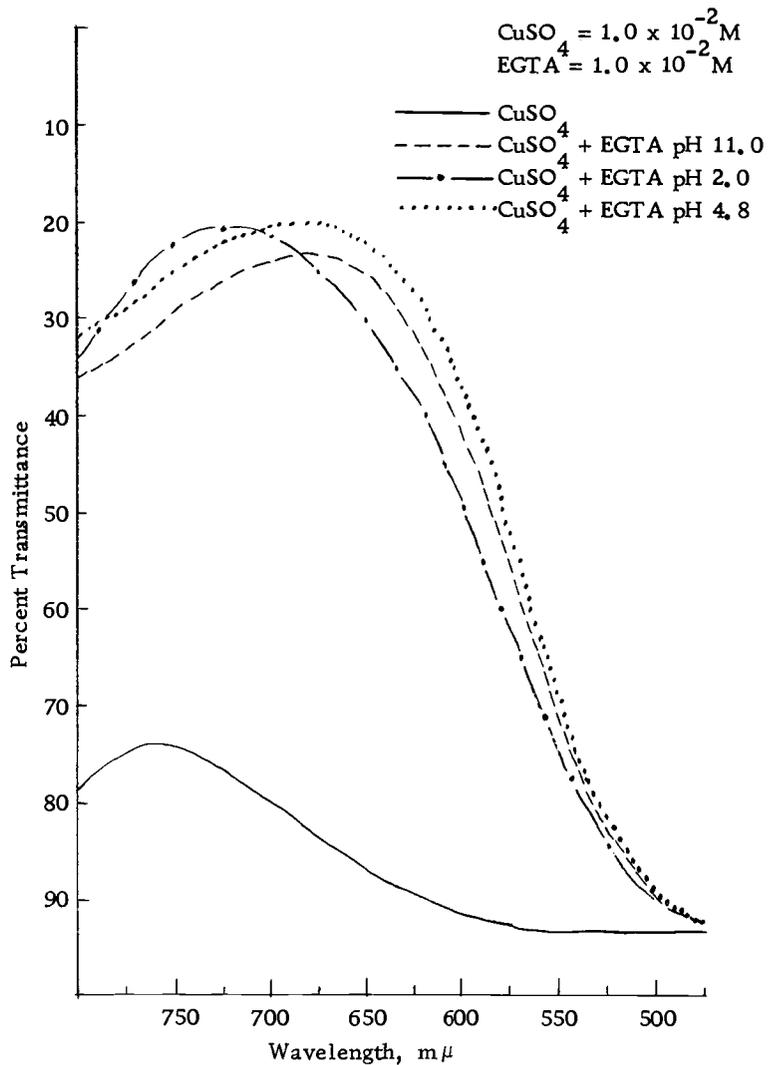


Figure 12. Copper (II) - EGTA spectra

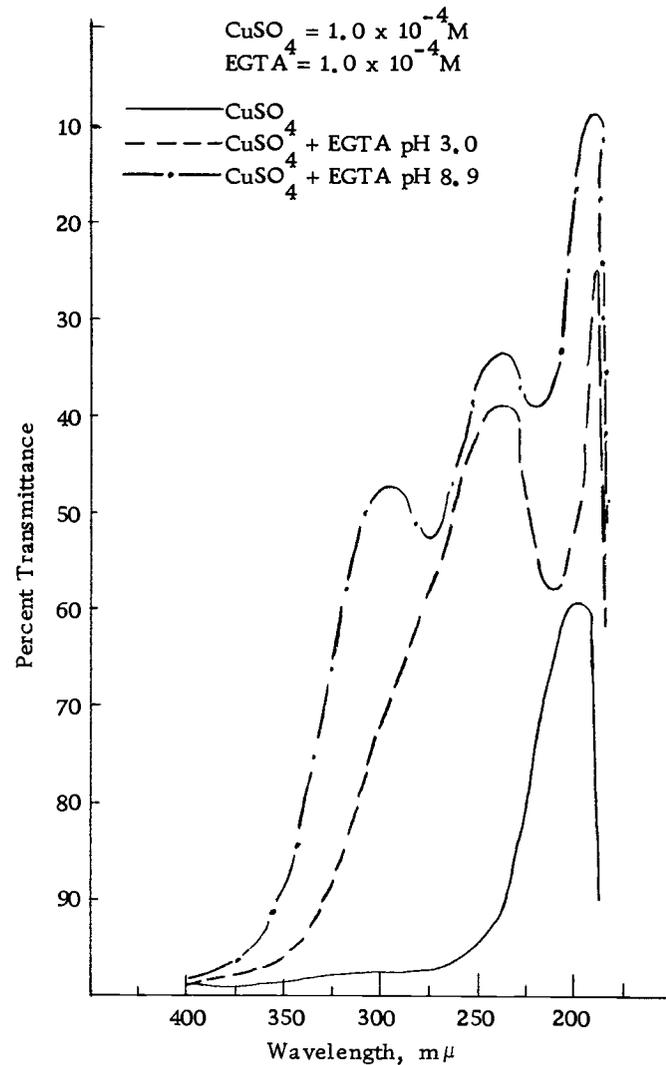


Figure 13. Copper (II) - EGTA spectra

Of the two copper UV peaks, the one at 298 m μ was chosen for possible quantitative analysis applications. Details concerning this part of the study are included in Chapter V.

Zinc

Two solutions of zinc sulfate were prepared in 1.0×10^{-2} M concentrations with EGTA added in equal concentration to one. Spectra were scanned at pH 2.6, 5.7, 8.6, and 11.3. No absorption was shown from 700 to 250 m μ by either the 1.0×10^{-2} M zinc sulfate solution or by the three solutions containing EGTA at pH 2.6, 5.7, and 8.6. Below 250 m μ only the characteristic EGTA absorption was observed. At pH 11.3 the spectrum gave evidence of colloid formation with a continually increasing ellipsoidal absorption curve from 575 (T = 99%) to 225 m μ (T = 0%). Zinc formed a chelate with EGTA (see Table II).

Rubidium

A spectral scan of this alkali metal ion was made with and without EGTA at 1.0×10^{-3} M concentration. As was expected, there was no absorption other than that characteristic of EGTA and the chloride ion associated with the rubidium.

Strontium

Strontium ion complexed with EGTA in a somewhat less stable manner than did calcium ion. Strontium chloride solutions were prepared with 1.0×10^{-2} M concentration. One contained 1.0×10^{-2} M EGTA. Spectra were scanned at pH 3.1, 7.1, and 10.1. Only chloride and EGTA spectra were observed.

Yttrium

A stock solution was prepared of yttrium sulfate in a concentration of 5.0×10^{-2} M. A spectral scan of this solution showed no absorption except for a very small peak at 300 $m\mu$, and then the solution (unlike sulfate ion absorbance) became totally absorbing from 240 $m\mu$ to the limit of the instrument. Two tenfold dilutions were prepared, one containing 1.0×10^{-2} M EGTA. Spectra were scanned at pH 3.0, 6.4, 9.1, and 11.3. At this concentration with EGTA there was no evidence of a peak at 300 $m\mu$, and the remainder of the spectra had only EGTA absorption characteristics.

Zirconium

The spectrum of a 1.0×10^{-2} M stock solution of zirconium sulfate showed no absorption maxima until the solution became totally absorbing at 210-215 $m\mu$. A tenfold dilution with EGTA added

showed some subtle differences after the settling of an initial trace precipitate. At pH 1.5 no additional precipitate formed, but the UV spectral region showed a slight absorption maxima (5% T less than base line) at 273 m μ . At pH 3.9 the peak was better developed (12% T less than base line), but at pH 9.6 the peak at 273 m μ was depressed with another maxima (5% T less than base line) appearing at 340 m μ .

Molybdenum

A molybdenum sulfate solution was prepared in approximately 1×10^{-3} M concentration by dissolving molybdenum metal in hot concentrated sulfuric acid. A dark yellow-green solution resulted. A hundredfold dilution of the strongly absorbing ionic form had absorption maxima at 296 m μ , 257 m μ , and 212 m μ . The addition of EGTA to a similar concentration increased the absorption of each peak (T decreased by 5%). The molybdenum ionic form reacted with the solution. The 296 m μ peak height diminished with time and the solution became transparent to 250 m μ .

Ruthenium

Ruthenium solutions were prepared from ruthenium trichloride in 1×10^{-4} M concentration. The solution without EGTA showed no characteristic absorption maxima. Beginning at 740 m μ the solution's absorption continually increased, with decreasing wavelength, in a

nearly linear fashion until it was absorbing all of the available radiation at 390 $m\mu$. The solution containing EGTA showed no differences from the reference solution. Both solutions, originally a greenish-brown color, became greener with increased pH, but their absorbing character did not perceptibly change.

Rhodium

A 5.0×10^{-3} M solution of rhodium (III) sulfate was prepared. Spectra were run on two tenfold dilutions, one containing 1.0×10^{-3} M EGTA. The yellow-orange solutions showed identical transmittance from pH 2.5 to pH 7.8. An absorption peak existed at 412 $m\mu$, followed (toward the shorter wavelength region) by increasing absorption until the solution was totally absorbing at 275 $m\mu$. EGTA caused no difference in absorption. At pH 10 the EGTA-rhodium solution was unchanged at 412 $m\mu$. At shorter wavelengths it transmitted up to 20% T less light than the lower pH solutions.

The preparation of the rhodium sulfate solutions required the addition of a sufficient sulfuric acid to keep the pH near 2.0 to prevent the formation of a finely divided brown precipitate on contact with water.

Palladium

A 4.8×10^{-3} M palladium (II) sulfate stock solution was

prepared. From this solution, two 2.4×10^{-3} M solutions were prepared with an equal concentration of EGTA in one. The two solutions are compared at pH 3.0 in Figure 29. The formation of a dark, finely divided precipitate took place when the original solution was prepared. The addition of sufficient sodium hydroxide to raise the pH near 5.0 had the same effect in the presence of EGTA.

The examination of the potential quantitative application of EGTA to palladium solutions was undertaken at the same time as a similar study of the EGTA-uranyl complex. The similarity between the two will be discussed in the uranium section.

Silver

Silver sulfate solution, 1.0×10^{-2} M, was prepared and an absorption spectra was scanned. The solution was completely transparent until a small, broad absorption band appeared between 375 and 250 $m\mu$. The peak occurred at approximately 300 $m\mu$. Between 250 and 235 $m\mu$ the solution became totally absorbing and remained so to 200 $m\mu$. Dilution of the original sample to 1.0×10^{-3} M resolved the totally absorbing region into a flat shoulder at 226 $m\mu$, a peak at 212 $m\mu$, and a peak at 200 $m\mu$.

Two solutions were then prepared, 1.0×10^{-4} in concentration, with EGTA present in one as 2.0×10^{-4} M. In Figure 14 the spectra are compared with the EGTA solution at pH 6.8. If the pH exceeded

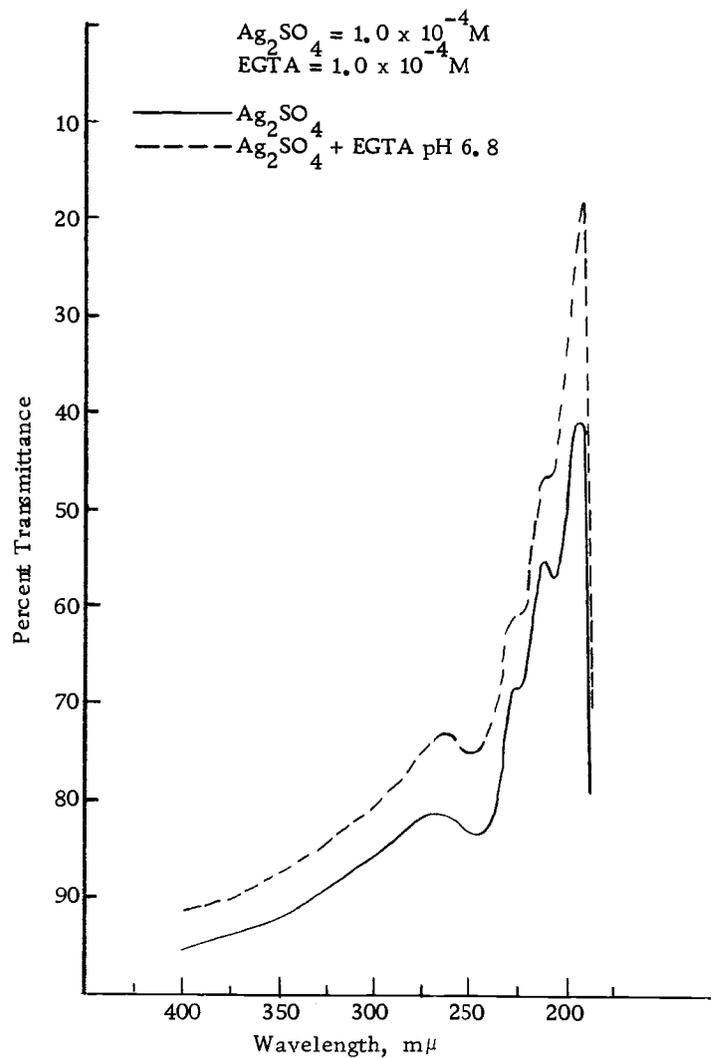


Figure 14. Silver - EGTA spectra

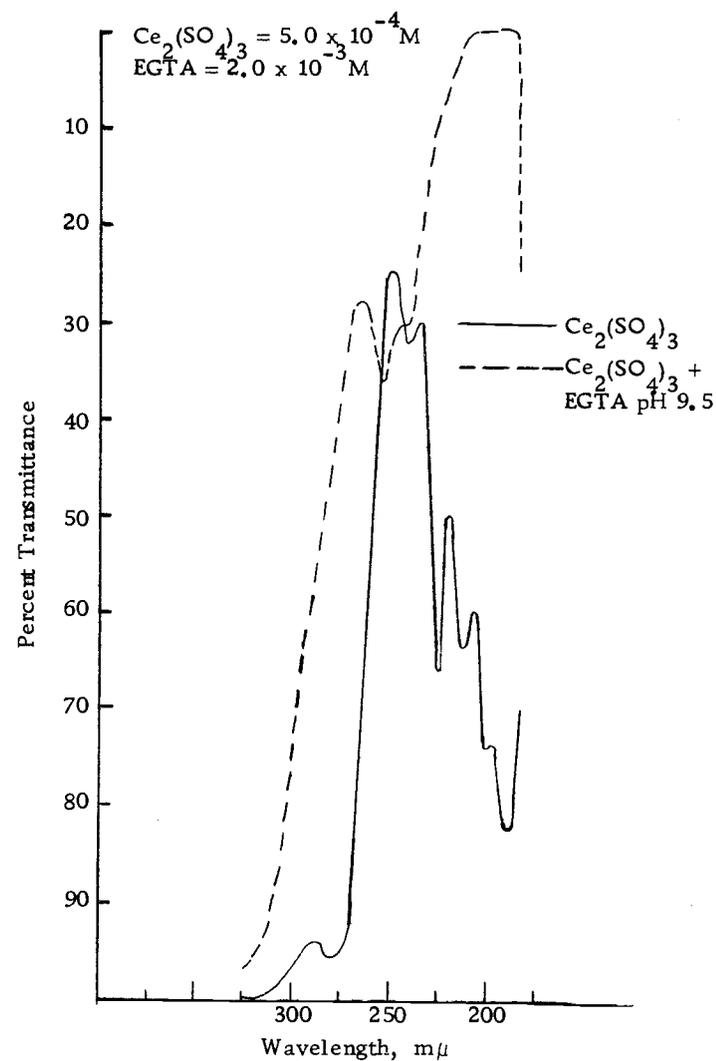


Figure 15. Cerium (III) - EGTA spectra

8, the peak at 300 $m\mu$ disappeared, whereas the shoulder at 226 and the peak at 212 $m\mu$ were obscured by the absorption of EGTA in this pH region. At pH 10.4 there was no absorption at this concentration until the wavelength diminished to 260 $m\mu$.

It was of interest to note that if EGTA was added to the silver ion below pH 4, no evidence (spectrally, at least) of chelation was noted. If the pH was raised to 6.0 the chelate was formed and the pH could then be lowered to 2.0 without changing the EGTA-silver ion absorption. The solutions were quite stable when protected from prolonged exposure to light.

The determination of a formation constant for the silver-EGTA complex has been reported (20).

Cadmium

Solutions containing 1.0×10^{-2} M cadmium sulfate and 1.0×10^{-2} M cadmium sulfate plus 1.0×10^{-2} M EGTA were prepared. The cadmium sulfate solution did not absorb from 700 $m\mu$ to 205 $m\mu$. The EGTA-cadmium solution showed only the absorption due to EGTA at pH 5.8, 3.2, 1.6, and 0.6 without formation of any EGTA precipitate. A very stable chelate was undoubtedly formed as indicated in Table II.

Indium

1.0×10^{-3} M indium perchlorate solutions, one containing equal concentration of EGTA, were scanned at pH 3.9, 6.6, 9.5, and 10.9. The solutions exhibited no absorption until the EGTA began absorbing in the ultraviolet region.

Tin

Solutions of tin (II) were prepared from stannous chloride. Spectra were obtained from 1.0×10^{-4} M tin (II) chloride and 1.0×10^{-4} M tin (II) chloride plus 1.0×10^{-4} M EGTA.

The spectra showed greater differences with pH variation than could be attributed to EGTA alone in the ultraviolet region, although the changes were not easily interpreted. At pH 2.0 and 5.4 the spectra were as expected from EGTA, with the exception of a slight shoulder at 235 m μ that the EGTA spectrum did not possess as it became totally absorbing in this region. When the pH was increased to 7.4, the width of the base of the peak became much wider with a shoulder at 225 m μ . Raising the pH to 10.6 caused the main peak to become narrower than under any other pH conditions, with a slight secondary peak forming at 220 m μ .

