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Metal-indicator systems in (ethylenedinitrilo) tetraacetic acid titrations

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METAL-INDICATOR SYSTEMS IN
(ETHYLENEDINITRILO)TETRAACETIC ACID TITRATIONS

by

William James Lane

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

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INTRODUCTION

The development of (ethylenedinitrilo)tetraacetic acid, hereafter referred to as EDTA, as a volumetric analytical reagent has reached a rank comparable with iodometric methods and the silver and halide titrations. EDTA, usually employed as the partially neutralized salt solution, derives its chemical utility from the two nitrilo and the four carboxylic acid functional groups. All of these groups can form bonds to a cation to satisfy its coordination habit. The resulting 1:1 chelate has greater stability because all the functional groups are linked in one molecule and react simultaneously. The analytical use arises when a reaction of EDTA with a desired cation can be determined. This is possible when one of the reactants possesses a measurable property, such as light absorption or reflection, acidity, ionic conductance, reduction potential, half-wave potential, diffusion current, or heat of reaction.

The property of light absorption is the one of immediate interest. The normal color of some cations is usually enhanced by chelation. This occurs in the ultra-violet region as well as the visible, and is the basis of some determinations. Most cations are not colored, so an indicator must be utilized. The number of inorganic indicator species, such as thiocyanate ions and ammonia, are limited in number and usefulness. The use of organic reagents as metal

indicators offers a much broader range of possibilities. Theoretically, nearly any combination of chelating group and chromophore may be combined in an organic molecule. A number of organic dyes have been applied as indicators. Indeed, the lake-forming dyes produce colors by a chelation reaction. Recently organic indicators have been synthesized with specific intent to contain certain groupings, to be water soluble or not, to function in a certain pH range, or to show some preference for a type of cation.

EDTA is quite unspecific as a reagent, and exhibits only a few selective characteristics in relation to pH or reaction rate. Indicators are generally little more selective. Hence, additional techniques must be applied, in the form of masking reactions or prior separations.

To solve a particular determination when all species are known with some certainty, a specific procedure may be devised. To investigate the potentialities of EDTA more fully, a more general approach may be made. Several possibilities exist. A series of indicators may be studied for use with a single cation or family of metals. A single indicator can be evaluated with a larger number of cations. In addition to the determinations of conditions and interferences of the titration, investigations of the masking of interferences, type of complex involved, and the nature of the end-point reaction are of value.

Work reported in this paper includes the application of three metal indicators. The first reagent is 7-(1-naphthylazo)-5-sulfo-8-hydroxyquinoline. This has been named Naphthyl Azoxine, and is one of a family of 7-aryloxo derivatives of 5-sulfo-8-hydroxyquinoline. The second reagent is 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid. The common name for this compound is Thorin. It is also called Thoren, Thoronol, Naphtharzin and APANS. It can also be named 1-(2-arsenophenylazo)-2-naphthol-3,6-disulfonic acid. Because the azobenzenearsonic acid is most likely the active center as a metal indicator with the ortho hydroxy group, the arsonic acid name is preferable in this application. The third indicator, a near isomer of Thorin, is 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-benzenearsonic acid. It has been named Arsenazo. This compound may also be named 3-(2-arsenophenylazo)-4,5-dihydroxy-naphthylene-2,7-disulfonic acid.

In Naphthyl Azoxine, the hydroxy group of the oxine function is ortho to the azo linkage, thereby offering two sites for chelation. The minimum pH at which the metal ions form the colored complex vary from pH 2 for copper to pH 5 for cadmium and lanthanum. This range is taken as a measure of relative stabilities. Only copper, cobalt, zinc and lead can be titrated directly; other cations require a trace of copper or zinc to provide a sharp end point transition.

As aryl arsonic acids exhibit selective reactivity to tri- and tetravalent cations, so do these azobenzene-arsonic acids form colored complexes with thorium(IV), trivalent rare earths, and others. Thorin forms a colored complex only with the lighter rare earths, so that indirect titration of the higher lanthanoids must be used. Lanthanum solution with Thorin indicator has been used for this back titration as well as for back titration of the excess EDTA in determinations of aluminum and some of the transition elements. The titration has also been applied to the determination of the excess lanthanum after precipitation of lanthanum fluoride.

In contrast to Thorin, Arsenazo forms highly colored complexes with all the rare earths, yttrium and scandium. In addition, Arsenazo is more sensitive owing to the high molar extinction coefficient of its complexes. This property has been utilized in photometric titrations of very dilute solutions of the rare earths. The complex formed with uranyl ion is blue and has a different spectrum from that of the rare earths. It has been shown that 1:1 complexes are formed and that the indicator as purchased may be purified by recrystallization as the acid form.

The measurement of light absorption has advanced from visual observation and the use of comparison apparatus, through photoelectric cells and electrical balancing systems, to electronic phototubes and amplifier circuits, all to

increase the accuracy and sensitivity of measurement. Simultaneously improvements have come in optical systems, added convenience of recording instruments, and features to broaden the applications of the instruments.

The technique of photometric titrations combines the features of a visual titration with those of spectrophotometric measurement. In addition to replacing human judgement of color change with an instrumental measurement, it permits an extension of titrations to a dilution level not otherwise possible. Further, the plot of the titration can reveal information concerning the end-point reaction.

The literature abounds with papers concerning the subjects of interest. Fortunately there are some reviews which complement the sampling presented here. Classification of topics cannot be mutually exclusive when they include EDTA titrations, indicators, and elemental determinations.

Of considerable interest is the extensive review of EDTA titration indicators, methods and techniques by Barnard, Broad, and Flaschka (16). Schwarzenbach's monograph (164) includes both theoretical considerations and procedures for EDTA titrations. The book by Martell and Calvin (122) treats the chemistry of chelation thoroughly and contains a tabulation of formation constants. Schwarzenbach and coworkers started publishing papers on EDTA in 1946. In 1947, he reported the acid dissociation constants (166), and in 1948 described the determination of EDTA titration end-points by

means of pH effects (165). Schwarzenbach presented theoretical considerations and a review of methods using EDTA in 1952 (163). Meanwhile, Diehl, Goetz and Hach (44) had applied the titration to water hardness determinations utilizing masking agents to prevent interferences from other metals, and Goetz, Loomis and Diehl (67) studied the stability of EDTA solution. Wehber (199) described a method of calculating formation constants. Other chelating agents of similar constitution are available. 1,2-Cyclohexylene-(dinitrilo)tetraacetic acid forms generally stronger chelates than EDTA. Others have more specific application.

Except for contemporary work by associates of the author, there appears little in the literature concerning analytical applications of Naphthyl Azoxine. In 1927 Matsumura (123) prepared 7-(1-naphthylazo)-5-sulfo-8-hydroxyquinoline along with other substituted oxine derivatives. Gutzeit and Monnier (69, 70, 71) in 1933 compounded a number of substituted oxines and investigated their use as reagents for qualitative and trace analysis of common metals. 5-(1-Naphthylazo)-8-hydroxyquinoline was included. Welcher's book (201) contains chapters on 8-hydroxyquinoline and derivatives (pp. 263-343) and azo-derivatives (pp. 344-356). On page 351, he described an isomer of Naphthyl Azoxine, 5-(4-sulfo-1-naphthylazo)-8-hydroxyquinoline. Hollingshead (76) has compiled a four volume treatise on oxine and derivatives with primary emphasis on analytical applications.