An additional observation suggested that a stable chelate was formed between tin (II) and EGTA. Upon standing overnight, the

solution containing EGTA was still clear, whereas the other tin (II) solution was already clouded.

Lanthanum

Lanthanum sulfate and lanthanum-EGTA solutions were prepared with lanthanum ion and EGTA concentrations of 1.0×10^{-2} M. Spectral scans were run at pH 3.8, 8.1, and 11.0. The typical EGTA absorption was all that existed. The solution otherwise was completely transparent from 700 m μ down to 250 m μ . Lanthanum did form a stable complex with EGTA, according to Mackey, Hiller, and Powell (22).

Rare Earth Elements

Among the so called rare earths, the spectral response to EGTA varied widely. All of the ions in this group were examined except promethium and lutetium. Each ion was examined in the +3 state and cerium was also studied as the ceric ion. Mackey, Hiller, and Powell (22) had determined formation constants for each element in the +3 state, and the values indicated that stable chelates were formed by all ions.

Spectrally the chelation with EGTA produced four general results. In some instances there was a definite increase in spectral absorption. With other ions there was a definite decrease in spectral

absorption. Some ions did not undergo any change in specific spectral absorption with EGTA. Most of the ions manifested a more intense background absorption in the ultraviolet region with the addition of EGTA.

Cerium

The cerium (III) ion was prepared in a concentration of 5×10^{-4} M. Figure 15 shows the difference that existed between a solution with EGTA added in 2.0×10^{-3} M concentration and one without EGTA. The cerium (III) sulfate solution had absorption peaks at 296 m μ , 255 m μ , 243 m μ , 224 m μ , and 213 m μ . At pH 2.0 the 213 m μ peak had been obscured by the addition of EGTA, the absorption of the 224 m μ peak had been increased (transmittance diminished 6%), and the twin peaks at 255 and 243 m μ had been shifted to 271 and 252 m μ , respectively. In addition, their absorption was decreased. At pH 3.9 the peaks at 295 m μ and 224 m μ no longer were present, whereas traces run at pH 6.6 and 8.8 were identical to the scan at pH 3.9. At pH 11.5 the solution became more strongly absorbing immediately following the cerium-EGTA maximum at 252 m μ . Cerium (III) solutions did not absorb from 700 m μ to 300 m μ .

The cerium (IV) ion had a much less complex spectra. The solution began to absorb at 400 m μ to form a large domed absorption maximum that peaked at approximately 262 m μ , and then the absorption

diminished somewhat, to 200 m μ . The addition of EGTA caused this broad peak to absorb a little more (transmittance decreased 5% at 262, 11% at 200 m μ) and increased its width.

The cerium (IV) sulfate solution was prepared from cerium (IV) bisulfate. The addition of EGTA slowly (in approximately 16 hours) reduced the cerium (IV) to cerium (III).

Praseodymium

Praseodymium sulfate solution (prepared as 2.4×10^{-2} M) had four sharp absorption maxima in the visible (700 to 400 m μ) spectral region. It had no absorption peaks in the ultraviolet except for the absorption due to sulfate ion. The addition of EGTA (see Figure 16) reduced the absorbing intensity of all four peaks while it very slightly shifted the wavelength of maximum absorption. The peak at 592 m μ was shifted about 6 m μ . The variation of pH from 3.8 to 10.6 had no effect upon the visible spectra and produced only a general increase in the ultraviolet. See Figure 19 or 22 for an example of this phenomenon.

The reduction of absorbing ability by praseodymium solutions upon EGTA addition made possible a qualitative identification of praseodymium in rare earth mixtures. This is discussed and described in Chapter V.

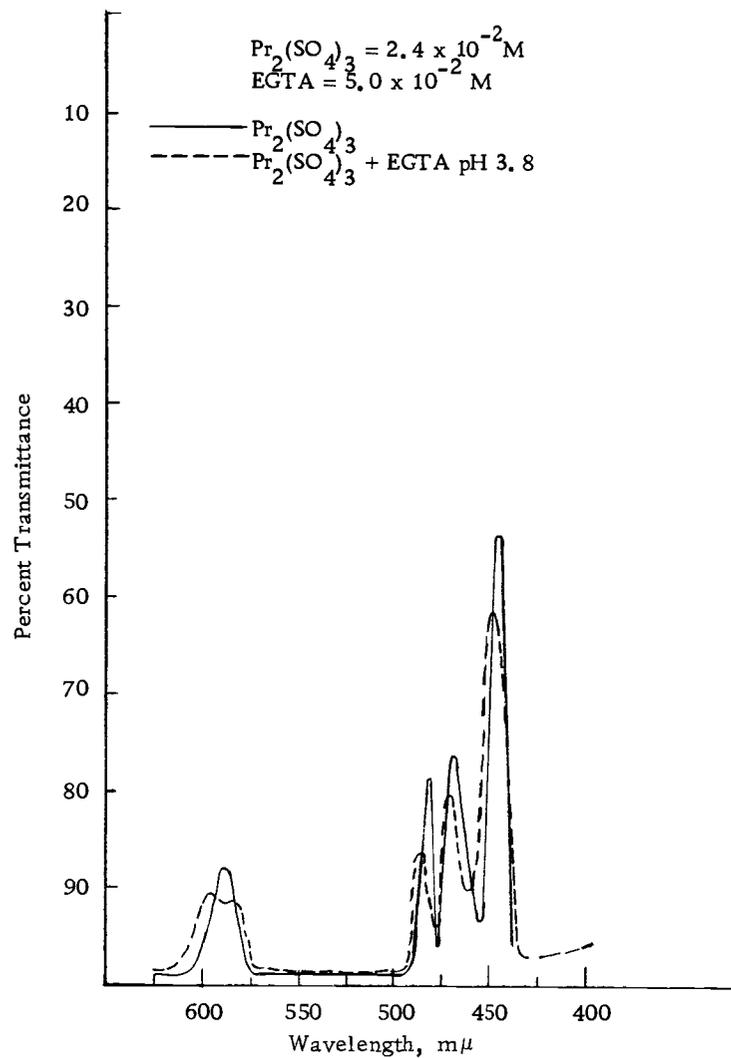


Figure 16. Praseodymium (III) - EGTA spectra

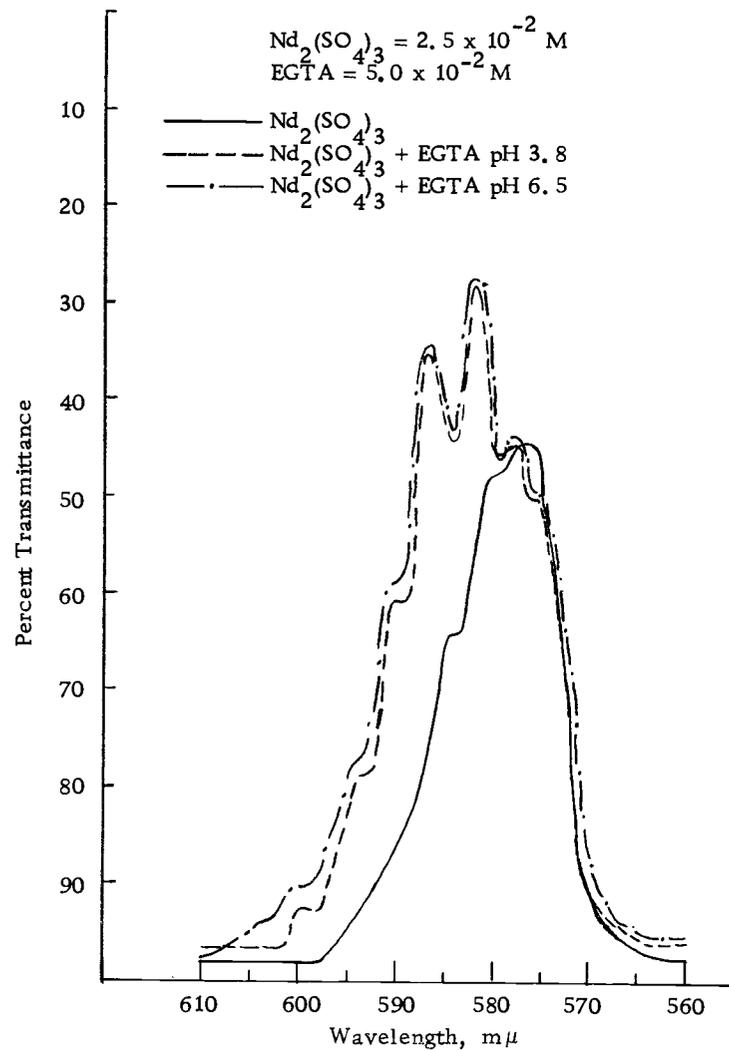


Figure 17. Neodymium - EGTA spectra

Neodymium

Neodymium sulfate solutions, one containing an equal concentration of EGTA, were prepared as 2.5×10^{-2} M (neodymium ion concentration equals 5.0×10^{-2} M). Between 800 $m\mu$ and 250 $m\mu$ this ion in aqueous solutions had five major peaks and sixteen minor peaks. The varying effects of EGTA upon the five major peaks will be discussed. Similar effects were measured on the minor absorption peaks.

The designation of major and minor absorption peaks was arbitrary. Any peak that absorbed at least one-half as much as the most strongly absorbing maximum was designated a major peak.

To examine the effect of EGTA upon the absorption of the neodymium spectra, the slow scan speed was used in the Beckman spectrophotometer. Figure 17 shows a typical neodymium peak and how EGTA changed its characteristics.

The neodymium peak occurring at 796 $m\mu$ was shifted by EGTA addition to 800 $m\mu$. The general configuration of the peak was not changed. Its transmittance changed by 4%. The next major peak occurred at 742 $m\mu$ with a side peak at 734 $m\mu$. EGTA addition shifted the peak by 2 $m\mu$ to 744 and 736 $m\mu$ and increased absorption (transmittance reduced 6%), but it did not change its general form. The major peak at 577 $m\mu$ (see Figure 17) experienced the greatest change upon complexing with EGTA. The single absorption maximum

was divided into three peaks and four shoulders. The highest of the three peaks that EGTA formed had 17% less transmittance and was shifted 5 μ into the longer wavelength region. The peak at 523 μ was split into two peaks and two shoulders. The highest of the two peaks formed was located at 526 μ . The last major peak of the five was located in the ultraviolet region at 356 μ . The effect of EGTA upon it was slight. The appearance of the peak was not changed. The transmittance decreased 8% and its position was shifted 3 μ to 359 μ .

The spectra were not changed with pH changes below pH 6.5. The solution became cloudy when the pH exceeded 7.0.

Europium

Europium solution (1.25×10^{-2} M europium sulfate) had only a trace of absorption at 465 μ , a small absorption peak at 394 μ , an even smaller peak at 362 μ , another equally small peak at 318 μ , and a similar one at 298 μ (see Figure 18). The solution began to absorb strongly at about 260 μ and was totally absorbing in the remainder of the UV region examined.

The addition of EGTA caused the trace of a peak at 465 to twin, whereas the small main peak at 394 μ developed a smaller side peak at 400 μ . The solution became even more strongly absorbing in the UV region which increased the background absorption at the

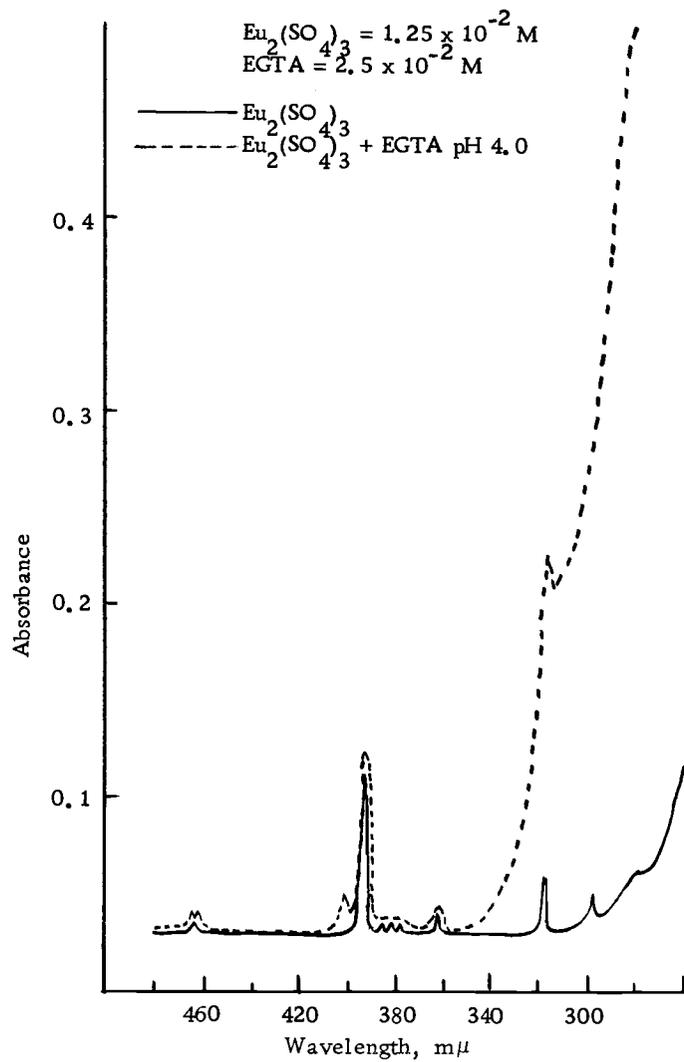


Figure 18. Europium (III) - EGTA spectra

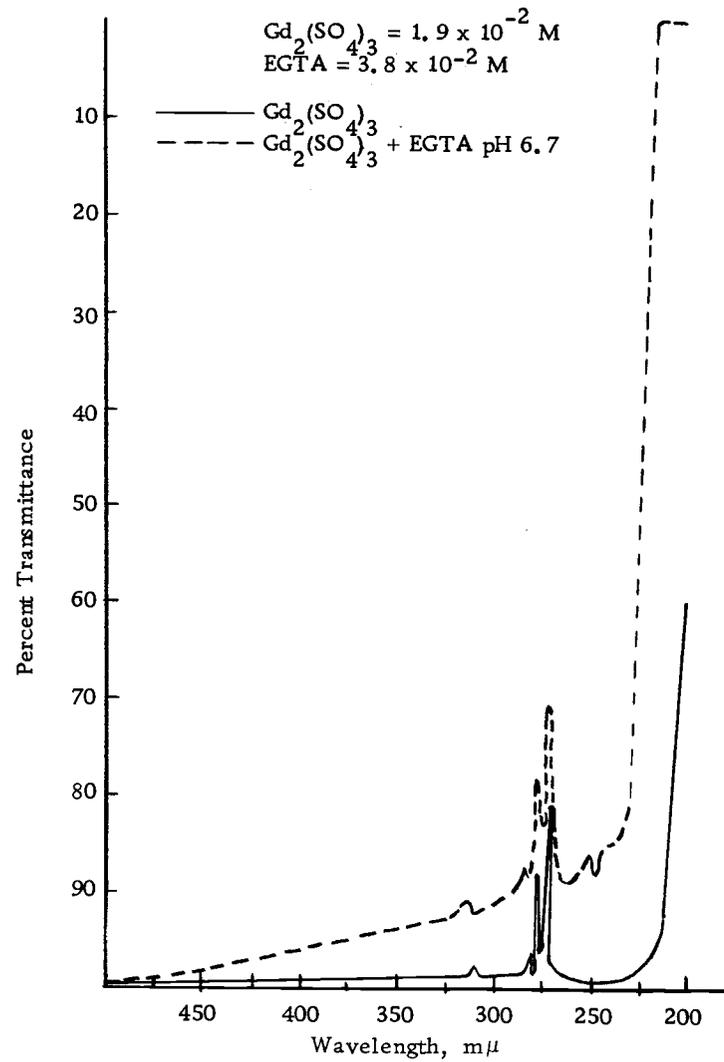


Figure 19. Gadolinium - EGTA spectra

319 $m\mu$ peak. A study was conducted to determine if this background increase at 319 $m\mu$ was proportional to concentration. The results are discussed in Chapter V.

Samarium

The addition of EGTA to samarium sulfate caused a trace of cloudiness that cleared in about five minutes. The samarium solutions were prepared as 3.5×10^{-2} M. Traces made with EGTA at pH 2.7, 6.4, and 10.1 were identical. The presence of EGTA had virtually no effect upon the samarium spectra. The most pronounced absorption took place at 403 $m\mu$ and at this wavelength there was only slight increase in absorption. In the ultraviolet spectral region the background increase by EGTA was much less than many of the rare earths.

Gadolinium

Gadolinium had no absorption from 700 $m\mu$ to 280 $m\mu$ (see Figure 19). The three spiked peaks at approximately 275 $m\mu$ were unchanged by the presence of EGTA except as the background level increased with increasing pH. As in the case of neodymium, the gadolinium-EGTA solution became cloudy at approximately pH 7.0.

Terbium

Terbium had no characteristic absorption in the spectral region that was examined. No increased absorption resulted from EGTA addition.

Dysprosium

The dysprosium background was increased with EGTA addition, and the six major peaks absorbed the same amount above the background (similar to gadolinium as illustrated in Figure 19) except for the peak at 351 m μ . This sharp absorption maximum was the same height with EGTA despite the background increase, but it was twice as wide, with a shoulder formed very near the peak. This solution also clouded with increased pH above 7.0.

Holmium

The holmium spectra was one of the more complex of the rare earths. It had eight major peaks and eight less significant ones. The addition of EGTA to holmium had not only the most pronounced effect of any of the rare earths but also the greatest variety of effects.