On pages 887 and 946, he discussed compounds of types related to Naphthyl Azoxine. Molland (135) has demonstrated that 5-sulfo-8-hydroxyquinoline forms inner complexes similar to oxine itself in ligand ratios of 3:1 and 2:1 for iron(III) and copper(II) respectively.

V. I. Kuznetsov (91-102) and associates have investigated analytical applications of a variety of organic indicators which have included both Thorin and Arsenazo. His report on preparation and properties of Thorin (93) has been clarified by Margerum, et al. (119). Mayer and Bradshaw (124) applied Thorin to the photometric determination of thorium in magnesium alloys; they claimed little interference when measured at pH 0.5-1.2. They postulate a 1:2 complex, absorbing at 555 μ . Banks and Byrd (12) have used Thorin to determine thorium in monozite sands following potassium hydrogen fluoride fusion and extraction with mesityl oxide. Clinch (37) studied the conditions and interferences of Thorin as a thorium reagent, and also reported the formation of a 1:2 chelate. Adamovitch and Mirnaya (2) used Thorin as a reagent for beryllium.

Kuznetsov (91), in 1941, reported the color reaction of Arsenazo among other reagents with thorium, uranium, rare earths, and other metals. He reported further reactions with rare earths in 1952 (92, 95), beryllium in 1955 (96), aluminum in 1955 and 1956 (98, 99), and zirconium in 1956 (97). Emi and Hayami (48) in 1955 determined fluoride by

by bleaching of the thorium-Arsenazo complex following a Willard-Winters distillation.

The review by Barnard, Broad and Flaschka (16) includes descriptions of these and many other indicators. There appear to be several general types. One is the triphenyl methane or phthalein type. Pyrocatechol violet or pyrocatecholsulfonphthalein has been applied by Malát, et al. (111, 112) to the determination of several cations, and has been diazotized by Kuznetsov and Nemodruk (102). Misumi (128) reported reaction of rare earths with Sunchromine Pure Blue B which is a fuchsone derivative. By coupling iminodiacetic acid groups to this type indicator, additional chelating power is provided. Anderegg, et al. (5) made phthalein complexone from cresolphthalein, and Diehl and Ellingboe (43) made Calcein from fluorescein in this manner. A second type is the azo compound substituted in either or both ortho positions to provide chelation sites. Biedermann and Schwarzenbach (22) have used Eriochrome Black T in the EDTA titration of alkaline earth and other metals. Flaschka and Abdine (53, 54) used 1-(2-pyridylazo)-2-naphthol, PAN, with copper as an EDTA indicator. Wehber (200) applied Eriochrome Red B to titrations of zinc, lead and copper. Schmid and Reilley (161) utilized acid and formation constants of Eriochrome Blue Black R, Calcon, to titrate calcium in the presence of magnesium. Zincon, used by Kinnunen and Merikanto (87), also is an azo indicator. Kuznetsov

(94) found rare earths formed colors with 2-(2-hydroxy-1-naphthylazo)-1-naphthalenesulfonic acid. Chromotropic acid is the base of a third type of indicator. Datta (40, 41, 42) has studied the complex of thorium with the 3,6-dinitroso derivative. The azo derivative of chromotropic acid, SPADNS, has been applied to both thorium and fluoride determinations by Banerjee (10, 11). Arsenazo also is an azo derivative of chromotropic acid. Naphazarin and alizarin are parent compounds for another type of indicator. Moeller and Tecotsky (134) have used naphazarin to detect rare earths photometrically and the derivative, Morin, was found by Fletcher and Milkey (56) to be useful for the determination of thorium. Fritz and Ford (60) used alizarin sulfonic acid, Alizarin Red S, for the EDTA titration of thorium. In addition there are indicators not so readily classified which can be used in EDTA titrations, such as dithizone as applied to the back titration of aluminum by Wänninen and Ringbom (197).

Analytical chemistry has always applied instruments as they became available. Müller (137) reviewed most of the modern instruments in 1941. Advances since then have been toward making apparatus more automatic, as described by Lingane (109), Malmstadt and Roberts (117) and Malmstadt (113). Müller (136) in 1939 described manual photometric titrations, and suggested the convenience of a recording spectrophotometer. Ringbom (153), in 1941, followed

photometrically the precipitation titration of barium with sulfate and discussed the general principles and applicability. He derived from Beer's Law the equation relating error to transmittance. Osborn, Elliot and Martin (1409) applied an interesting photometric balancing system to manual phototitrations. Ayers (7) considered the minimum error derivation in the evaluation of photometric analyses. Later Ringbom and Wänninen (154) treated the theory of complexometric titration when followed photometrically. A similar paper by Fortuin, Karsten and Kies (57) was applied to EDTA titrations. Goddu and Hume (64) considered the requirements of phototitrations of weak acids. Underwood (190) reviewed generally the advantages and examples of photometric titrations. In their review of the subject, Goddu and Hume (65) described the adaptation of the Beckman Model B spectrophotometer for titrations. Shapiro and Brannock (169) described a simple colorimeter instrument and a coupled recorder-titrator. The titration assembly used in part of the work of this paper was described by Klingman, Hooker and Banks (88). Malmstadt made several contributions to automatic titrations. With Gohrbandt (115), he adopted a Cary recording spectrophotometer and titrated thorium with EDTA using the copper-EDTA complex as the indicator. Malmstadt and Fett (114) devised an electronic instrument to take the second derivative of a potentiometric titration curve and to control the buret or other mechanism. With

Roberts (117), he added a third derivative unit to provide the same control to a photometric titration. Malmstadt and Roberts (116) also combined the technique of electrolytically generated titanium(III) with a photometric titration to determine vanadium in titanium metal. The third derivative instrument was applied to the photometric titration of iron in titanium with electrolytically generated titanium(III) by Malmstadt and Roberts (118). Sweetser and Bricker (182, 183) determined a number of metals by photometric EDTA titration. Underwood (189) followed the formation of copper-EDTA to determine both iron and copper, and with Wilhite (202) titrated both lead and bismuth using their EDTA complex absorbances. Cohen and Gordon (38) and Gedansky and Gordon (62) have described photometric EDTA titrations of small amounts of barium and silver respectively. Redox titrations are also suited to photometric titrations. Bricker and Sweetser (25) used the absorbance of cerium(IV) to signal the end of the titration of arsenic(III). Marple, Przybylowicz and Hume (121) titrated cerium(III) with permanganate photometrically. Miles and Englis (129) utilized ferrous sulfate to titrate chromium(IV) plus vanadium(V) after bromate oxidation, then arsenious acid to titrate chromium(VI) only. Sweetser and Bricker (181) conducted photometric titrations with a bromate-bromide solution to determine unsaturation, phenols, amines, and oxidizable functions. Miller and de Ford (130) used electrolytically

generated bromine to titrate olefins in a photometric titration.

Because of the chemical similarity of the members of the rare earth series, photometric determinations and complexometric titrations are generally non-specific. Exceptions usually are based on oxidation states other than the common trivalency. Quill and Rodden (148) have collected many analytical procedures for scandium, yttrium and the rare earths. Vickery (191) has described the chemical behavior of the members of the series. Jones (83) postulated that the rare earth-EDTA chelates exhibit ionic bonding. Rhinehart (152) reported that Alizarin Red S can be used to determine a separated rare earth or total rare earths photometrically. Moeller and Tecotsky (134) found that naphthazarin can similarly be used. Holleck, Eckhardt and Hartinger (74) have used aurintricarboxylic and sulfosalicylic acids to form mixed complexes with the rare earths for analysis. Kuznetsov (91, 92, 94, 95) reported reagents forming colors with the rare earth group and other elements. Charlot (35) and Misumi (128) have also investigated color reactions for the rare earths. Brunisholz and Cahen have titrated rare earths with EDTA using a mixed indicator of Alizarin Red S and Methylene Blue (26) and using Eriochrome Black T (27). Wunsch (206) has titrated scandium with EDTA using Eriochrome Black T; he used malic acid and an elevated temperature in the direct titration because of the

irreversibility of the reaction between scandium and the indicator. Beck (18) titrated scandium with nitrilotriacetic acid and murexide indicator. Flaschka (51) developed three techniques for direct and indirect EDTA titrations of rare earths. Bamann and Heumuller (9) measured the excess phosphate by the molybdenum blue method after precipitating rare earth phosphates. Conca and Merritt (39) have measured the absorbance of cerium(IV) in strong carbonate solution. Foster and Kremers (58) reduced europium with zinc and made the indirect determination by dichromate titration of the iron which was reduced by the europium(II); samarium and ytterbium were not reduced by zinc and did not interfere. Banks and O'Laughlin (14) have determined cerium and chromium indirectly by using the selective oxidation of chromium only by fuming perchloric acid and of both elements by peroxydisulfuric acid. Carron, Skinner and Stevens (32) have separated thorium from rare earths by sebacic acid; thorium precipitates at pH 2.5, while rare earths precipitate at pH 9. Beck (20) found that rare earths precipitated with pyrocatechol and ethylenediamine, piperidine, pyridine or quinoline were more dense than if ammonia were used, and were less soluble than the oxalates. Popov and Wendlandt (144) reported that cupferron and neocupferron formed a more easily filterable precipitate than oxalate but was not as selective; ignition to the oxide was required for determination. Beck (19) and Boulanger (24) have noted the fractionation of the

rare earths by oxalate precipitation from EDTA or nitrilotriacetic acid solution as a function of pH. Banks and Klingman (13) have published visible and ultra-violet absorption spectra of rare earths. Holleck and Hartinger (75) have also recorded absorption spectra of the rare earths. Banks, Spooner and O'Laughlin (15) applied the precision analysis of neodymium in the presence of yttrium. Fassel, et al. (49) and Hunemorder and Hess (79) have investigated line pairs and conditions for emission spectrographic analysis for rare earths; the latter authors used a recording spectrophotometer. Spedding and Powell (175, 176, 177) have discussed the theory and behavior of rare earth separation by means of ion exchange resin.

Aluminum may be determined by several methods, few of which are as readily performed as a titration. Classical methods are included in analytical texts such as Walton (196, pp. 44, 96, 291, 363) and Willard and Diehl (203, pp. 142, 153). Among new organic indicators for aluminum are Stilbazo, a bis-(azobenzene) derivative of stilbene studied by Jean (82) and Kuznetsov, Karonovich and Drapkina (100), and Arsenazo investigated by Kuznetsov and Golubta (98, 99). Millner (131), Miller and Kunos (132) and Hill (73b) have used Eriochrome cyanine R as a photometric reagent. Two direct EDTA titrations of aluminum have been reported. Aarnes and Klerstrand (1) have used haematoxylin and 80° temperature in an empirically standardized titration. Theis (186)

also heated the solution to 80° for the EDTA titration with Chrome Azurol S indicator. Several indirect aluminum titrations have been proposed. Flaschka and Abdine (53) added a trace of copper, and titrated with EDTA using PAN. Ter Haar and Bazan (72) titrated the excess EDTA with thorium and Alizarin Red S indicator. Wänninen and Ringbom (197) used dithizone for the back titration with zinc. Flaschka and Abdine (52) developed a potentiometric back titration of excess EDTA with zinc using a ferri-ferrocyanide and 3,3'-dimethylnaphthidine system. Goon, et al. (68) have described the colorimetric determination after chloroform extraction of aluminum oxinate. Sprain and Banks (178) extracted aluminum oxinate from ferrous tris-(1,10-phenanthroline), and determined both elements photometrically. Margerum, Sprain and Banks (120) masked thorium from extraction with 4-sulfo-benzenearsonic acid and acetate ion, and reextracted copper, cobalt, nickel and zinc with cyanide. Beck and Szabó (21) and Paulson and Murphy (142) have applied acidimetric titrations of aluminum with and without added fluoride salt. Flaschka and Zavagyl (55) determined aluminum by difference after titrating iron with ascorbic acid using thiocyanate ion for an indicator and determining the sum of iron and aluminum gravimetrically. Přibil, Koudela and Matepka (146) have used a potentiometric back titration of excess EDTA with iron(III) to determine aluminum, iron and other metals; they have determined both aluminum and iron by titration at two

pH's. Bobtelsky and Welwart (23) applied the heterometric principle to titration of aluminum with oxine and followed the formation of turbidity with a photometer. Turner (188) reported a neutron activation analysis in which aluminum is determined by a (n,α) reaction producing sodium-24 of a fifteen hour half-life. Szabó and Beck (184) have included aluminum in a mathematical approach to analysis by complex formation as a function of pH.

The reactivity of fluoride ion with higher valent cations is the basis of numerous methods for detecting fluoride, but few methods exist for separating fluoride from these same metals prior to determination. McKenna (125) compiled an annotated bibliography of fluorine analysis from 1816-1950. Batchelder and Meloche (17) in 1931 had included a list of references. Standard methods are described in works such as Scott (167, pp. 403-410), Walton (196, pp. 115, 157, 353) and Willard and Diehl (203, p. 371). The Willard-Winter distillation (205) has become the core of most fluoride determinations. Huckabay, Welch and Metler (78) described an improved, all glass apparatus for the distillation. Willard and Winter (205) titrated the fluoride with thorium using the zirconium-Alizarin Red S complex as an indicator. Willard and Horton (204) later found purpurin, Alizarin Red S, Eriochrome cyanine R, dicyanoquinizarin, and Chrome Azurol S provided the best equivalence point detection. The Association of Official Agricultural Chemists