The solutions were prepared as 2.5×10^{-2} M holmium sulfate with 5.0×10^{-2} M EGTA present in one solution. The pH was varied from 4.1 to 10.1 without causing any additional spectral change in the

holmium-EGTA system, except for the characteristic EGTA changes below 250 $m\mu$. There was no evidence of any cloudiness in the solutions with pH change.

At 642 $m\mu$ the first major peak had a 8 $m\mu$ wide shoulder that disappeared when EGTA was added. The peak itself was shifted to 646 $m\mu$ and its transmittance decreased 6%. The peak at 539 $m\mu$ was divided into two peaks by EGTA with less absorption than the reference peak. A minor absorption maximum at 488 $m\mu$ was divided into two peaks without significant change in absorption. This was the only small peak to be appreciably changed by the EGTA.

The peak at 543 $m\mu$ (see Figure 20) had a transmittance decrease of 25%. This increased absorption was examined for analytical use and is discussed in Chapter V.

A holmium peak at 418 $m\mu$ was unchanged by EGTA except for a transmittance decrease of 6%. In the ultraviolet region a peak at 364 $m\mu$ had a significant absorption increase (transmittance diminished 15%) and was twinned into two peaks. Peaks at 289 $m\mu$, 280 $m\mu$, and 243 $m\mu$ were unchanged relative to the background.

Erbium

The erbium spectrum was nearly as complex as the holmium spectrum. It had six characteristic major absorption peaks and seven minor ones. The minor peaks were as significantly changed

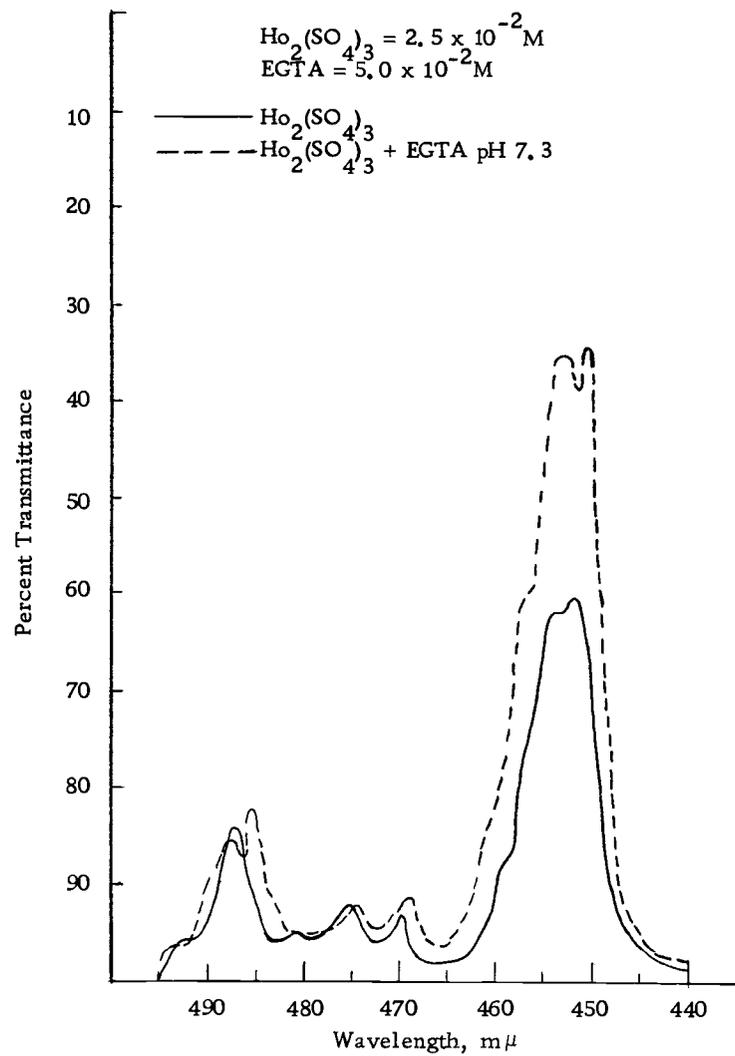


Figure 20. Holmium - EGTA spectra

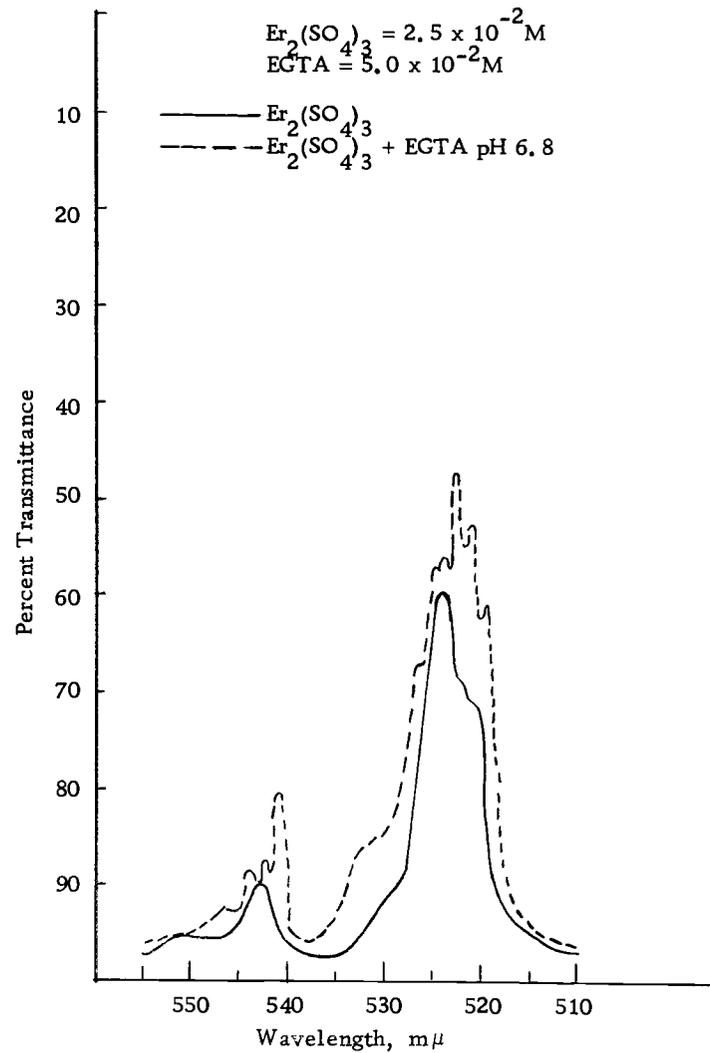


Figure 21. Erbium - EGTA spectra

by EGTA as were the major ones. None of the peaks had major absorption changes.

The peak at 654 $m\mu$ was broadened, diminished in absorption, and shifted to 653 $m\mu$. A minor peak at 543 $m\mu$ was divided into a triplet. The major peak at 525 $m\mu$ (see Figure 21) was changed by EGTA into five subpeaks. The peak at 489 $m\mu$ was shifted to 491 $m\mu$ and diminished in absorption intensity. A minor peak at 452 $m\mu$ that interfered with the spectrophotometric analysis of holmium, according to Kolthoff and Elving (20), retained its identical absorption when EGTA was added. This led, during this study, to the early belief that differential absorption would permit the elimination of this interference using EGTA, whereas the absorption of holmium at this wavelength was at a maximum. The erbium peak at 381 $m\mu$ was divided into a triplet by EGTA. A minor peak at 366 $m\mu$ formed a doublet of reduced absorption. The major peak at 257 $m\mu$ was unchanged with respect to the increased base line. Changing the pH had no effect upon the spectra except for the formation of a cloudy solution above pH 7.0. The solutions were 2.5×10^{-2} M with respect to erbium sulfate and 5.0×10^{-2} M with respect to EGTA.

Thulium

The thulium spectra shown in Figure 22 was only moderately changed by EGTA. The concentration of thulium sulfate was

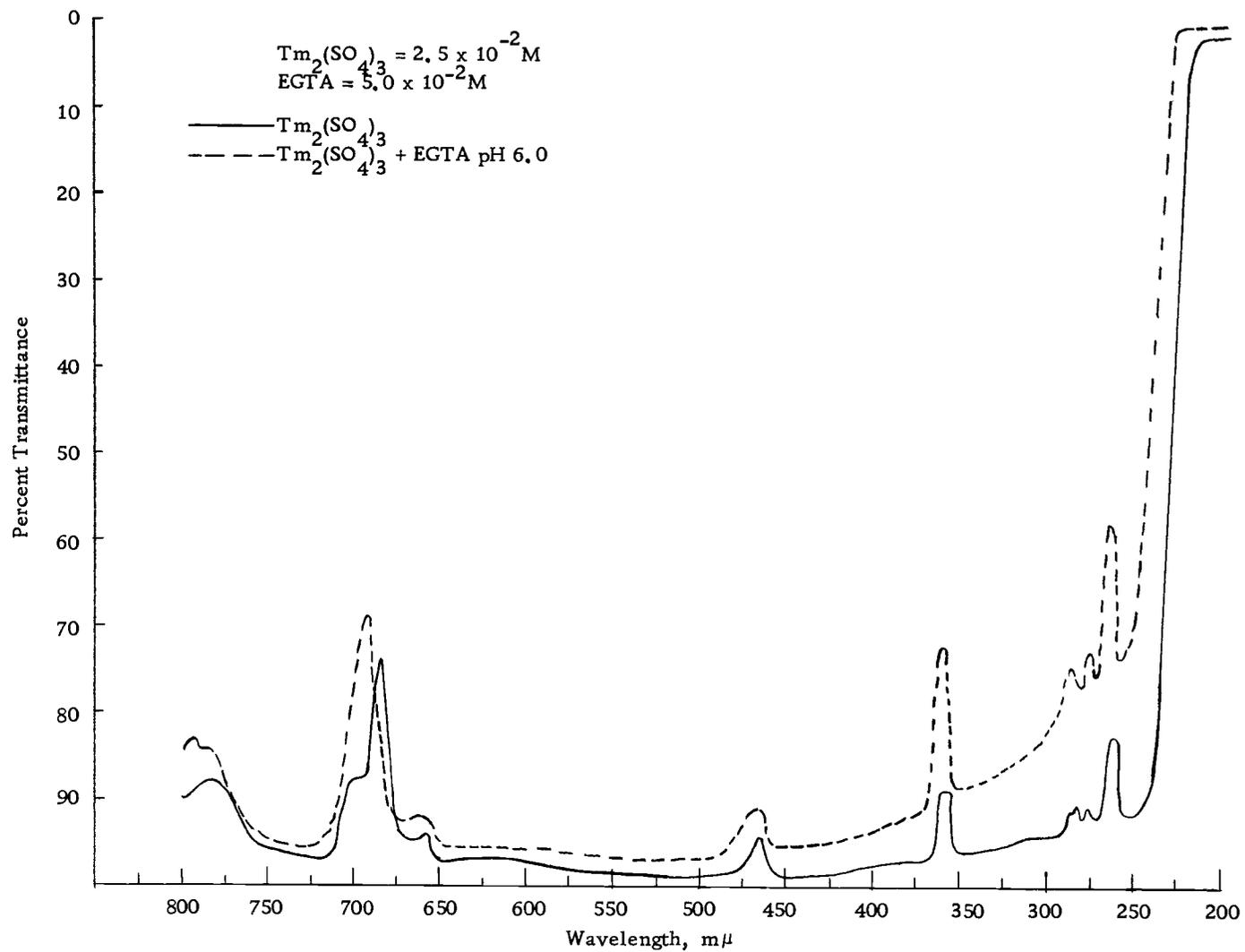


Figure 22. Thulium - EGTA spectra

2.5×10^{-2} M and the EGTA was 5.0×10^{-2} M. The spectra illustrated the typical spectral shifts induced by EGTA as well as the background increase in the ultraviolet.

Ytterbium

Ytterbium, like terbium, had no spectral absorption peaks in the visible and ultraviolet regions examined. EGTA addition did not change this situation.

Rhenium

Rhenium was available only as rhenium (III) chloride. The compound was slightly soluble, yielding an intense burgundy colored solution that rapidly interacted with water to produce a grey-black precipitate. A 1×10^{-4} M solution was stabilized at a pH 1.5 but at this pH did not spectrally change upon EGTA addition. The rhenium solution had an absorption peak at 505 m μ and a broad peak with shoulders on either side at 307 m μ .

Iridium

Solutions of iridium were prepared from iridium (III) bromide and iridium (IV) chloride. In Figures 23 and 24 are compared the spectra that resulted, both with and without EGTA.

The iridium (III) bromide solution had a violet color with a slight

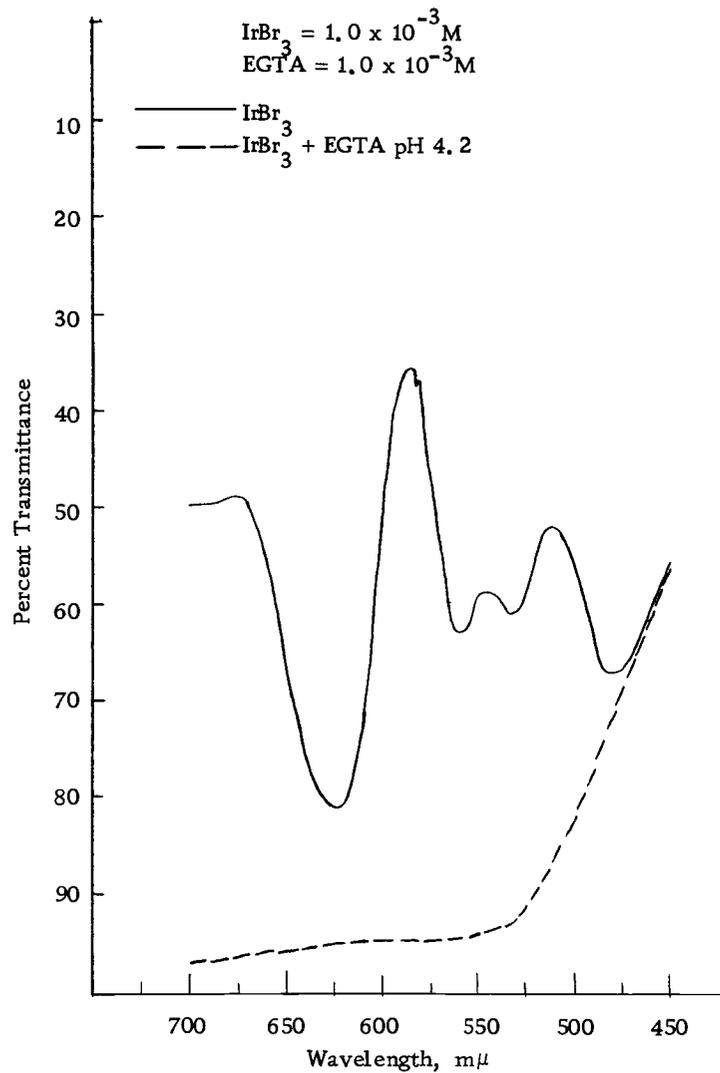


Figure 23. Iridium (III) - EGTA spectra

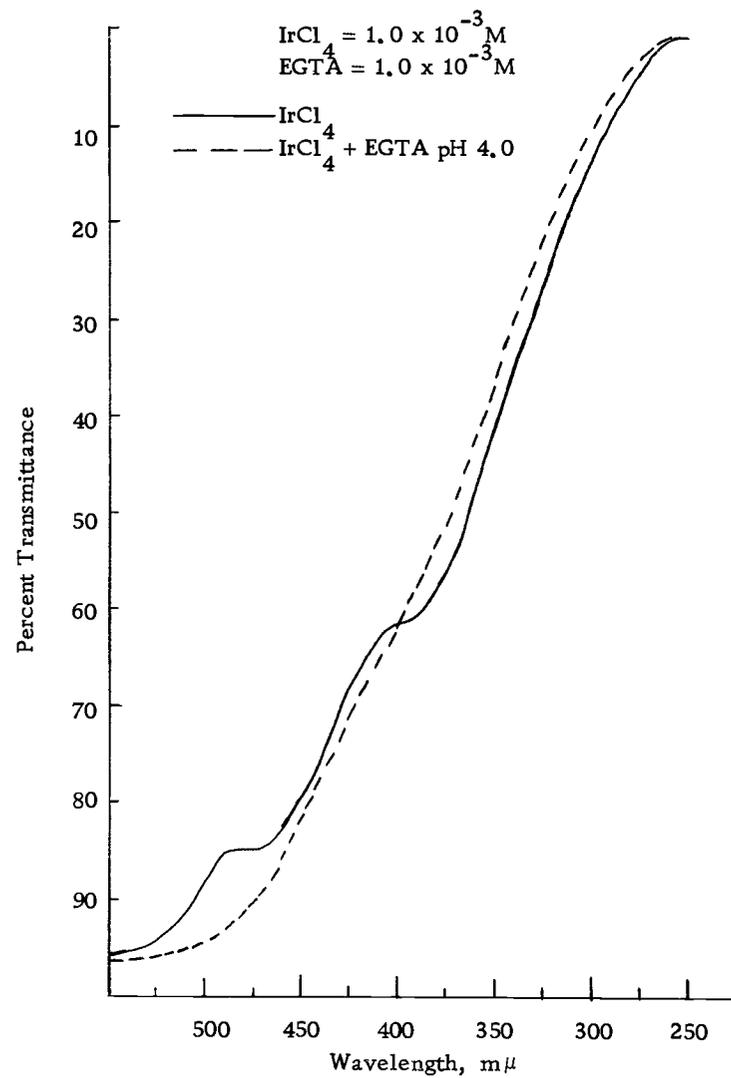


Figure 24. Iridium (IV) - EGTA spectra

brownish-yellow iridescence. The addition of the dark violet crystals to water produced a slight amount of brown precipitate. As the iridium stock solution was added to a volumetric flask already containing an equal amount of EGTA, the dark solution turned a yellow-tan color.

The iridium (III) solution had four distinct peaks, prior to EGTA addition, at 675 $m\mu$, 587 $m\mu$, 545 $m\mu$, and 512 $m\mu$. The spectra shown in Figure 23 were for 1.0×10^{-3} M solutions.

The iridium (IV) solutions were also 1.0×10^{-3} M. The color of the solution without EGTA was a reddish bronze. The addition of EGTA produced a slight visible change.

Whereas the two solutions had spectra with similar slopes after EGTA addition, the wavelengths where the solutions absorbed equally well were separated by approximately 50 $m\mu$. It was possible that the iridium (III) solution reacted with the EGTA and became a different ionic form. If the iridium (III) had oxidized to iridium (IV), then the difference in spectra would have had to be explained on the basis of the difference between the bromide and chloride ion effect on iridium (IV).

Platinum

Solutions of platinum (IV) chloride were examined at various concentrations for possible interaction with EGTA. The negative

complex of platinum with excess chloride ion showed no tendency to chelate with EGTA.

Gold

Solutions of 1.0×10^{-4} M gold (III) chloride were prepared both with and without EGTA. In Figure 25 is compared the spectrum of the yellow colored solution of gold (III) with the reddish-violet solution that resulted from EGTA addition. An identical trace resulted at both pH 5.2 and 10.8. However, upon acidification the peak at 535 m μ began to absorb less and the absorption at 700 m μ began to increase. The solutions were not stable and upon standing, the gold deposited on the walls of its container.

A spectral scan started at 800 m μ after acidification of the solution showed a broad plateau from 725 m μ to 525 m μ .

Mercury

The most stable EGTA metal complex listed in Table II was the mercury (II)-EGTA chelate. Solutions of mercury (II) chloride were prepared as 1.0×10^{-4} M; one contained an equal concentration of EGTA.

Spectral scans run at pH 4.4, 6.4, and 10.8 revealed only the absorption of EGTA. At that concentration the solution was transparent from 700 to 260 m μ .

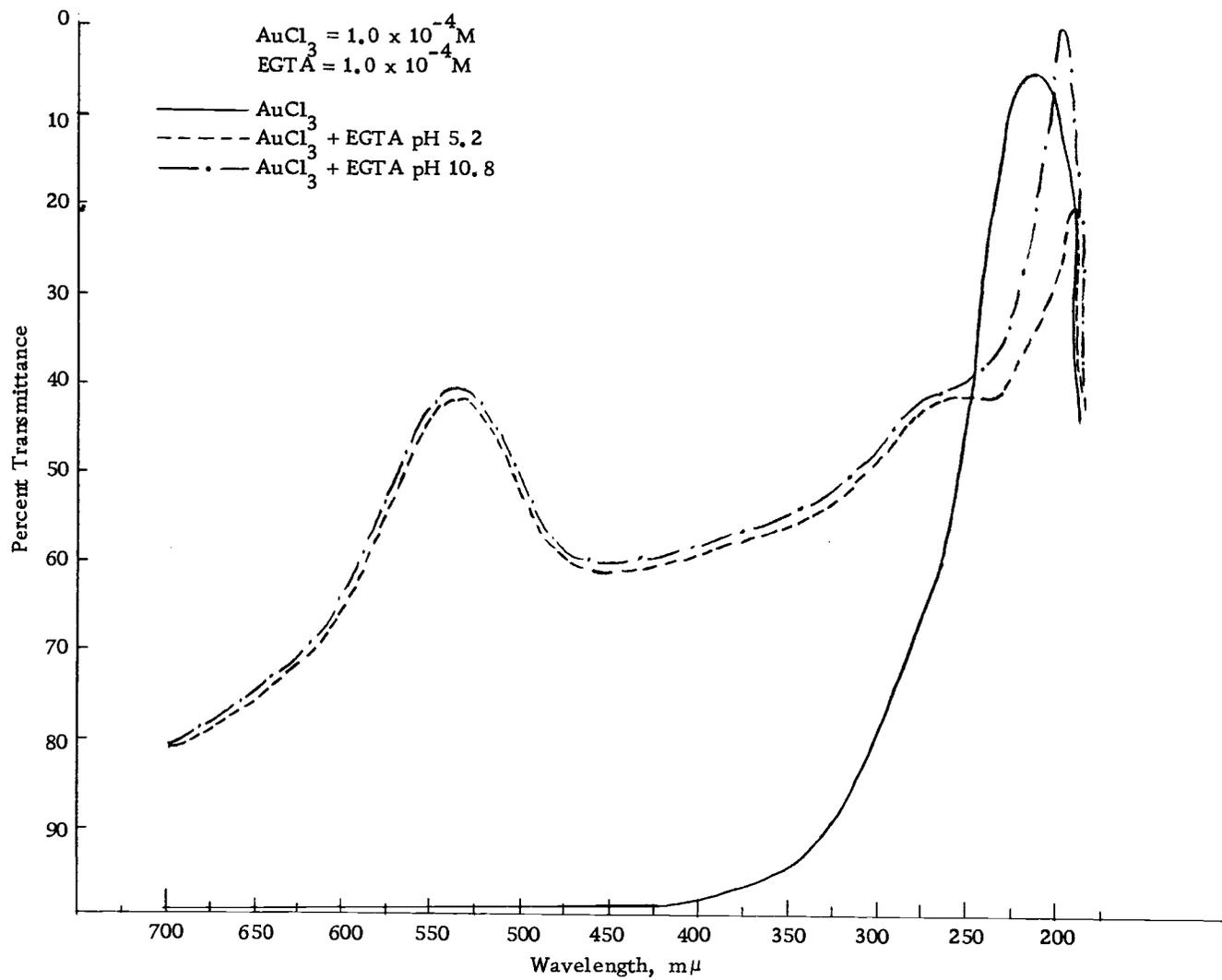


Figure 25. Gold (III) - EGTA spectra

There was no precipitation below 2.2, indicating that the chloride had not prevented the EGTA from chelating with the mercury. At pH 1.8 the spectral scan showed just a slight deviation between 245 m μ and 220 m μ from the other lower pH traces with EGTA at this concentration.

Thallium

The thallium (I) sulfate solutions were prepared 2.5×10^{-2} M with 5.0×10^{-2} M EGTA added to one solution. The two spectra are compared in Figure 26. A very slight turbidity formed on addition of EGTA. It was allowed to settle out prior to the spectral scan. The absorption of the thallium (I)-EGTA solution appeared to be significantly greater than the scan of the two separate solutions at that concentration. The pH of the EGTA solution was 6.2. The spectrum of the solution was unchanged to pH 4.0. Precipitation resulted at pH 2.0 and cloudiness appeared at pH values above 7.5.

A tenfold dilution of the EGTA-containing solution showed no evidence of the shoulder associated with the 303 m μ thallium (I) spectral peak.

Thallium (III) chloride solutions were spectrally examined. The solution had to be acidic to prevent the formation of a cloudy precipitate. The thallium (III) solution did not absorb from 800 m μ to about 350 m μ , depending on the concentration. The solution did

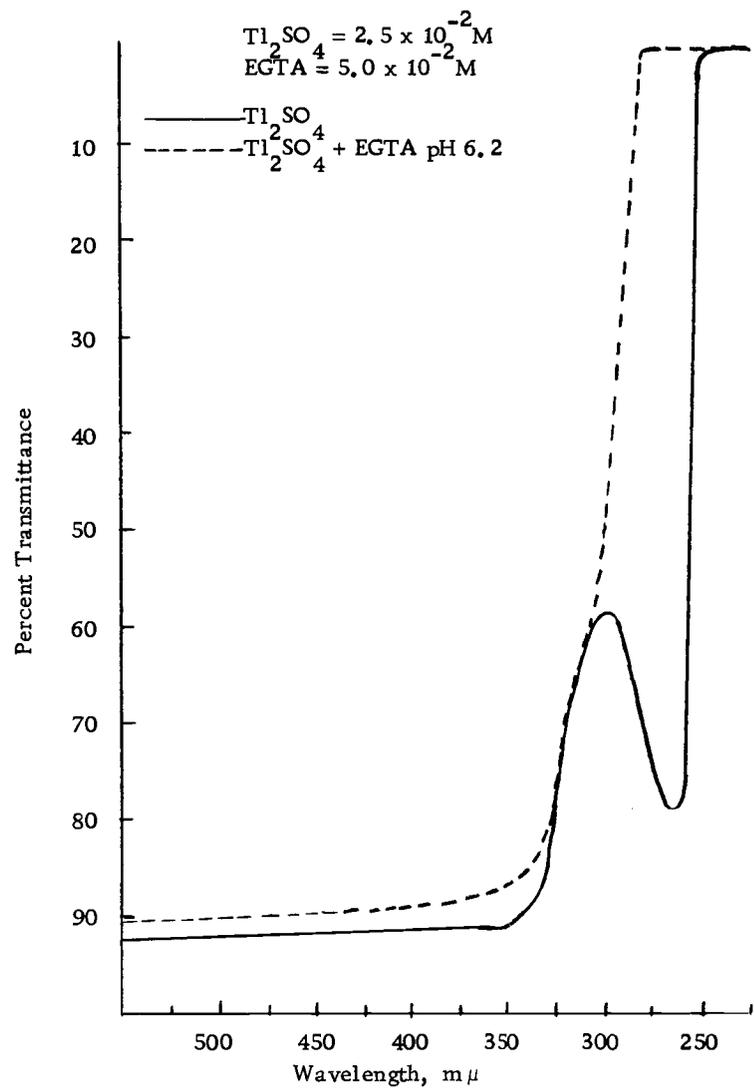


Figure 26. Thallium (I) - EGTA spectra

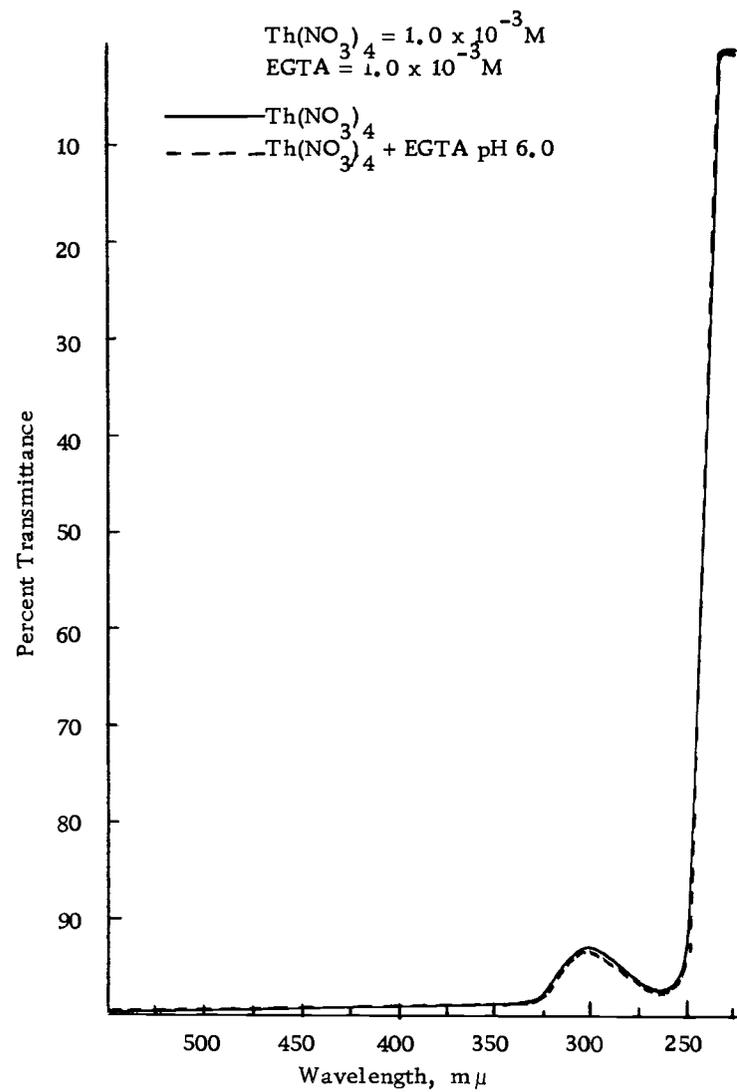


Figure 27. Thorium (IV) - EGTA spectra

absorb strongly below 300 m μ at concentrations as low as 5.0×10^{-4} M. The addition of equal concentration of EGTA caused a slight change in the slope of the increasing absorption curve. To decrease the transmittance from 90% T to 10% required a 30 m μ change in wavelength for thallium (III) solution. With EGTA added, the same change in transmittance required a 41 m μ change in wavelength. The comparison was made in the vicinity of 315 m μ .

Thorium

A 1.0×10^{-3} M solution of thorium (IV) nitrate was prepared. A spectral scan was run from 700 to 200 m μ , showing only the nitrate spectra in the UV region. When EGTA-thorium solution was prepared in equal concentration no additional absorption occurred. Figure 27 was included to demonstrate the reproducibility of the instrument and the solution preparation procedure. The two spectral traces on the original chart paper overlapped each other except where the first nitrate peak at 300 m μ descended toward 275 m μ .

Uranium

Figure 28 shows the spectrum of 1.0×10^{-2} M uranyl nitrate with scans run of 1.0×10^{-2} M uranyl nitrate plus 1.0×10^{-2} M EGTA at five different pH values from 2.1 to 9.3. Precipitation took place at pH 9.7.

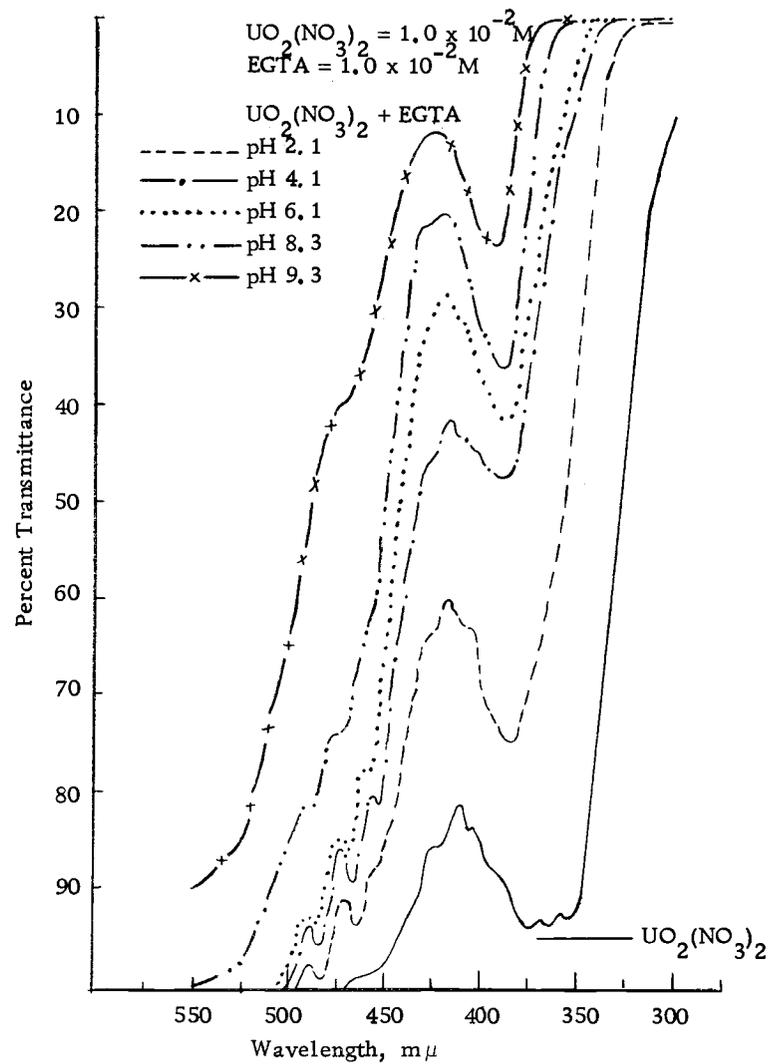


Figure 28. Uranium (VI) - EGTA spectra

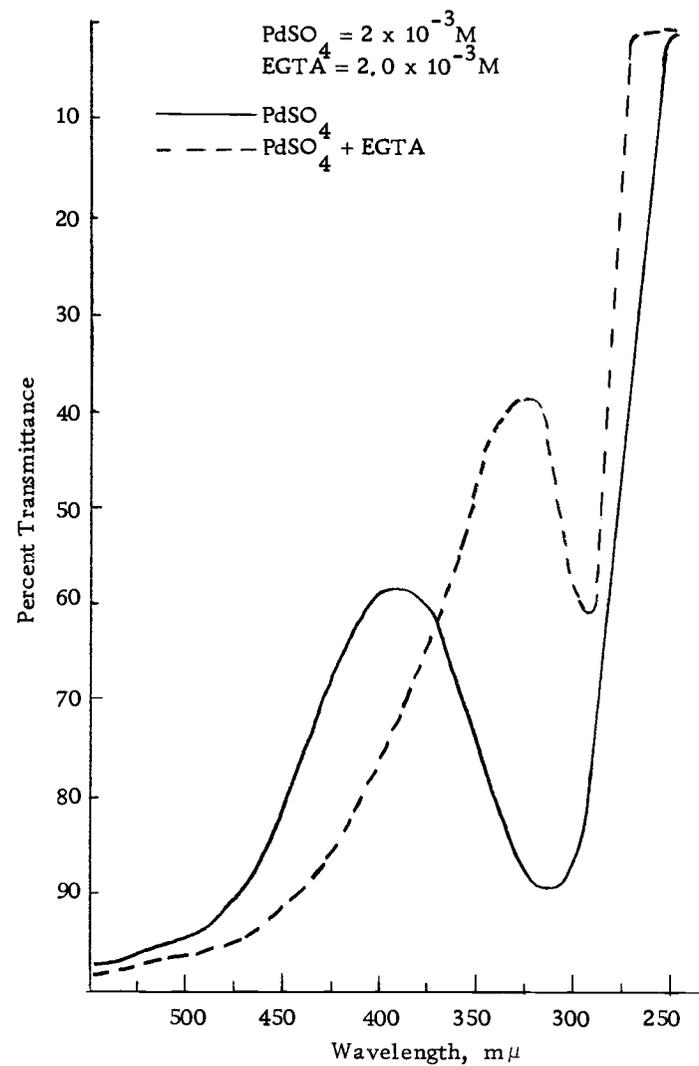


Figure 29. Palladium (II) - EGTA spectra 37

An attempt was made to develop quantitative colorimetric procedures for both the uranyl ion and the palladium (II) ion (Figure 29). It was found, however, that the spectra of both of these ions were not only pH dependent but also dependent upon the complexes formed with each of the buffer systems that were prepared to keep the ions at a fixed pH for spectrophotometric measurements.