(6) recognized calcium hydroxide as a fluoride fixative in the Willard-Winters distillation and back titration with thorium as its official method. Eberz, Lamb and Lachele (46) has studied and altered the distillation and titration procedure. Reynolds and Hill (151) also investigated the method with emphasis on treatment of phosphate rocks. Wadhvani (192, 193, 194, 195) postulated that distillation at 130-145° produced H_2SiF_6 which titrated to H_2ThF_6 , while distillation at 140-145° provided ThF_4 stoichiometry. Adams and Koppe (3) have studied the pH effect and recommended pH 2.90 for the thorium titration. Rowley and Churchill (155) showed that an alcoholic solution was not necessary for the thorium titration. Saylor and Larkin (158) titrated fluoride with aluminum chloride using Eriochrome cyanine R indicator. Brunisholz and Michod (28) titrated fluoride in 50% methanol with cerium(III) and murexide indicator. Banerjee (10) used SPADNS indicator for the thorium titration. A number of procedures have been used which incorporate bleaching of a colored metal indicator complex by fluoride ion. Included are thorium-Chrome Azurol S by Revinson and Harley (150), thorium-Thorin by Horton, Thomason and Miller (77), thorium-amaranth by Lambert (103), thorium-Alizarin Red S by Icken and Blank (80), thorium-Arsenazo by Emi and Hayami (48), thorium-Chromotrope 2B by Liddell (108), and thorium-N-4-(o-arsonophenylazo)-1-naphthyl -ethylenediamine by Liddell (107);

zirconium-Eriochrome-cyanine R by Megregian (126), zirconium-alizarin by Bumsted and Wells (29), zirconium-Alizarin Red S by Sanchis (157), and zirconium-Azodye by Kamado, Onishi and Ota (85); ferric thiocyanate by Ingols, et al. (81), iron- β -resorcyldaloxime, iron 5-phenylsalicylic acid, and iron-resacetophenone by Nichols and Condo (138); aluminum-hematoxylin by Price and Walker (147), aluminum-Eriochrome-cyanine by Thrun (187); and pertitanic acid by Parrish, et al. (141) and titanium-ascorbic acid by Schall and Williamson (159). Sen (168) postulated a novel, but unsuccessful, colorimetric approach to fluoride determination, then determined the sensitivity of several systems from plots of change in absorbance versus log concentration. Acid-base effects were utilized in the titration of fluoride with potassium alum in partial non-aqueous solvent by Chilton and Horton (36) and Schleibs (160). Long (110) titrated with aluminum chloride. Kurtenacker and Jurenka (90) titrated with aluminum, cerium(III) and iron(III) solutions. Precipitation with lanthanum has been studied by Meyer and Schulz (127), Fisher (50) and Giammarino (63); the determinations were made by weight. Popov and Knudson (143) determined the excess lanthanum after precipitation by cupferron. Batchelder and Meloche (17) titrated the excess cerium(III) with permanganate. Ehrlich and Pietzka (47) converted the lead bromofluoride precipitate to silver bromide and determined the excess silver by a thiocyanate titration with iron(III)

indicator. Laszlovszky (105) dissolved the lead chlorofluoride and titrated the lead with EDTA using Eriochrome Black T. Stevens (179) developed a nephelometric procedure using the turbidity of calcium fluoride. Shell and Craig (170) studied the alkaline fusion method for extracting fluoride and found zinc oxide to be useful. Pyrohydrolysis of metal fluorides was studied by Warf, Cline and Tevebaugh (198), and apparatus changes were advocated by Susano, White and Lujan (180). Freier, et al. (59) utilized a combustion method for determining fluoride in organic material. Samuelson (156, p. 150) reported the use of cation exchange resins to separate fluoride from aluminum, beryllium and iron. Zipkin, Armstrong and Singer (207) separated microgram quantities of fluoride from 500 fold amounts of phosphate on an anion exchange resin. Nielson and Dangerfield (139) concentrated fluoride ions from air sampling by means of anion resin. Langer (104) titrated fluoride amperometrically with lanthanum and thorium nitrates, the nitrate ion being the reducible species. Similarly Castor and Saylor (33) titrated with the aluminum complex of Superchrome Garnet Y and measured the diffusion current of the liberated dye. Baker and Morrison (8) have determined fluoride from the current of an electrolytic cell. Singer and Armstrong (171) collected hydrofluoric acid, diffused from perchloric acid solution, in a sodium hydroxide and titrated with thorium nitrate. Cabral and Götte (31) counted the radio-phosphorous liberated

from zirconium phosphate by fluoride. Smolyak (174) measured the intensity of the molecular bands of calcium fluoride emission spectra using calcite impregnated electrodes.

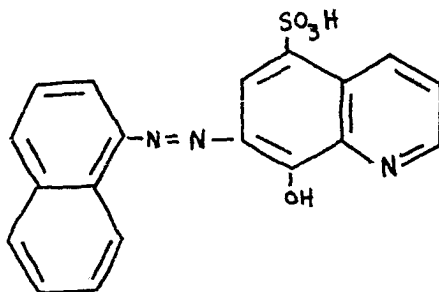
The literature discloses a current trend toward faster analytical techniques. This is evident in the development of improved and more automatic instruments and an increase in spectrophotometric and, with the advent of reagents of the EDTA type, titrimetric methods. The photometric and titrimetric procedures require metal sensitive indicators, and many dyes and indicators have been investigated. This paper presents results of the application of three indicators to EDTA titrations and of the use of photometric detection to titrate very dilute solutions.

7-(1-NAPHTHYLAZO)-5-SULFO-8-HYDROXYQUINOLINE;

NAPHTHYL AZOXINE

Reagent

This compound, 7-(1-Naphthylazo)-5-sulfo-8-hydroxyquinoline, has been prepared in this laboratory and is one of a family of 7-(aryldazo) derivatives of 5-sulfo-8-hydroxyquinoline. The trivial name of Azoxine has been assigned to the family and this compound has been named Naphthyl Azoxine. The structural formula is



The reagent was prepared by coupling diazotized 1-Naphthylamine with 5-sulfo-8-hydroxyquinoline and recrystallized from warm dimethylformamide by the addition of water. The preparation was described by Fritz, Lane, and Bystroff (61). Naphthyl Azoxine is very soluble in dimethylformamide, moderately soluble in acetonitrile and isopropanol, slightly soluble in water and ethyl acetate, and insoluble in diethyl ether. In aqueous solution, it is red-violet below pH 3.5,

red-orange in the intermediate range and yellow-orange above pH 8.5.

Naphthyl Azoxine forms a bright yellow complex with a number of metal ions. The minimum pH at which some representative cations form the yellow complex are copper, pH 2.5; thorium, pH 3.0; cobalt, pH 4.0; and cadmium and lanthanum, pH 5.0. These figures are interpreted to be a measure of the stability of the metal-Naphthyl Azoxine complexes; i.e., copper is the strongest and lanthanum is the weakest of these elements. Evidence will be presented to show that copper forms 1:1 and 1:2 complexes and the latter has a formation constant of 1.9×10^{15} .