V. ANALYTICAL APPLICATIONS OF EGTA-METAL ION ABSORPTION SPECTRA

Qualitative Application to Certain Rare Earths

The lack of distinctive chemical tests for individual rare earth elements (20, p. 62) placed more than ordinary emphasis upon their unique absorption spectra. All of the rare earths did not possess characteristic spectra in the visible and near ultraviolet spectral regions, and those which did varied greatly in the complexity of their spectra.

Because of the complexity of the spectra of neodymium, holmium, and erbium, it was often difficult to establish the presence or absence of other rare earths in low concentration when these three were predominately present individually or collectively. The spectral absorption peaks of holmium overlapped all but one of the absorption maxima of erbium. Both holmium and erbium obscured the main spectral absorption peaks of praseodymium, whereas the presence of neodymium in any significant concentration obscured the one additional minor praseodymium peak.

The response of praseodymium to EGTA was unique among the rare earths. The depression of the absorption peaks of praseodymium appeared undesirable. However, when the absorption of praseodymium-EGTA solution was measured versus a solution containing

only praseodymium, the result was a characteristic negative absorbance spectrum as the solution in the reference cell began to absorb more strongly than the sample cell containing praseodymium and EGTA.

Figure 30 illustrates the spectrum that resulted when the Cary spectrophotometer measured the spectral differential between solutions of holmium plus praseodymium versus holmium, praseodymium, and EGTA. The metal ion concentrations were 2.0×10^{-3} M and the EGTA concentration was 5.0×10^{-3} M. The spectral plots in Figure 30 were traced directly from the chart paper.

To illustrate the differences that occurred, there was included in Figure 30 the absorption spectrum of holmium (D) at those wavelengths where praseodymium absorption existed. Figure 30 (C) shows the differential spectrum of holmium versus holmium plus EGTA. The changes caused by EGTA addition to holmium were the components of this spectral difference. The smaller absorption peaks at 467 m μ and 472 m μ that EGTA did not change were completely missing from the differential plot. Figure 30 (A) shows the strong negative absorbance due to the presence of praseodymium. The negative characteristic praseodymium absorption was clearly distinguishable when the concentration of praseodymium was lowered fivefold and the holmium was increased tenfold.

Negative absorbance spectra also resulted from the major shift

- A. Instrumentally plotted difference between HoPr solution and HoPr EGTA solution
- B. HoEr versus HoEr EGTA
- C. Ho versus Ho EGTA
- D. Ho versus H_2O

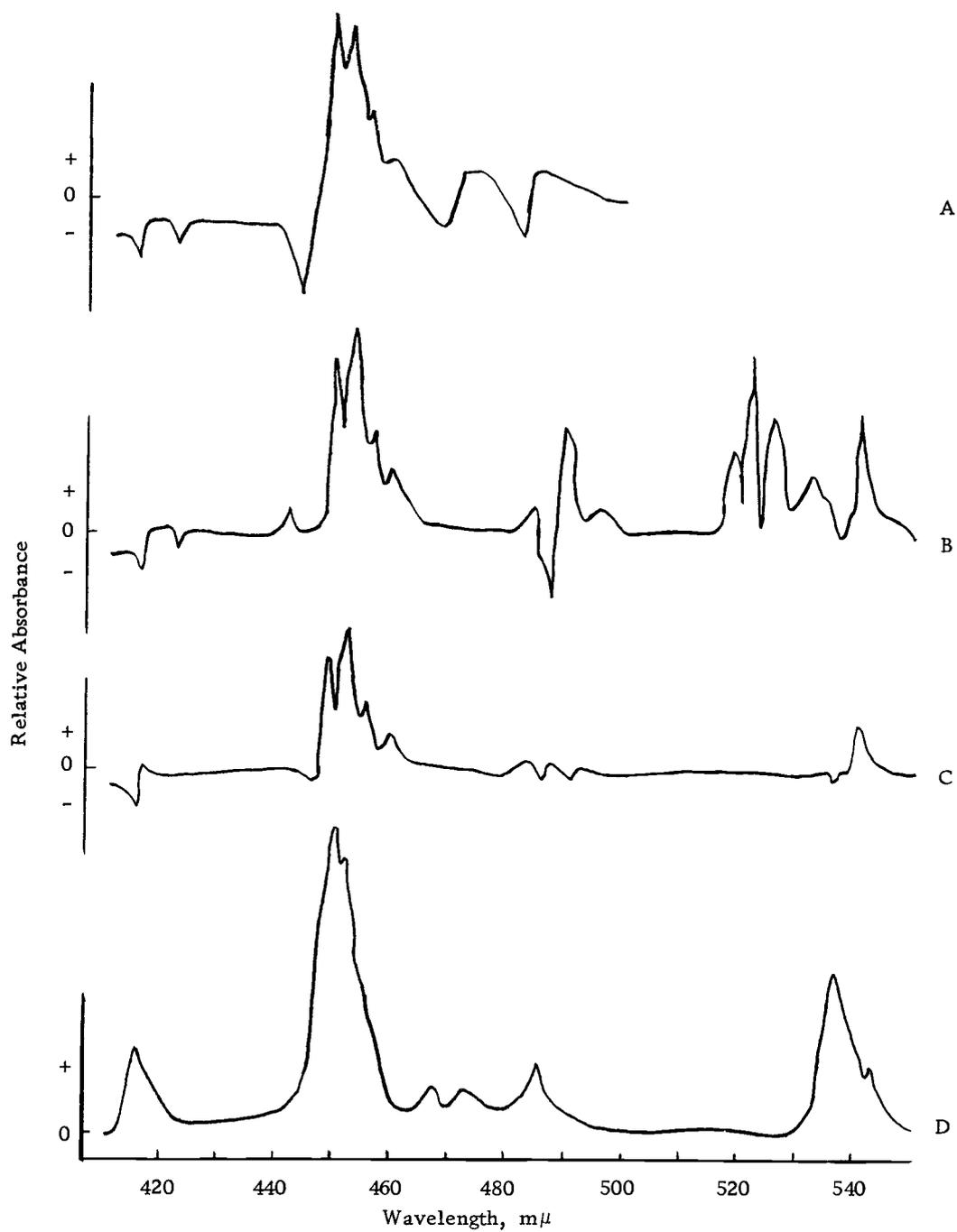


Figure 30. Differential spectra compared with holmium spectrum

of an absorption peak. Erbium had an absorbing maximum overlapping the holmium peak at 485 $m\mu$. The addition of EGTA shifted this peak far enough that the original peak in the reference solution containing erbium plus holmium absorbed more strongly than the solution with EGTA added. In Figure 30 (B) is shown the differential spectrum as recorded by the instrument. A characteristic negative peak at 487 $m\mu$ persists as the erbium concentration is reduced tenfold.

In practice the differential spectra were determined by pipetting equal aliquots of a rare earth ion mixture into two equal volumetric flasks. Equal volumes of buffer (selected with a pH less than 6.0) were added to each flask and sufficient EGTA solution added to one flask to exceed the estimated total rare earth ion concentration. When diluted to volume and mixed, the flask containing the EGTA provided the contents of the spectrophotometer sample cell, and the reference cell was filled from the other flask.

Quantitative Application to Certain Rare Earths

Spectrophotometric analysis procedures for the individual rare earths have been summarized by Woyski and Harris in the treatise edited by Kolthoff (20, p. 101-118). The molar absorptivities of the rare earth ions in aqueous solutions were listed (20, p. 102) with the wavelengths used for analysis.

Although the addition of EGTA to solutions of rare earth ions did not produce truly spectacular increases in their absorption, it did for certain ions, notably holmium, produce a significant improvement in the absorptivities of certain major absorption peaks.

The amount of EGTA reagent utilized by various rare earth ions in forming chelates was determined by varying the mole fraction of the rare earth ion with respect to the total concentration of the ion plus EGTA. As the concentration of the rare earth ion increased and the EGTA concentration decreased, the absorbance of the color formed by the chelate at a particular wavelength reached a maximum and then declined. The ion-mole ratio of maximum absorption (within experimental error) for the rare earth chelates with EGTA was 1:1.

The linearity of the Beer's Law plot of each chelate solution was determined with the minimum concentrations to which the instrument would respond.

Attempts were made to verify the formation constants (see Table II) of the chelates by the spectrophotometric method described by Martell and Calvin (23, p. 99). No detectable difference in absorbance could be measured, whether the ion and EGTA were present in equal concentration or the EGTA in great excess. This indicated that at the concentrations available for this study, the formation of the colored chelate had been so complete that the addition

of excess reagent did not produce an equilibrium shift.

The reagents that were used in the study of the neodymium-EGTA system were 1.11×10^{-2} gram-ion/liter Nd^{+++} stock solution, 1.00×10^{-2} M EGTA stock solution, and 1.00×10^{-1} M potassium hydrogen phthalate pH 4.0 buffer stock solution prepared as described by Bates (1, p. 159).

The neodymium solution was prepared from anhydrous neodymium sulfate supplied by the City Chemical Company as 99% pure. The compound was dried at 115° C for five hours. No loss in weight occurred after the first three hours of drying.

The solutions used for the variation of the mole fraction of neodymium and EGTA were prepared by adding X ml of neodymium stock solution and $10-X$ ml of EGTA stock solution to a 25 ml volumetric flask. To the flask was then pipetted 10 ml of the pH 4.0 buffer stock solution and the flask diluted to volume. The absorbance was measured by the Cary recording spectrophotometer as the wavelength region from 600 to 560 $\text{m}\mu$ was scanned. The reference cell contained neodymium ion and buffer in the same concentration that existed in the sample cell. The absorbance of the 580 $\text{m}\mu$ differential peak was measured versus the base line at 575 $\text{m}\mu$. The absorbance values listed in Table IV thus represent only the increased absorption due to the chelate form. Figure 31 shows the graphical plot of the data. A one-to-one ratio of ion to chelon was

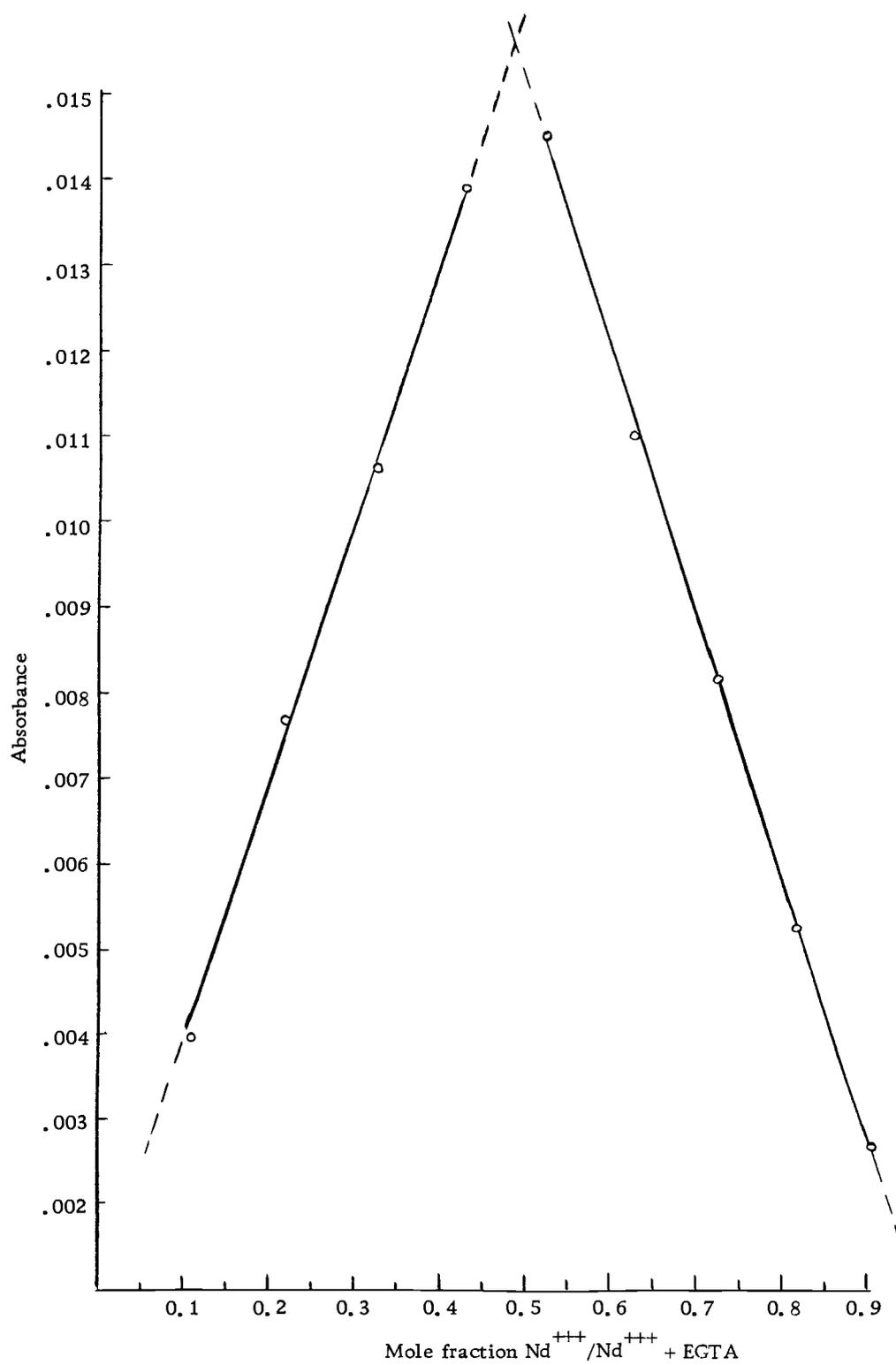


Figure 31. Continuous variations plot of Nd-EGTA system at 580 mμ.

clearly indicated.

Table IV. Continuous variations data for the neodymium-EGTA system at 580 m μ .

X ml Nd ⁺⁺⁺	mole fraction	absorbance
1.0	.110	.00395
2.0	.217	.00765
3.0	.322	.0106
4.0	.425	.0139
5.0	.526	.0145
6.0	.625	.0110
7.0	.722	.00818
8.0	.817	.00528
9.0	.908	.00268

To determine if the neodymium-EGTA chelate concentration was linearly related to the solution's absorbance, four solutions containing excess EGTA were scanned versus a blank containing buffer and EGTA. The absorbance of the peak at 580 m μ was determined in reference to the base line at 560 m μ . The values are plotted in Figure 32.