Titration of Metals

This reagent gives sharp end-points as a metal-indicator for EDTA titrations. Metals such as copper, cobalt, nickel, zinc and ytterbium, form sufficiently strong complexes with Naphthyl Azoxine that they may be titrated directly. Metals such as cadmium and lanthanum form weak complexes which do not give sharp color changes. Titrations of these metals require the addition of a copper blank to obtain a sharp end-point. The titration of thorium at pH 3.0 to 3.5 also requires the addition of copper. Several complexing agents of the carboxylic acid and inorganic types do not interfere

in the titration of some of these divalent cations, and so may be used as masking agents.

Successful titrations of cadmium, cobalt, copper, lanthanum, nickel, thorium, ytterbium, yttrium and zinc have been performed. In the titration of the divalent ions the uranyl ion has been successfully masked by the tartrate ion, but not by sulfosalicylate ion. Masking of uranyl ion was not achieved in the titration of thorium or the rare earths.

Solutions

EDTA was prepared by dissolving the proper amount of disodium or diammonium salt in water to make a 0.05 M solution. This was standardized by the titration of a standard zinc solution at pH 10 using Eriochrome Black T indicator.

All metal solutions were made 0.05 M.

Copper, nickel and zinc solutions were prepared by dissolving weighed amounts of the metals. The copper was cleaned copper wire. Nickel used was C. P. shot with 0.05% total listed impurities. Zinc metal was better than 99.9% pure by spectrographic analysis. An aliquot of this copper solution was diluted tenfold to serve as the copper blank solution for some of the titrations.

Cadmium solution was prepared from reagent-grade cadmium nitrate which was standardized by EDTA titration using a zinc blank and Eriochrome Black T indicator.

Cobalt solution was prepared from reagent-grade cobalt perchlorate. It was standardized by passing aliquots through a cation exchange resin column in the hydrogen form. The equivalent perchloric acid was titrated with standard sodium hydroxide.

Lanthanum, ytterbium and yttrium solutions were prepared by dissolving column purified oxides in acid. The lanthanum solution was standardized by EDTA titration using Thorin indicator by a method described in the next chapter. Ytterbium and yttrium solutions were standardized by lanthanum titration of the excess EDTA using Thorin indicator.

Thorium nitrate was prepared by dissolving the reagent-grade salt in water. It was standardized with EDTA titrations using Alizarin Red S indicator by the method of Fritz and Ford (60). Uranyl nitrate solution, 0.1 M, was prepared by dissolving the salt, but was not standardized. This solution was used to check the masking of uranyl ion in other determinations.

Naphthyl Azoxine solution was made to be 0.2% in dimethylformamide.

Titrations

The titrations were carried out according to this general procedure. Aliquots of approximately 0.5 millimoles were taken for titration with 0.05 M EDTA. The sample was diluted to 100 ml. Ammonium acetate was used as a buffer

for the pH 5.5 region and was added as the solid. From 1 to 2 grams sufficed. The pH was checked with a meter and adjusted with ammonia or nitric acid. For titrations of copper at pH 4 or of thorium at pH 3.0 to 3.5, sodium formate or sodium chloroacetate were used respectively. Masking agents if desired were added. About 10 drops of 0.2% naphthyl azoxine were used. Personal preference and the color of the solution itself could make a different amount of indicator desirable. When the copper blank was required to provide a sharp end-point, 1.00 ml. of 0.005 M solution was usually added when the titration was about 95% completed. Often, the end-point without copper was noted, then the copper was added and the titration was carried to the second end-point. The end-point was taken when the solution had attained the maximum red color. When the copper blank was included, the maximum color change was taken if the blank correction were also determined in this manner.

The results of the titrations are given in Table 1. Figures in both columns "No copper added" and "Copper added" mean that the end-point of the titration was noted, and then the copper blank was added. The titration was continued to a second end-point and the value of the copper blank was subtracted. When end-points were obtained both ways, they were in good agreement. The blank values for 1.00 ml. of 0.0049 M copper were well confirmed. The differences

Table 1. Titration of metal ions

Ion	Mg. taken	Mg. found		pH at e.p.
		No Cu added	Cu added	
Cd ⁺²	60.0		59.9, 59.9	5.5
Co ⁺²	29.12	29.12	29.19	5.0
		29.12	29.12	5.6
Cu ⁺²	30.99	30.95		5.2
		30.95		3.0
		31.02		3.6
La ⁺³	69.69		69.71, 69.63	5.3
			69.71	5.4
			69.78, 69.49	5.6
			69.86, 69.78	6.3
			69.71	6.4
Ni ⁺²	29.33	29.38	29.24	5.2
		29.35	29.29	5.9
		29.38	29.38	5.9
Th ⁺⁴	52.36		54.52	3.2
	108.73		109.04, 108.79	3.2
			109.04	3.4
Y ⁺³	47.10		47.40, 47.26	5.4
			47.21	5.2
Yb ⁺³	91.49	91.50	91.59	5.2
		91.59	91.50	5.2
			91.50	5.2
Zn ⁺²	32.23	32.20		5.1
		32.12	32.12	5.2
		32.10	32.13	5.1

between end-points when succeeding 1.00 ml. aliquots of copper were added were always 0.09 to 0.10 ml. Ten independent titrations of similar aliquots resulted in five at 0.09 and five at 0.10 ml. In practice, 0.09 ml. have been subtracted from the titration value producing the maximum red color

Masking of uranyl ion

It has been demonstrated that tartrate ion will mask equal molar amounts of uranyl ion in titration of cadmium, cobalt, copper, nickel and zinc. The end-point in the titration of ytterbium was more orange than red and was not as sharp. It closely approximated the correct result however. No end-points at all could be observed for the titrations of lanthanum, thorium and yttrium with tartrate present. The tartrate complex with uranyl ion was yellow, and tended to obscure the end-point. Nevertheless, the color change was observed. The sulfosalicylate ion did not mask the uranyl ion. The uranyl sulfosalicylate color produced was more intense than with the tartrate ion. The results of the titrations with uranyl ion masked by tartrate are given in Table 2.

Related information

Associates also working with Naphthyl Azoxine indicator have investigated other interferences and masking agents. Fritz, Lane and Bystroff (61) found that calcium and

Table 2. Masking of uranyl ion with tartrate ion in titration of metal ions

Ion	Mg. taken	Mg. U	Mg. found	pH
Cd ⁺²	60.0	10	59.9	5.6
Co ⁺²	29.12	100	29.2	5.8
	29.12	100	29.3	5.3
Cu ⁺²	31.86	6	31.81	3.8
Ni ⁺²	29.33	100	29.35	5.7
Yb ⁺³	91.49	100	91.8	5.8
Zn ⁺²	32.23	50	32.20	5.3

magnesium in equal molar amounts did not interfere in the titrations of 0.25 millimole of cadmium, cobalt, manganese, nickel and zinc. Aluminum, iron(III) and zirconium(IV) do not interfere in one-tenth those amounts but do in higher proportions. Also, ions such as fluoride, bromide, iodide, sulfate, phosphate, cyanide and thiocyanate can be tolerated in zinc titrations up to 2:1 mole ratio. Similarly, ascorbic acid, citric acid, malonic acid, oxalic acid, tartaric acid, iminodiacetic acid, and ethylenediamine do not interfere in ratios from 2:1 for most to 20:1. These agents have been used successfully to mask other cations in the titration of zinc. These are chloride for silver, iodide for mercury(II), fluoride for beryllium, niobium and

titanium, citrate for aluminum, tin(II), tin(IV), thorium and zirconium, tartrate for antimony(II), and thiourea for copper. Additional masking possibilities might be suggested in a review of masking agents and their applications which has been made by the Ames Laboratory Staff (4).