The constant increase of the background absorption in the ultraviolet region by many of the rare earth ions including europium (III) (see Figure 18) upon addition of EGTA, aroused interest in the concentration dependence of this absorption. Accordingly, a 2.50×10^{-2} M stock solution of europium sulfate octahydrate was prepared. One milliliter of this solution was added to three milliliters of 0.100 M EGTA in a 25 ml volumetric flask. Ten milliliters of buffer stock

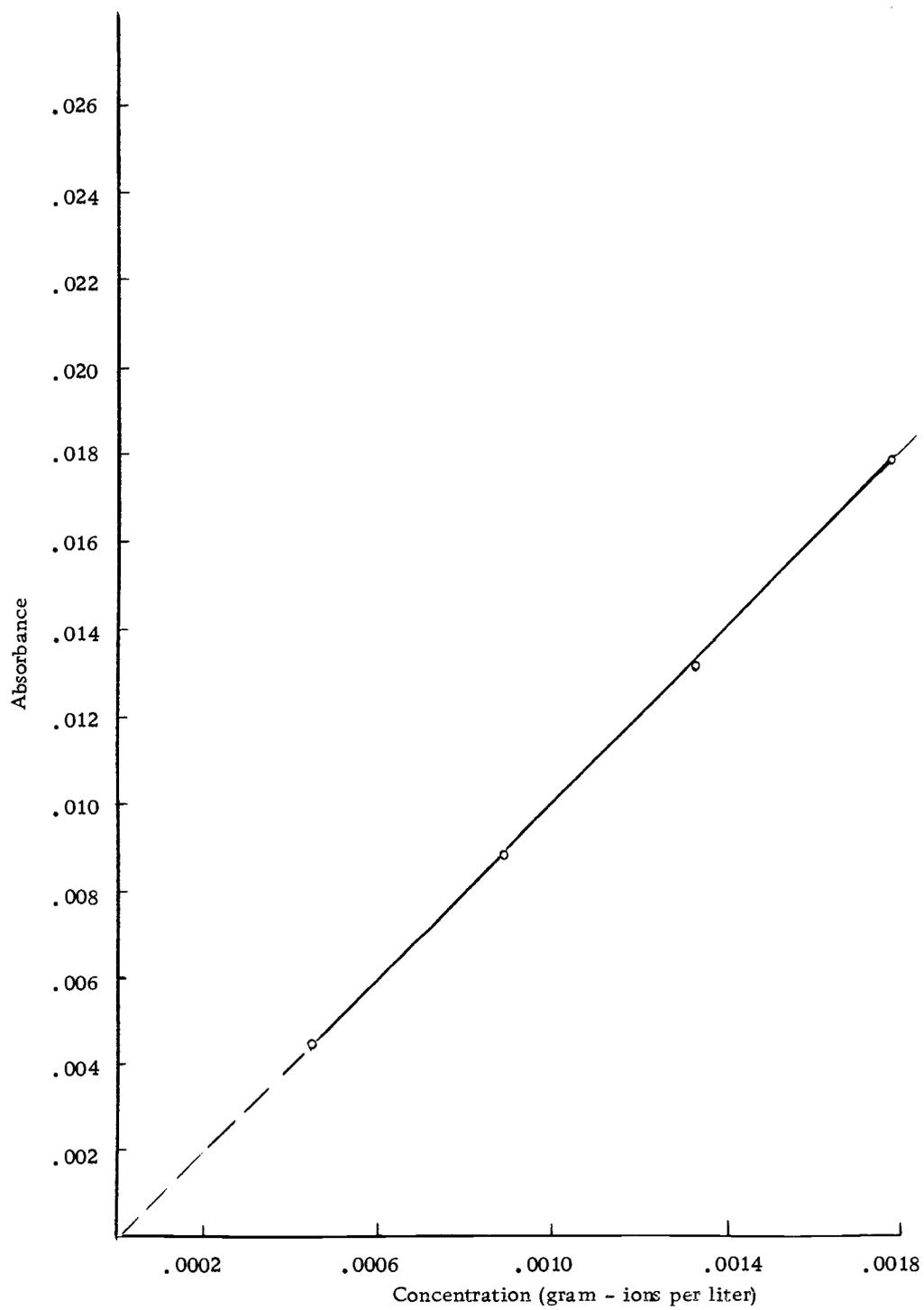


Figure 32. Beer's Law relationship of Nd-EGTA system at 580 mμ

were added to give pH 4.0 upon dilution to volume. In a similar manner solutions of 2, 3, and 4 times this concentration of chelate were prepared. The absorbance of the solutions was measured against a reference blank containing identical amounts of EGTA and buffer stock. Figure 33 graphically shows the linear increase in absorbance with changing concentration. The straight line, however, did not pass through the origin. Its orientation suggested that the 99.9% europium sulfate octahydrate supplied by Alfa Inorganics, Inc. was of lesser purity, probably due to absorbed water.

The absorbance values plotted in Figure 33 were the difference between the base line at 345 $m\mu$ and the 318 $m\mu$ peak. The background intensity increased but the height of the peak itself, that extended above the background, did not noticeably change in size.

The most pronounced increase in absorbance with the addition of EGTA to rare earth ions was with holmium at 450 $m\mu$. The molar absorptivity of the 537 $m\mu$ holmium peak, also used for spectrophotometric analysis, was 4.97 (20, p. 102). The molar absorptivity of the holmium-EGTA complex at 450 $m\mu$ was determined to be 10.1.

To study the holmium-EGTA system, a 2.155×10^{-2} gram-ion/liter stock solution was prepared from anhydrous 99.9% holmium sulfate which was dried for 10 hours to constant weight at 120^o C. The solutions used to determine the ratio of Ho^{+++} to EGTA were prepared by the addition of X ml of the holmium sulfate solution and 10-X

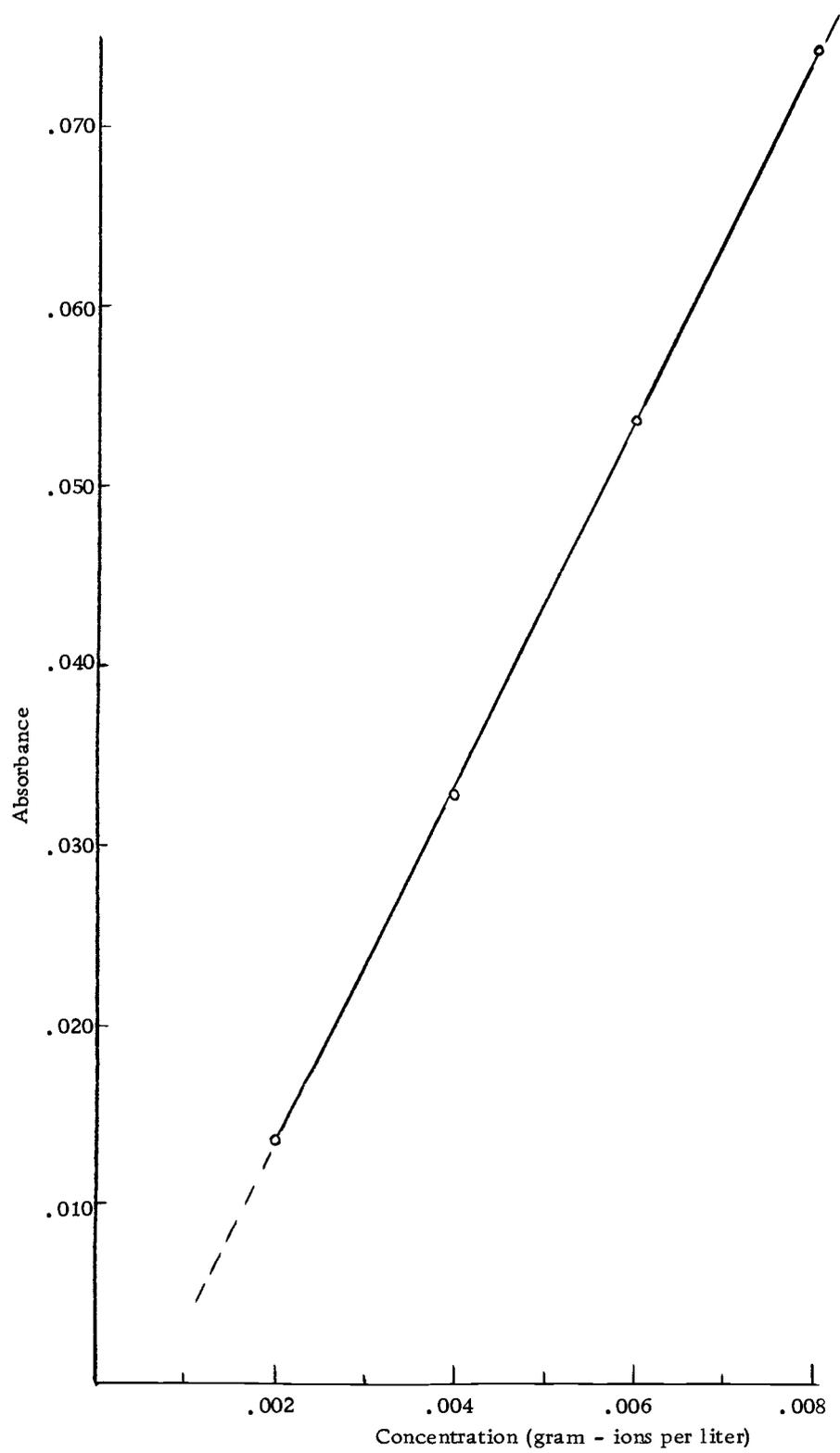


Figure 33. Beer's Law relationship for Eu-EGTA system at 318 $m\mu$

ml of 2.50×10^{-2} M EGTA to a 25 ml volumetric flask. Buffer stock solution (12 ml) was added by pipet and the contents of the flask were diluted to volume. A blank solution was also prepared each time containing X ml of holmium and the buffer aliquot.

The differential absorbance resulting only from the chelate was plotted by the instrument as scans were run from 475 to 440 $m\mu$. The maximum absorbance was determined by reference to the baseline at 440 $m\mu$. The differential spectra of holmium had two peaks, one at 450 $m\mu$ and one at 453 $m\mu$. In Figure 34 are graphed the results obtained from the determination of the ratio of holmium (III) to EGTA in the chelate based upon each of the two absorption maxima. The 1:1 ratio is evident. The data is listed in Table V.

Table V. Continuous variations data for the holmium-EGTA system.

X ml Ho ⁺⁺⁺	mole fraction	450 $m\mu$ absorbance	24 hour stability	453 $m\mu$ absorbance	24 hour stability
1.0	.0873	.0035	.0035	.0025	.0028
2.0	.177	.0063		.0053	
3.0	.270	.0103	.0105	.0085	.0087
4.0	.365	.0145	.0145	.0118	.0120
5.0	.453	.0185	.0187	.0161	.0165
6.0	.565	.0185	.0187	.0168	.0168
7.5	.721	.0130	.0130	.0120	.0118
8.0	.777	.0108		.0104	
8.5	.830	.0085	.0080	.0073	.0072

The solutions prepared for the continuous variations study were stored for 24 hours and the absorbance values rechecked. These are

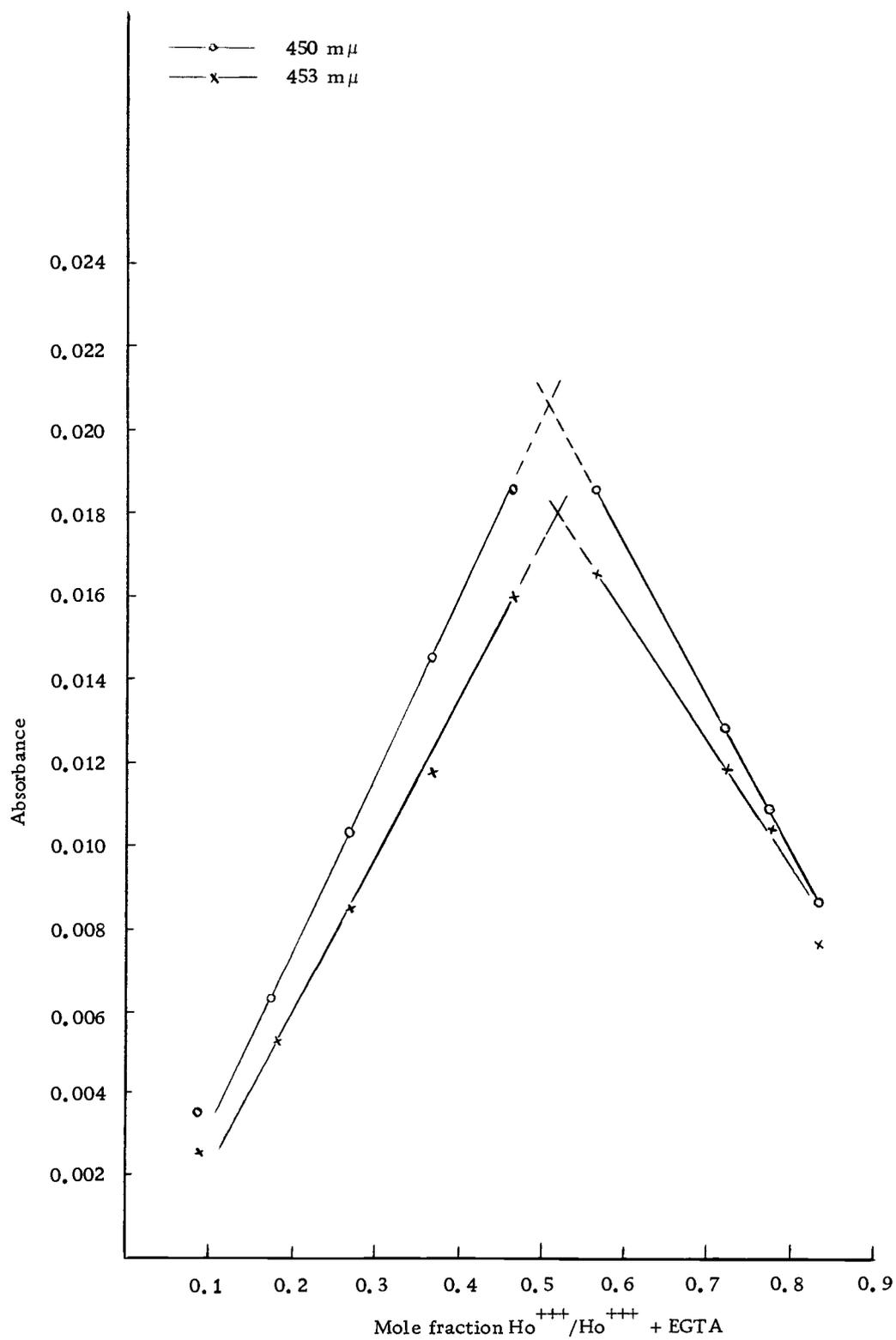


Figure 34. Continuous variations plot of Ho-EGTA system at 450 and 453 m μ .

also tabulated in Table V. Additional measurements taken over a period of months indicated complete stability.

The Beer's Law conformity of the holmium-EGTA solutions was carefully examined for the total absorbance by holmium plus EGTA at 450 m μ . In Figure 35 is graphed the linearity of the more dilute concentrations examined. Beer's Law was obeyed from a concentration of 8.62×10^{-4} gram-ions/liter to 1.77×10^{-2} gram-ions/liter. No greater concentrations were examined. Table VI lists the absorbances of the various concentrations measured.

Table VI. Absorbances of various holmium-EGTA solutions at 450 m μ .

Solution	Concentration (gram-ions/liter) of holmium ion	Absorbance
A	8.62×10^{-4}	.0087
B	1.72×10^{-3}	.0175
C	2.58×10^{-3}	.0260
D	3.45×10^{-3}	.0348
E	3.54×10^{-3}	.0363
F	4.30×10^{-3}	.0435
G	7.08×10^{-3}	.0710
H	1.06×10^{-2}	.1060
I	1.41×10^{-2}	.1414
J	1.77×10^{-2}	.1758

In each instance a pipet was used to add a portion of the stock solution to a 25 ml volumetric flask. To this were added a

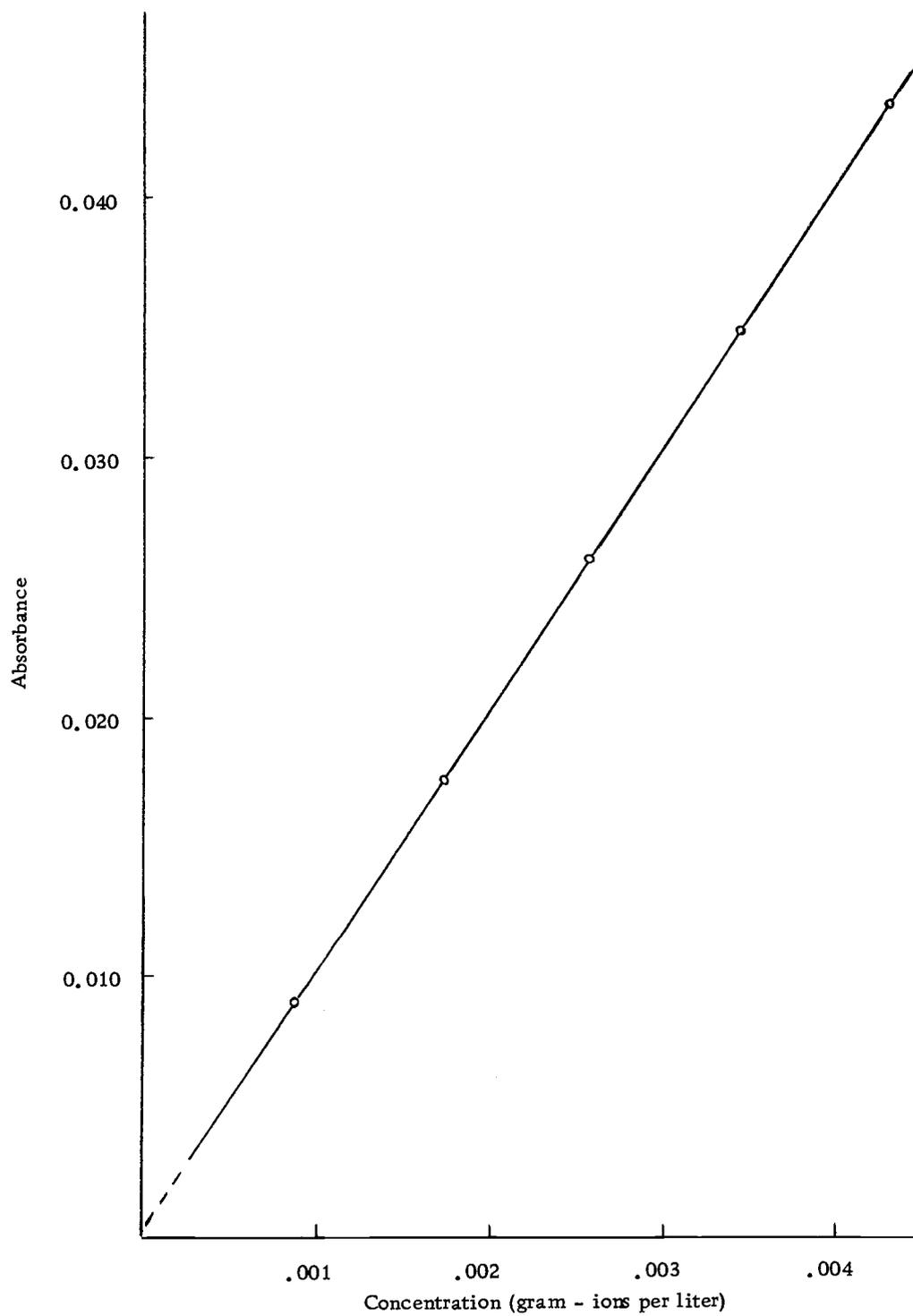


Figure 35. Beer's Law relationship of Ho-EGTA system at 450 m μ

stoichiometric excess of 0.100 M EGTA solution and 12 ml of stock pH 4.0 buffer solution. The flask was diluted to the mark with distilled water and carefully mixed.