Spectrophotometric Data and Titrations

Equipment

Absorption spectra were obtained from a Cary Model 12 recording spectrophotometer. Two Corex cells of 2.01 cm. path length were used. Photometric titrations were conducted with a Beckman Model DU spectrophotometer. The titration assembly was that built by Klingman, Hooker and Banks (88). The photometric titration beakers were of borosilicate glass and had a light path length of about 4 cm.

Interpretation of spectra

The spectra of Naphthyl Azoxine at pH 4, 6, and 8 are given in Figure 1. The isobestic point at 512 m μ indicates that there are two species of the indicator in equilibrium. Other spectra have shown that the peak of the acid form at pH 1 and 2 developed prominently at 540 to 550 m μ . The peak of the basic form at 480 m μ continued to rise with pH to pH 11. The molar extinction coefficient for the indicator at 500 m μ and pH 6 is 13,000.

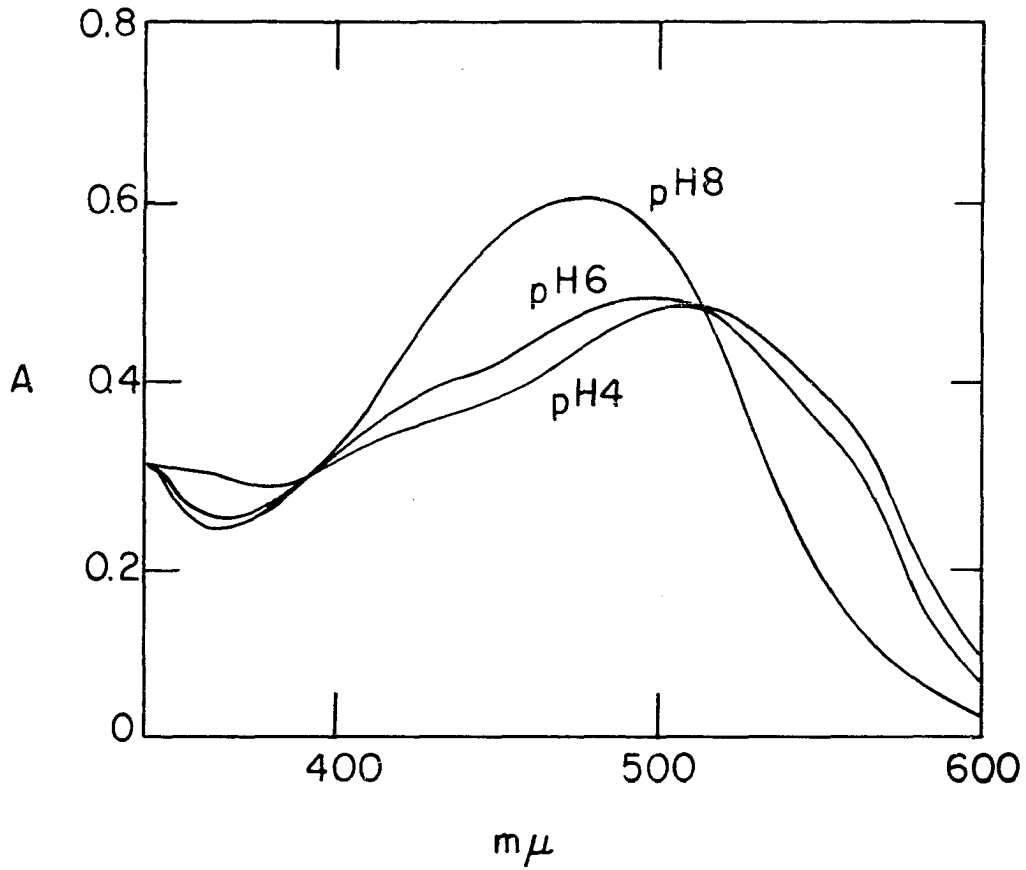


Figure 1. Spectra of Naphthyl Azoxine at pH 4, pH 6 and pH 8, 1.89×10^{-5} M, 2.01 cm. cells

Figure 2 and Figure 3 show the spectra of the copper complex as the ratio of Naphthyl Azoxine is raised from 1:1 to 3:1 at pH 6. These spectra indicate that both 1:1 and 1:2 complexes are formed. The 1:1 species absorption maximum is at 440 m μ and the 1:2 species absorption peak is at 455 m μ . The addition of a third ratio mole of reagent causes no further shift in wave length of the maximum. That the differences between the 1:1 and 1:2 spectra is not due to free indicator is shown by curve 2'. This spectrum of the 1:2 ratio solution is scanned versus a 1 equivalent mole indicator blank. The difference between curves 1 and 2' denote that different species were absorbing. The similarity of curves 2 and 3' show that the 1:3 ratio spectrum is due to the sum of the absorbances of the 1:2 complex plus one equivalent mole of reagent. These same spectra are plotted on a log absorbance scale in Figure 3, and show these similarities and differences more rigorously. From curve 2, the molar extinction coefficient for the complex at pH 6 and 455 m μ was calculated to be 35,600.

Photometric titrations

Photometric titrations were undertaken both to use the technique for dilute titrations and to study the end-point reaction. To compare photometrically determined end-points with visual titrations, a number of similar titrations were made both ways. For both types, the same 5 ml. micro-buret