Routine analyses were run on five synthetic unknowns with the results shown in Table VII.

Table VII. Analyses of synthetic holmium unknowns.

Sample	Concentration taken gram-ions/liter	Concentration found gram-ions/liter	Deviation, %
A	1.07×10^{-3}	1.07×10^{-3}	0.0
B	1.72×10^{-3}	1.77×10^{-3}	+2.9
C	1.04×10^{-3}	1.07×10^{-3}	+2.8
D	2.59×10^{-3}	2.67×10^{-3}	+3.1
E	2.93×10^{-3}	2.96×10^{-3}	+1.0

The initial spectral traces run on erbium-EGTA systems indicated that the low erbium interference with the holmium 450 m μ peak would be completely eliminated due to the shifting of the erbium peak involved. Unfortunately, the shift in the erbium wavelength, upon EGTA addition, was not sufficient to remove this interference completely. Whenever holmium is analyzed in the presence of erbium a subtractive correction for the erbium interference must be made (20, p. 114) as all major holmium peaks have erbium interferences.

An investigation was made of the erbium-EGTA chelate, even

though EGTA caused the least absorption increase in the erbium spectrum when compared with the three rare earth ions previously discussed. The continuous variations study measuring the absorbance of the erbium chelate at 521 $m\mu$ is summarized in the graph shown in Figure 36, whereas the Beer's Law relationship at 521 $m\mu$ is shown in Figure 37. This information was desired as erbium and holmium generally occur together in natural substances. If EGTA were used to enhance the analysis of holmium, it would still be possible to determine erbium in the same solution as the erbium-EGTA chelate also conforms to Beer's Law.

Quantitative Application to Copper

The copper (II)-EGTA system was examined in the ultraviolet region for the possible analytical application of the 298 $m\mu$ absorption maximum. The copper stock solution was prepared by dissolving the calculated amount of 99.9% copper sulfate pentahydrate in sufficient distilled deionized water to produce a 1.00×10^{-1} M solution. The concentration of this solution was checked by standard electrogravimetric procedures that yielded a concentration of $0.1003 \pm .0002$ M. This solution was then quantitatively diluted as required in subsequent procedures.

Copper was known to form two chelates with EGTA. Holloway and Reilley (16) had observed an unusual potential versus pH curve

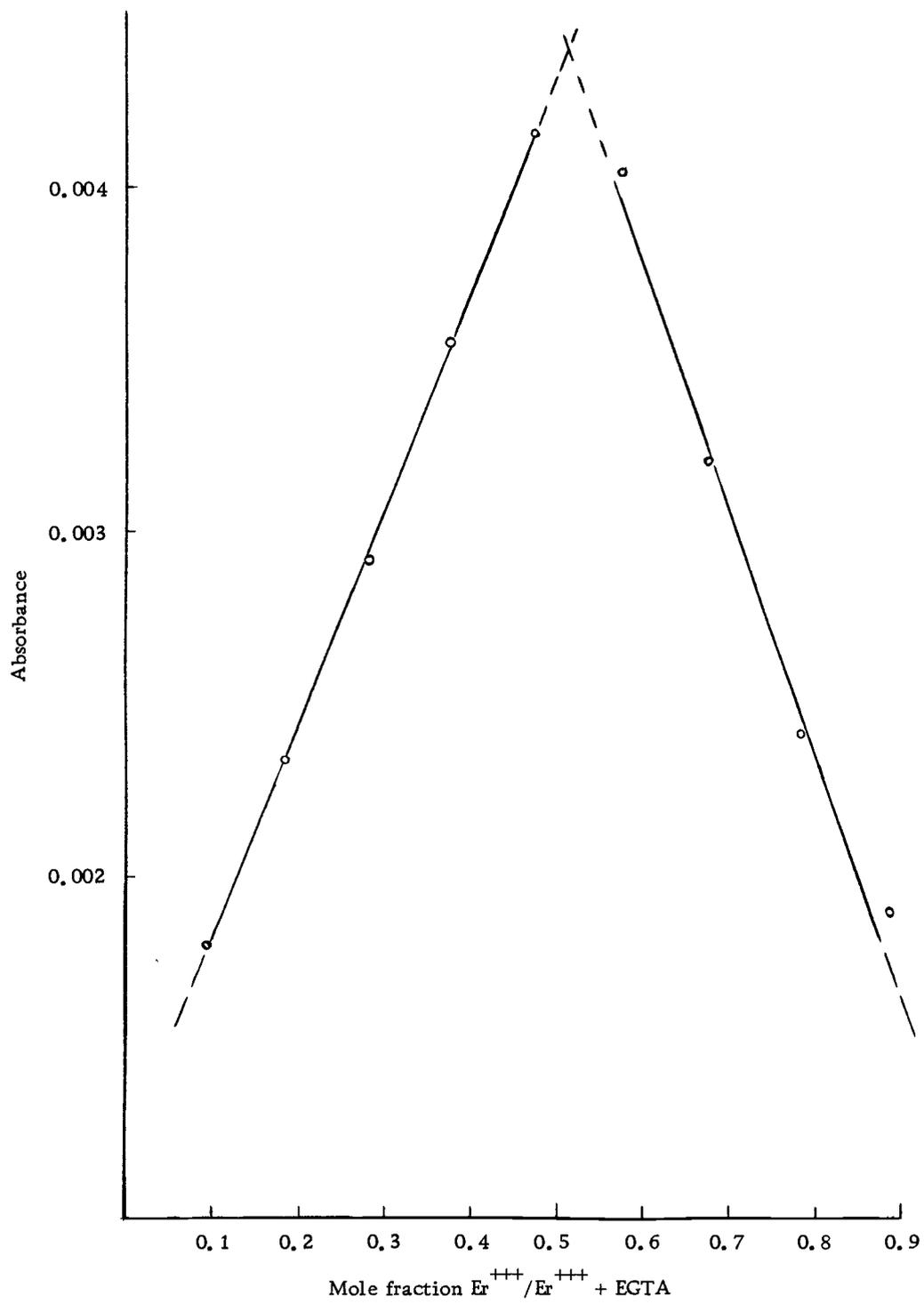


Figure 36. Continuous variations plot of Er-EGTA system at 521 m μ

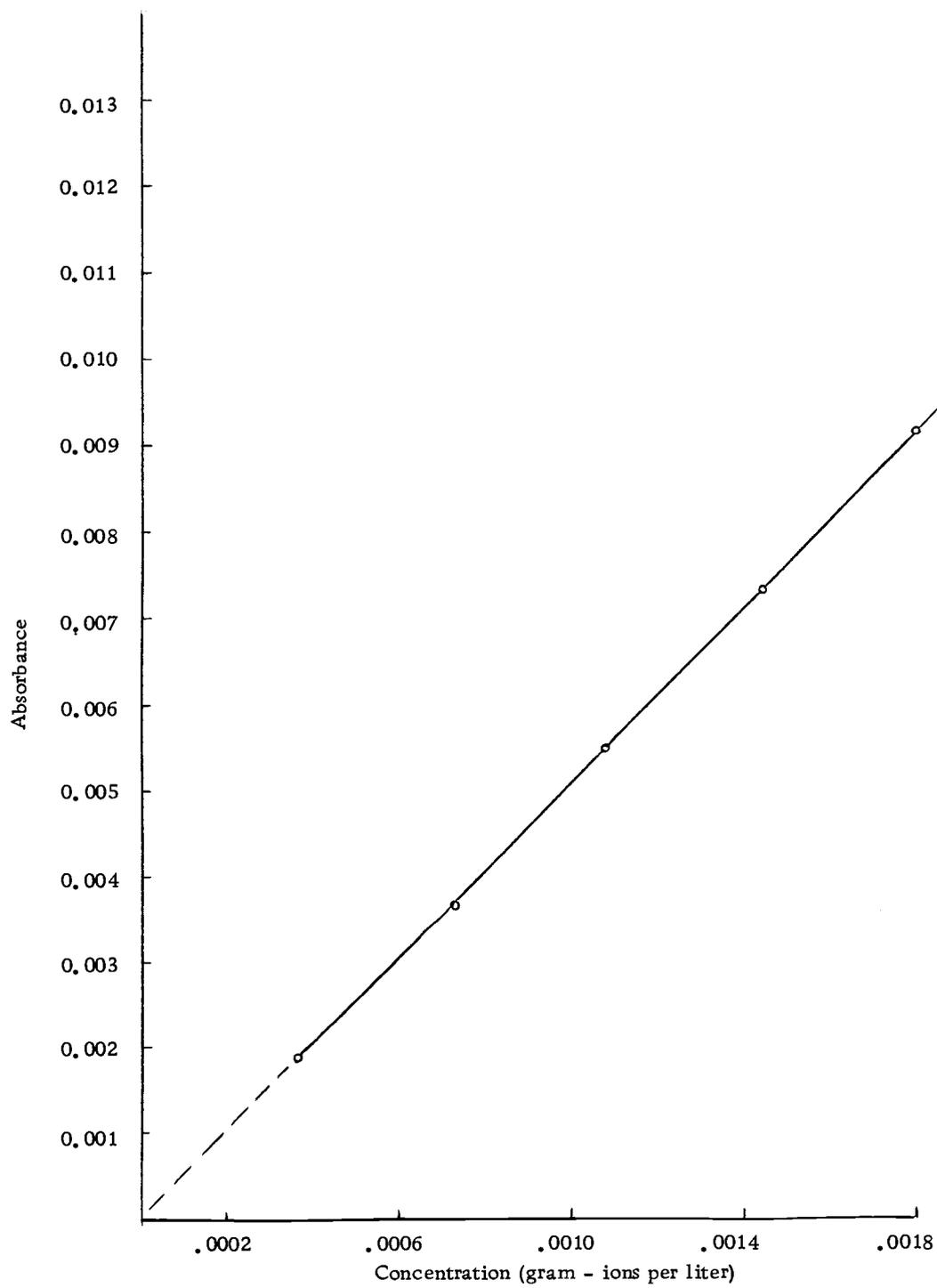


Figure 37. Beer's Law relationship of Er-EGTA system at 521 m μ

for copper when attempting to determine its stability constant with EGTA. Jacobsen and Saetre (18), da Silva and Calado (6), and Schrøder (38) polarographically examined the copper (II)-EGTA chelate system and suggested, with varying degrees of refinement, that both a mononuclear and binuclear chelate were formed. Holloway and Reilley determined the formation constant to be 17.8 (log K) for the 1:1 chelate and Schrøder (38) determined the formation constant of the binuclear complex to be 4.31 (log K).

In the initial phase of this study, copper (II) was observed to form two distinct absorption peaks in the ultraviolet, one at 298 m μ and one at 243 m μ (see Figure 13). The lowering of the pH past 3.5 caused the 298 m μ absorption maximum to disappear. It was also observed that the addition of excess copper (II) ions would produce the same disappearance in a solution buffered at pH 6.0. The removal of the 298 m μ peak did not change in any detectable way the appearance of the maximum at 243 m μ . When the reference cell of the Cary spectrophotometer contained a copper (II) ion concentration equal to the copper (II) chelate concentration in the sample cell, the peak at 243 m μ was reduced in intensity to approximately that of the peak at 298 m μ . Further investigation showed that the intensity of the 243 m μ maximum did not increase with increasing concentration as rapidly as the peak at 298 m μ . Accordingly, the 298 m μ peak was selected for possible analytical use at a pH above 4 and with excess

EGTA for quantitative analysis. Another factor recommended this choice as well. Greater interferences existed at the shorter wavelength.

The mole ratio of the copper (II) ion to EGTA was determined by a continuous variation of the copper (II) and EGTA concentrations, keeping the total concentration of the two constant. For this study a 1.00×10^{-3} M copper (II) sulfate solution was prepared by the volumetric dilution of an aliquot from the stock solution. A pH 6.0 buffer stock solution was prepared as described by Bates (1, p. 160) from potassium dihydrogen phosphate and sodium hydroxide solution prepared as 1.0×10^{-1} M in freshly boiled deionized water. 1.00×10^{-3} M EGTA was prepared by the volumetric dilution of 1.00×10^{-1} M stock solution. Additions of X ml of copper (II) solution were carefully made to 25 ml volumetric flasks from a 50 ml buret. $10-X$ ml of EGTA solution were added from a 50 ml buret, 5 ml of the buffer stock was introduced by pipet, and the solution was diluted to volume. The absorbance of the solutions was measured versus a reference blank containing EGTA and buffer solution in the same concentrations as present in the sample solutions. A scan was made of the spectral region from 400 m μ to 240 m μ . The peak height was measured in absorbance units above the base line at 400 m μ . At the time this study was in progress the Cary spectrophotometer would, at irregular intervals, quickly shift its base line absorbance approximately .006 unit. A positive shift was always followed by a negative

one and vice versa. Accordingly, it was necessary to make a scan of the complete spectral region and then make a mechanical correction to the absorbance value obtained based upon any shifts that took place between 400 m μ and the 298 m μ peak. The changes in the base line were quite obvious except on the steeper portions of the spectrum. The results are listed in Table VIII and graphically plotted in Figure 38.

Table VIII. Continuous variations data for the copper (II)-EGTA system at 298 m μ .

X ml Cu ⁺⁺	mole fraction	corrected absorbance
1.0	0.10	0.126
2.0	0.20	0.256
3.0	0.30	0.374
4.0	0.40	0.495
5.0	0.50	0.605
5.5	0.55	0.490
6.0	0.60	0.348
6.5	0.65	0.217
7.0	0.70	0.162
8.0	0.80	0.202

The peak absorbance increased with increasing mole fraction of copper (II) until copper (II) and EGTA were 1:1, the peak then diminished. At a mole fraction of 0.60 copper the peak was only a shoulder on the side of the increasing absorbance of the peak at 243 m μ . Continued measurements at the same wavelength (298 m μ) reached a minimum and then increased again. This minimum

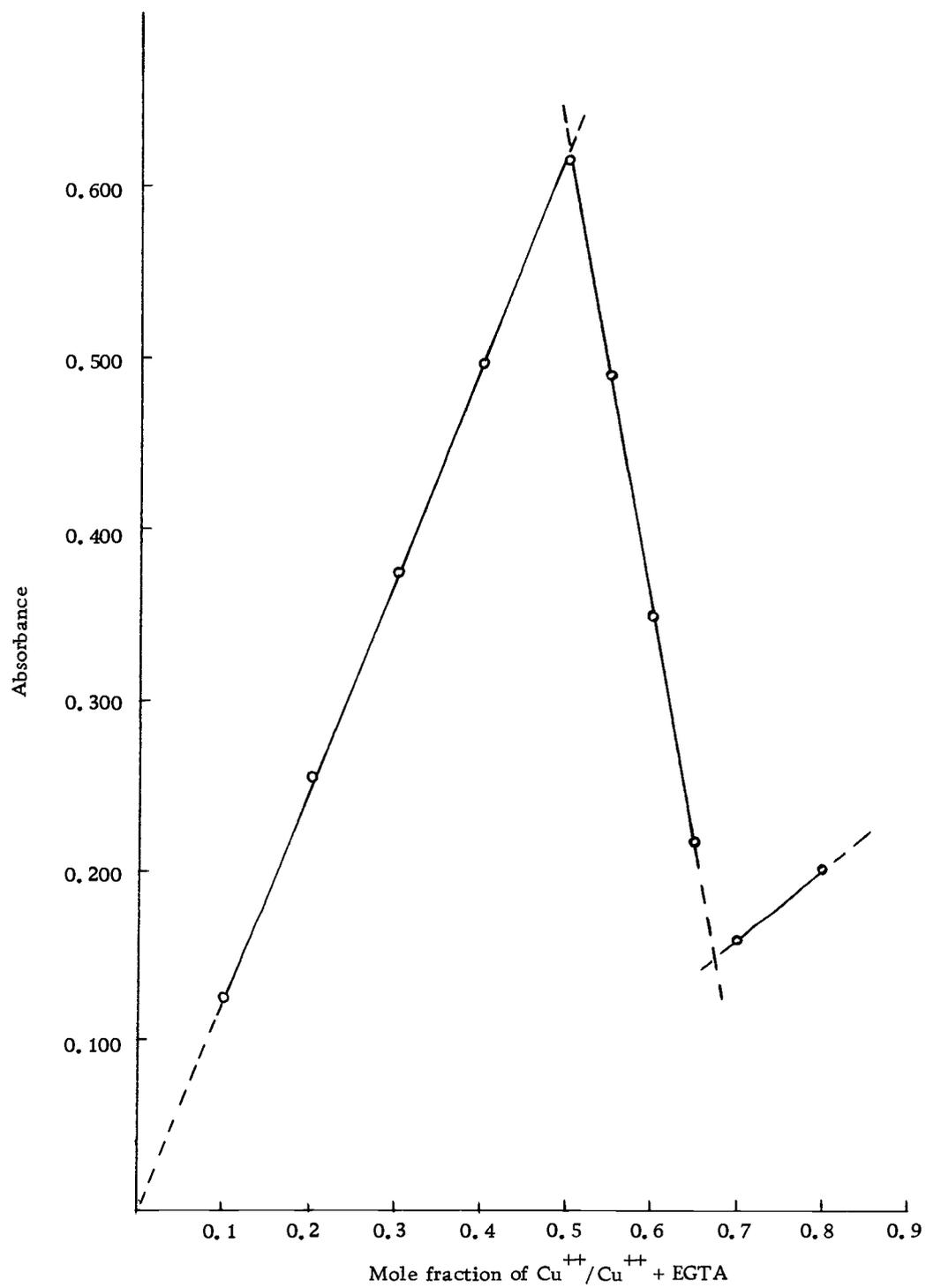


Figure 38. Continuous variations plot of Cu-EGTA system at 298 m μ .

corresponded to the 2:1 copper (II)-EGTA chelate reported by a number of investigators (6, 18, 38). The formation of a vaguely clouded solution at mole fraction 0.85 copper (II), probably due to a hydrolysis reaction of the copper ion with water at pH 6.0, prevented an intelligible extension of the graph.

The conformity of copper (II)-EGTA solutions to Beer's Law was examined. Solutions were prepared by volumetric additions of copper (II) ion to 25 ml volumetric flasks followed by excess EGTA and then the buffer. The buffer was always added last to reduce any tendency for hydrolysis reactions to occur. The chelate formed immediately upon addition of EGTA. A reference blank was prepared containing the same excess of EGTA and the required amount of buffer. The spectrum was scanned from 400 to 240 $m\mu$ and the 298 $m\mu$ peak height above the baseline at 400 $m\mu$ was measured in absorbance units. Correlation was made for instrumental fluctuations. Table IX lists the corrected values obtained. Figure 39 is a graphical presentation of the data.

The slope of the line in Figure 39 corresponds to a molar absorptivity of 3065 with an uncertainty, corresponding to the instrumental uncertainty, of ± 40 . The copper (II)-EGTA molar absorptivity at pH 6.0 in the visible region at 700 $m\mu$, according to da Silva, Calada, and de Moura (7), is 68.

An investigation of absorbance changes resulting from different

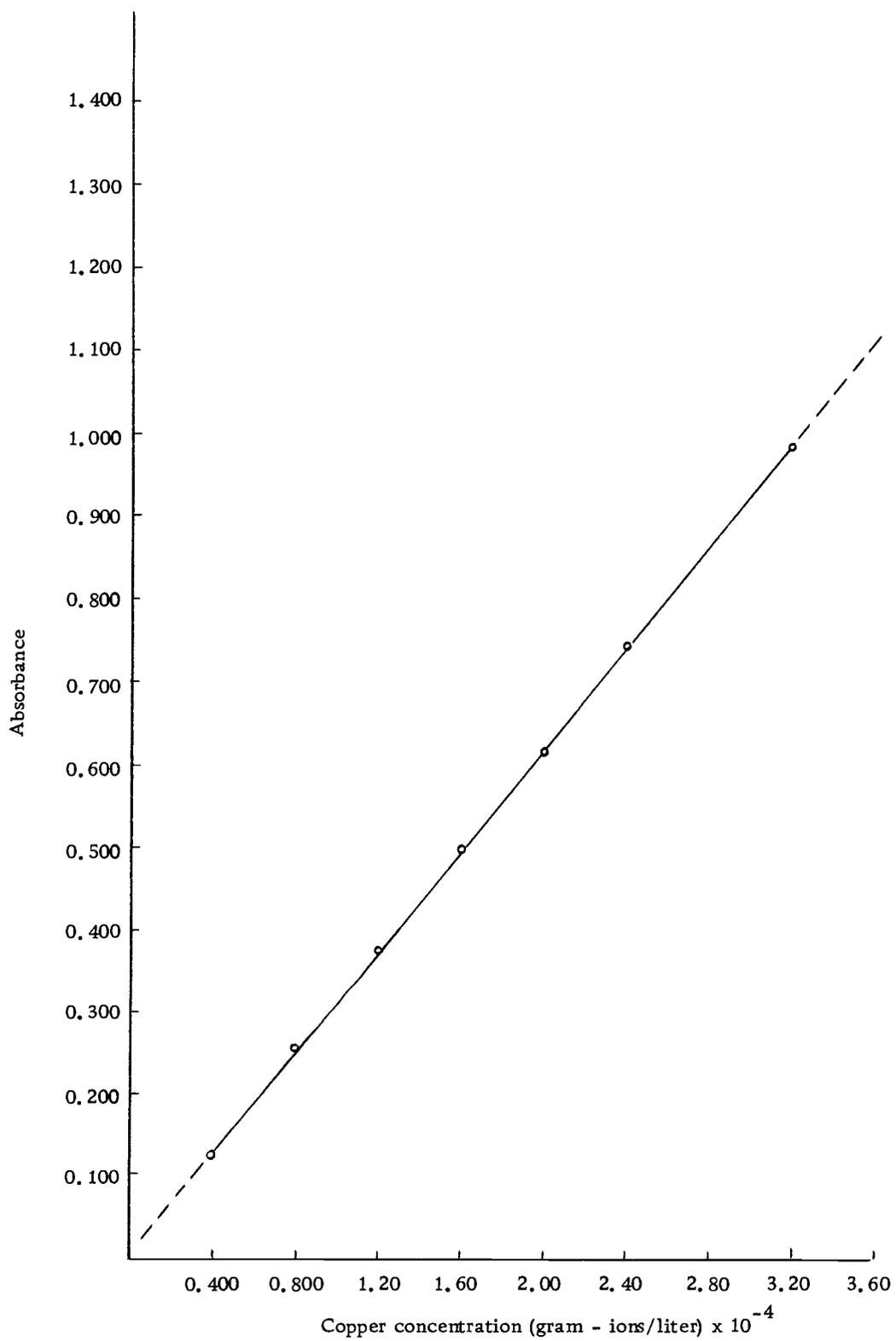


Figure 39. Beer's Law relationship of Cu-EGTA system at 298 m μ

ionic strengths revealed no change in the absorbance as the ionic strength was varied from .01 μ to 0.1 μ . Appropriate quantities of 0.50 M potassium chloride were used to change the ionic strength.

Table IX. Absorbances of various copper (II)-EGTA solutions at 298 m μ .

Solution	Concentration (gram-ions/liter) of copper (II) ion	Corrected Absorbance
A	4.00×10^{-5}	0.126
B	8.00×10^{-5}	0.256
C	1.20×10^{-4}	0.374
D	1.60×10^{-4}	0.496
E	2.00×10^{-4}	0.612
F	2.40×10^{-4}	0.741
G	3.20×10^{-4}	0.982
H	4.00×10^{-4}	1.214

The stability of the copper (II)-EGTA chelate was determined by periodically measuring the spectrum of the same solution over a period of six months. No changes in absorption were detected.

The application of the method to routine analysis was examined. Synthetic unknowns of copper (II) solution were prepared to yield copper concentrations from 4.00×10^{-5} M to 4×10^{-4} M. The solutions were prepared free of nitrate ion. Other common anions without strong complexing ability did not interfere at 298 m μ . An aliquot of the unknown solution was added to a 25 ml volumetric flask followed by the addition of 2 ml of 1.00×10^{-2} M EGTA. Five milliliters of buffer were added by pipette and the solution was diluted

to volume.

The absorbance was measured versus a reference cell filled with a blank solution prepared by adding 2 ml of EGTA and 5 ml of buffer to a 25 ml volumetric flask followed by dilution to volume.

The analytical results are listed in Table X.

Table X. Analyses of synthetic copper unknowns.

Sample	Concentration taken gram-ions/liter X 10 ⁻⁴	Concentration found gram-ions/liter X 10 ⁻⁴	Deviation %
A	1.12	1.12	0.0
B	1.12	1.11	-0.9
C	1.12	1.13	+0.9
D	0.400	.418	+4.5
E	0.400	.415	+3.7
F	0.400	.406	+1.5
G	0.400	.408	+2.0
H	0.400	.417	+4.2
I	4.00	4.01	+0.3
J	4.00	3.99	-0.3
K	4.00	3.98	-0.5
L	.800	.792	-1.0
M	.800	.819	+2.4
N	.800	.802	+0.3
O	2.00	1.99	-0.5
P	2.00	1.99	-0.5
Q	2.00	1.98	-1.0

Average percentage deviation equals 1.4%.

The ability of the instrument to reproduce its scan of the absorbance of a solution was determined. A solution of 1.2×10^{-4} M copper chelate was placed in the spectrophotometer sample cell with a suitable blank in the reference cell. Without moving the

sample cell or changing the solution the absorbance was measured five different times. The absorbance values that resulted were 0.348, 0.350, 0.348, 0.347, and 0.346. The average deviation was 0.0010.

A determination was also made to discover if the reproducibility of rinsing the sample cell, filling and replacing the cell, and scanning a sample would be less than the reproducibility of the instrument. Another 1.12×10^{-4} M copper chelate solution was prepared and the sample cell was repeatedly rinsed, filled with the solution and the absorbance measured. The absorbance values were 0.353, 0.352, 0.349, 0.351, and 0.348. The average deviation was 0.0017.

A determination of the reproducibility of sample preparation was made. Five samples of the same concentration were prepared using the same volumetric glassware. The final solutions were 4.0×10^{-5} M copper chelate concentration. The five absorbance values were 0.130, 0.129, 0.126, 0.127, and 0.130. The average deviation was 0.0015.

In Table XI are listed those metal ionic forms that had spectra when EGTA was present that would interfere with the determination of copper spectrophotometrically at 298 m μ and pH 6.0. Also included in the table are the maximum concentrations that certain ions could reach before causing interference.

Table XI. Ions that spectrophotometrically interfere with copper-EGTA absorbance at 298 m μ and pH 6.0.

Ionic form	Maximum concentration (gram-ions/liter) without interference
Sc	5.0×10^{-3}
Ti (III)	
V (II, III, IV)	
Cr (III)	1.0×10^{-3}
Mn (VII)	
Fe (II, III)	
Co (II)	1.0×10^{-2}
Ni (II)	1.0×10^{-2}
Zr	1.0×10^{-4}
Mo (IV)	
Rh (III)	
Pd (II)	
Ag (I)	1.0×10^{-4}
Sn (II)	1.0×10^{-3}
Rare earths	1.0×10^{-3}
except Ce (III)	1.0×10^{-4}
Ce (IV)	
Ho	1.0×10^{-4}
Ir (III, IV)	
Pt (IV)	
Au (III)	
Tl (I)	1.0×10^{-4}
Tl (III)	
Th (IV)	1.0×10^{-4}
U (VI)	

VI. SUMMARY AND DISCUSSION

The reactions of EGTA, [ethylene bis (oxyethylenenitrilo)] tetraacetic acid, with 51 metal ions have been studied spectrophotometrically in aqueous solutions. The absorption spectra of the chelates formed were measured with a recording spectrophotometer between 200 and 700 m μ . The pH of each solution was varied and a spectrum was scanned at different acidity levels.

The spectra of 25 metal ions showed measurable differences in the presence of EGTA. The majority of the solutions that formed characteristic spectra were stable.

The most pronounced spectral changes in the ultraviolet region resulted from EGTA chelation with the following ions: iron (II), copper (II), palladium (II), europium (III), and thallium (I). In the visible region praseodymium (III), neodymium, holmium, erbium, iridium (III), gold (III), and uranyl ions had significant spectral differences resulting from the addition of EGTA.

The variety of spectral changes induced in various rare earth ions by complexation with EGTA made possible a specific qualitative identification of praseodymium in the presence of much greater concentrations of erbium, holmium, and neodymium.

The combining ratio of metal ion to EGTA was determined by a spectrophotometric method of continuous variations for copper (II),

neodymium, holmium, and erbium. All ions formed 1:1 chelates. The conformity of the EGTA-metal ion solutions to Beer's Law was determined for copper, neodymium, europium, holmium, and erbium complexes.

A study was made of the quantitative use of the copper (II)-EGTA absorption maximum at 298 m μ and the holmium-EGTA absorption peak at 450 m μ . Though the spectral absorption sensitivity of the holmium-EGTA complex was not large, the complex did have a molar absorptivity of over twice that of holmium ion. The absorption of the copper (II)-EGTA complex at 298 m μ , with a molar absorptivity of 3065, made possible routine analysis of copper ion in concentrations above one part per million.

The method herein described for the analysis of copper utilized a wavelength region that was not previously employed for the spectrophotometric determination of copper (36, p. 443).

No attempt was made to extend the analytical method to its minimum concentration conditions. The use of the lower absorbance range of the Cary spectrophotometer should extend the analysis limit of copper ion to concentrations of 3×10^{-6} gram-ion/liter.

The behavior of the copper (II)-EGTA complex as the pH of the solution was lowered and the similar absorption changes that took place when the binuclear chelate was formed suggest that an interesting nuclear magnetic resonance study could be made to settle the

question of the chelate structures. Bryson and Nancollas (3) studied the N. M. R. spectra of alkaline earth-EGTA complexes but found part of the results difficult to explain.

A further investigation of the iron (II)-EGTA system may be justified. The conditions that must exist to form the chelate may possibly be controlled to permit the development of a quantitative system. Preliminary attempts in this direction indicate an absorption sensitivity equal to the copper chelate in the ultraviolet region.

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APPENDIX

Chemical Sources

Compound	Company	Reported % Purity
Aluminum potassium sulfate	J. T. Baker Chemical Co.	99.9
Calcium chloride	J. T. Baker Chemical Co.	99
Cadmium sulfate	J. T. Baker Chemical Co.	99.9
Ceric hydrogensulfate	Mallinckrodt Chemical Works	99
Cerous sulfate	City Chemical Company	98 +
Chromium potassium sulfate	J. T. Baker Chemical Co.	99.8
Cobaltous sulfate	J. T. Baker Chemical Co.	99.7
Cupric sulfate	J. T. Baker Chemical Co.	99.9
Dysprosium sulfate	Goldsmith Chemical and Metal Corp.	99
EGTA	K and K Laboratories, Inc.	98 +
Erbium sulfate	City Chemical Company	99.9
Europium sulfate	Alfa Inorganics, Inc.	99.9
Ferric nitrate	J. T. Baker Chemical Co.	98.9
Ferrous sulfate	J. T. Baker Chemical Co.	99.8
Gadolinium sulfate	City Chemical Company	99
Gold trichloride	Goldsmith Chemical and Metal Corp.	99

Compound	Company	Reported % Purity
Holmium sulfate	City Chemical Company	99.9
Hydrochloric acid (solution 37.0%)	Allied Chemical Corporation	
Indium perchlorate	G. Frederick Smith Chemical Co.	98 +
Iridium tribromide	Goldsmith Chemical and Metal Corp.	99
Iridium tetrachloride	Goldsmith Chemical and Metal Corp.	99
Lanthanum sulfate	Goldsmith Chemical and Metal Corp.	99.9
Magnesium sulfate	J. T. Baker Chemical Co.	99.7
Manganous sulfate	J. T. Baker Chemical Co.	99.9
Mercuric chloride	J. T. Baker Chemical Co.	99.2
Molybdenum metal	Mackey, Inc.	99
Neodymium sulfate	City Chemical Company	99
Nickelous sulfate	J. T. Baker Chemical Co.	99.9
Palladium chloride	Matheson, Coleman, and Bell	98 +
Palladium sulfate	City Chemical Company	99
Platinum chloride (solution 5%)	City Chemical Co.	99
Potassium dihydrogen orthophosphate	Allied Chemical Corporation	99
Potassium hydrogen phthalate	Allied Chemical Corporation	99
Potassium hydroxide	Mallinckrodt Chemical Works	85AR

Compound	Company	Reported % Purity
Praseodymium sulfate	City Chemical Company	99
Rhenium trichloride	Alfa Inorganics, Inc.	99
Rhodium sulfate	Goldsmith Chemical and Metal Corp.	99
Rubidium chloride	E. H. Sargent and Company	99
Ruthenium chloride	Fischer Scientific Company	Purified
Ruthenium trichloride	City Chemical Company	98
Samarium sulfate	City Chemical Company	99
Scandium sulfate	Alfa Inorganics, Inc.	99.9
Silver sulfate	J. T. Baker Chemical Co.	99.7
Sodium bromide	J. T. Baker Chemical Co.	99.2
Sodium chlorate	J. T. Baker Chemical Co.	99.4
Sodium chloride	J. T. Baker Chemical Co.	99.9
Sodium hydroxide	Allied Chemical Corporation	97 +
Sodium nitrate	J. T. Baker Chemical Co.	99.1
Sodium phosphate (monobasic)	J. T. Baker Chemical Co.	99.1
Sodium sulfate	J. T. Baker Chemical Co.	99.8
Stannous chloride	J. T. Baker Chemical Co.	99.6
Strontium chloride	J. T. Baker Chemical Co.	99.5
Sulfuric acid	Allied Chemical Corporation	98.0
Terbium sulfate	Alfa Inorganics, Inc.	99.9

Compound	Company	Reported % Purity
Thallium trichloride	Goldsmith Chemical and Metal Corp.	99
Thallosulfate	Goldsmith Chemical and Metal Corp.	99
Thorium nitrate	J. T. Baker Chemical Co.	99.1
Thorium sulfate	City Chemical Company	99
Thulium sulfate	Alfa Inorganics, Inc.	99.9
Titanium oxysulfate	E. H. Sargent and Company	98
Titanium trichloride (solution 20%)	Matheson, Coleman, and Bell	
Tris(hydroxymethyl) amino methane	Matheson, Coleman, and Bell	
Uranyl nitrate	J. T. Baker Chemical Co.	99.2
Uranyl sulfate	Mackay, Inc.	98
Vanadium sulfate	City Chemical Company	98 +
Yttrium sulfate	Goldsmith Chemical and Metal Corp.	99.9
Ytterbium sulfate	Alfa Inorganics, Inc.	99.9
Zinc sulfate	J. T. Baker Chemical Co.	99.8
Zirconium sulfate	E. H. Sargent and Company	98 +
Zirconium tetrachloride	City Chemical Company	99