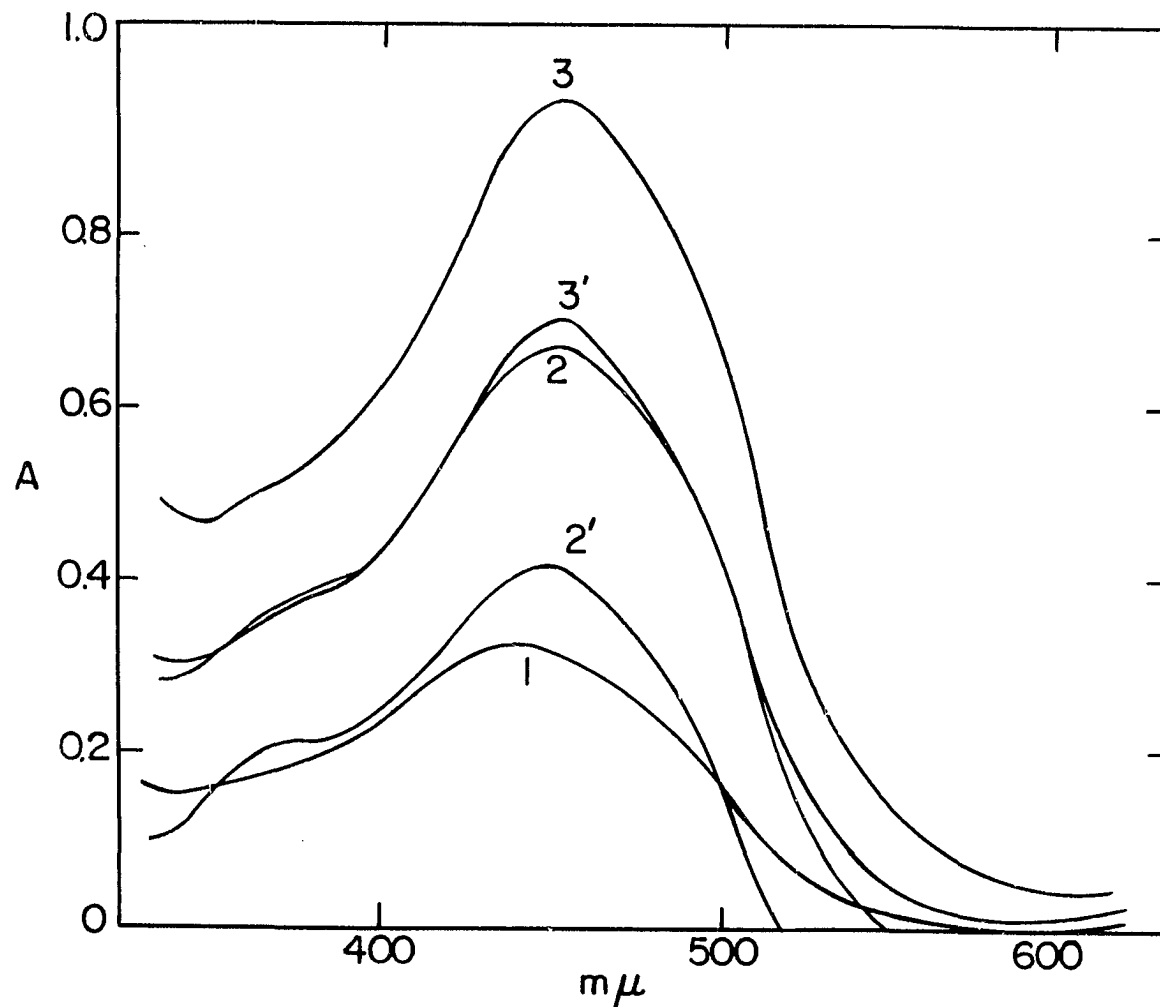


Figure 2. Spectra of 10^{-5} M copper plus Naphthyl Azoxine: curve 1, 1:1; curve 2, 1:2; curve 3, 1:3 mole ratios vs. water and curve 2', 1:2 and curve 3', 1:3 mole ratios vs. 1 equivalent mole blank, 2.01 cm. cells

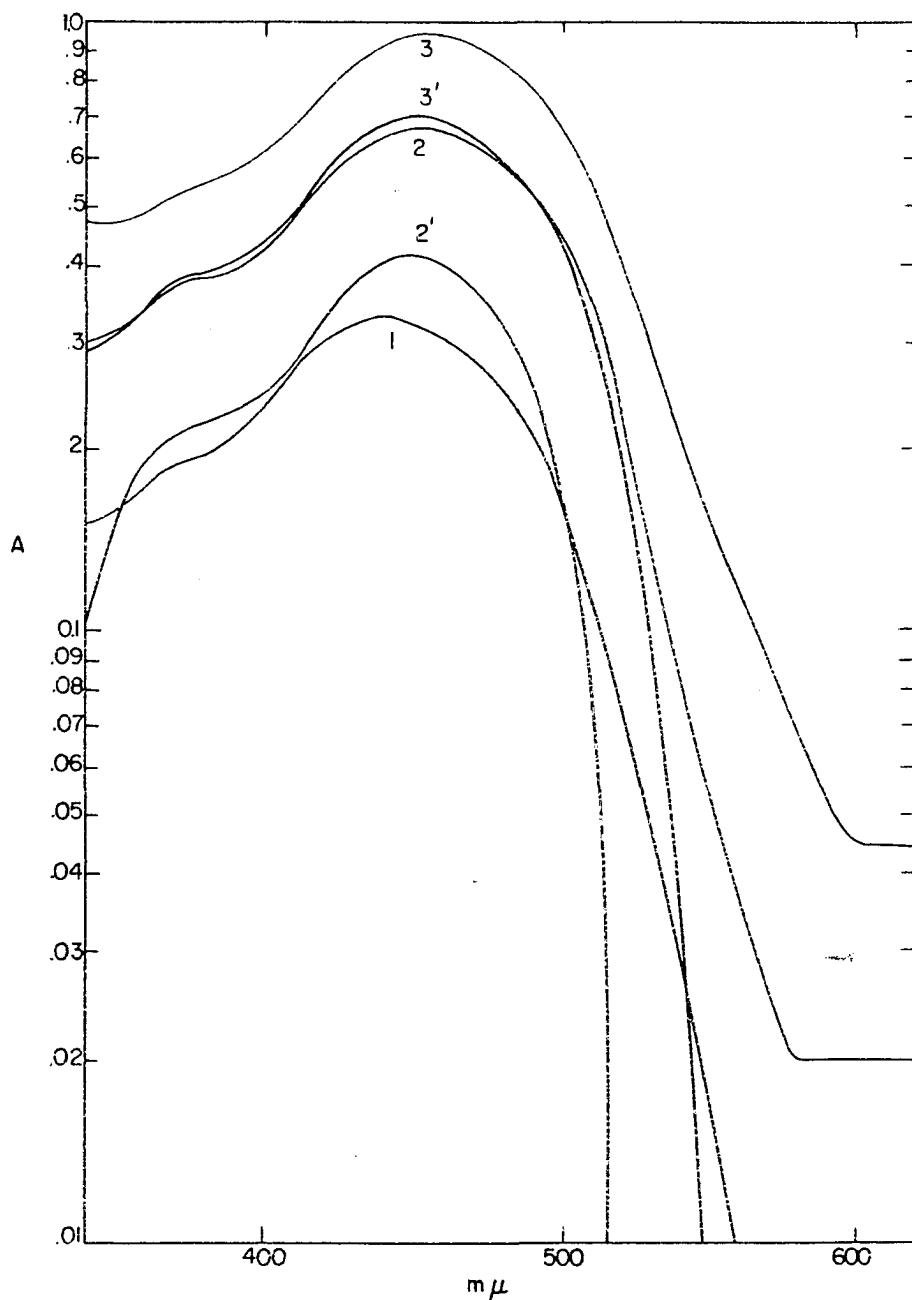


Figure 3. Spectra of 10^{-5} M copper plus Naphthyl Azoxine: curve 1, 1:1; curve 2, 1:2; curve 3, 1:3 mole ratios vs. water and curve 2', 1:2 and curve 3', 1:3 mole ratios vs. 1 equivalent mole blank, 2.01 cm. cells

was used. Graduated in 0.005 ml, it could be read to plus or minus 0.001 ml. The titrant was 10^{-2} M EDTA and, by using very small increments, the color changes were noted very accurately. The phototitrations gave results higher than the visual values by 1%. The results are included in Table 3. The photometric values are obtained from extrapolation of the curves in Figure 4. The wavelengths are those of the absorption maxima assigned to the 1:1 complex and 1:2 complex and the free indicator respectively.

Table 3. Visual and photometric titrations of copper
(0.649 mg. copper taken)

<u>ml. visually</u>			
0.986	0.991	0.989-0.993	0.991-0.999
Average 0.992			
<u>ml. photometrically</u>			
440 m μ	452 m μ	500 m μ	
1.000	1.003	0.985	
Average 0.996			

A higher proportion of indicator was added to the solutions for the photometric titrations than is normal for visual titrations. This was done to provide a large absorbance change and to study the shape of the curves. These titrations in Figure 4 confirm the existence of 1:1 and 1:2 copper-Naphthyl Azoxine complexes.

Each of the titrations plotted in Figure 4 is identical except for the wave length at which the absorbances were measured. The amount of Naphthyl Azoxine included was such that if only a 1:1 complex were found, the copper from this complex would be titrated from 0.7 ml. The absorbances change would then be a straight line to the equivalence point, after which it would become horizontal. If a 1:2 complex only were formed, the absorbances should be constant nearly to 0.85 ml., at which point they should change sharply to the equivalence absorbance. The changes for a 1:1 complex being transformed into a 1:2 complex during the titration can be predicted from the spectra of the indicator and complexes (Figures 1 and 2). At 452 μ , the absorbance would rise slightly from 0.70 to 0.85 ml., then drop to the lower level at 1.0 ml. At 440 μ the absorbance should drop slightly from 0.7 to 0.85 ml., then drop more rapidly to its lower level at 1.0 ml. At 500 μ , the absorbance should rise from 0.7 ml. to 0.85 ml., then continue the rise to 1.0 ml. at a somewhat slower rate. The closeness to the observed behavior confirms the last hypothesis. Both curves

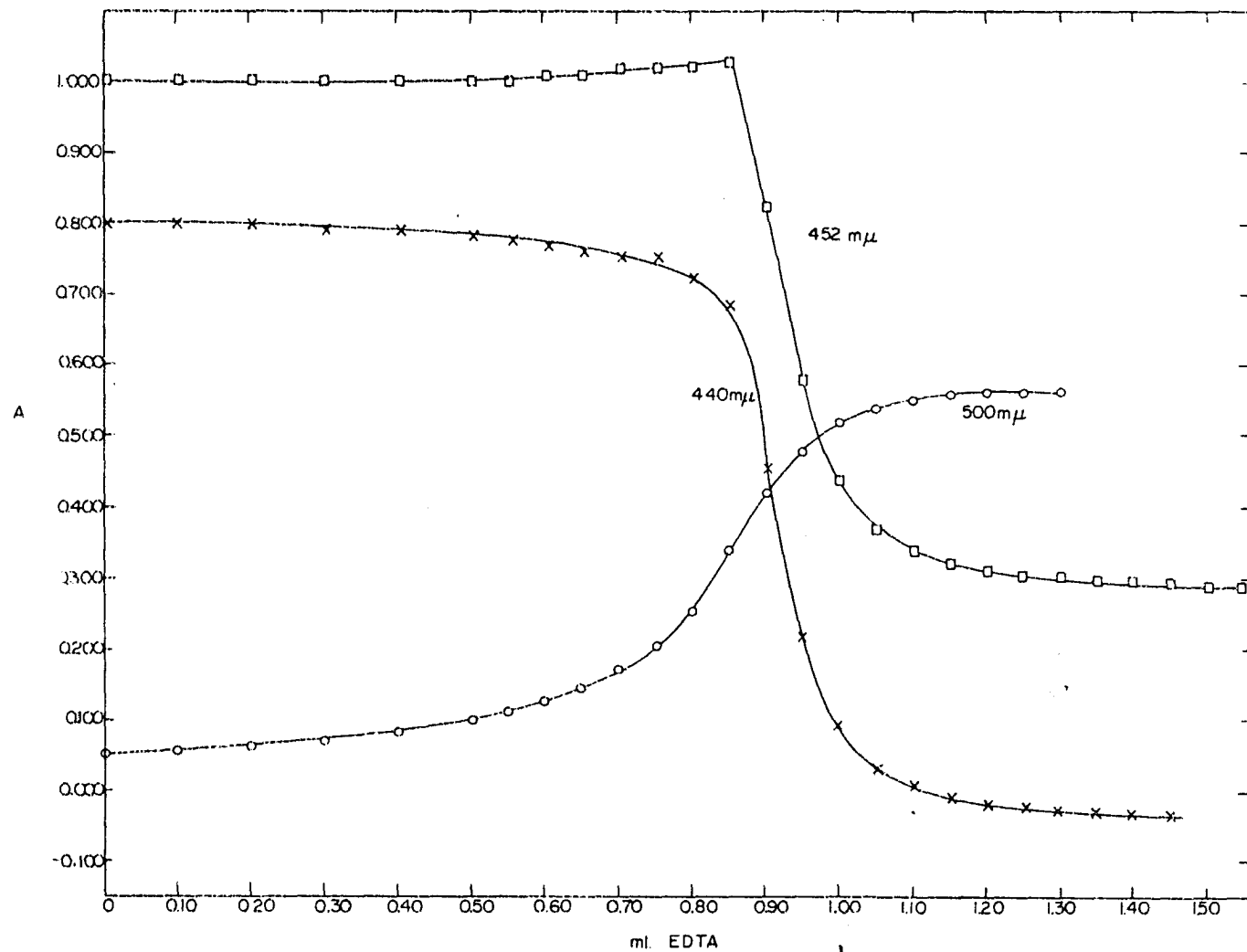


Figure 4. Photometric titrations of 100 ml. $0.99 \times 10^{-4} \text{ M}$ copper with $1.0 \times 10^{-2} \text{ M}$ EDTA

at 452 and 440 μ start their descent at 0.85 ml., and the extrapolated end-points are at 1.0 ml. The extrapolations of the rising portion of the 500 μ curve with the horizontal portions intersect at 0.7 and 1.0 ml. The rounded portions would be due to dissociation of the various complexes.

The phototitrations of Figure 5 were mole ratio type titrations in which 3×10^{-3} millimoles of Naphthyl Azoxine were titrated with 5×10^{-3} M copper solution. The formation of a 1:2 complex would produce a break at 0.3 ml., of a 1:1 complex at 0.6 ml. The breaks came at 0.20 ml. at 452 μ and at 0.25 ml. and 0.6 ml. at 440 μ , and curvature started at 0.25 ml. at 500 μ .

Formation constant

The method of Harvey and Manning (73a) of determining dissociation constants of complexes from their mole-ratio plots has been adapted to data from the absorption spectra of copper-Naphthyl Azoxine complexes. Absorbances were taken from the maxima of curves 2 and 3' of Figure 2, p. 32. Absorbance of curve 2 was assumed to be due to the 1:2 complex as dissociated when the reactants were in stoichiometric proportions. Absorbance of curve 3' was assumed to be due to the complex when driven toward complete association by a 50% excess of indicator, but which excess had been compensated in the blank. Therefore, α , the degree of

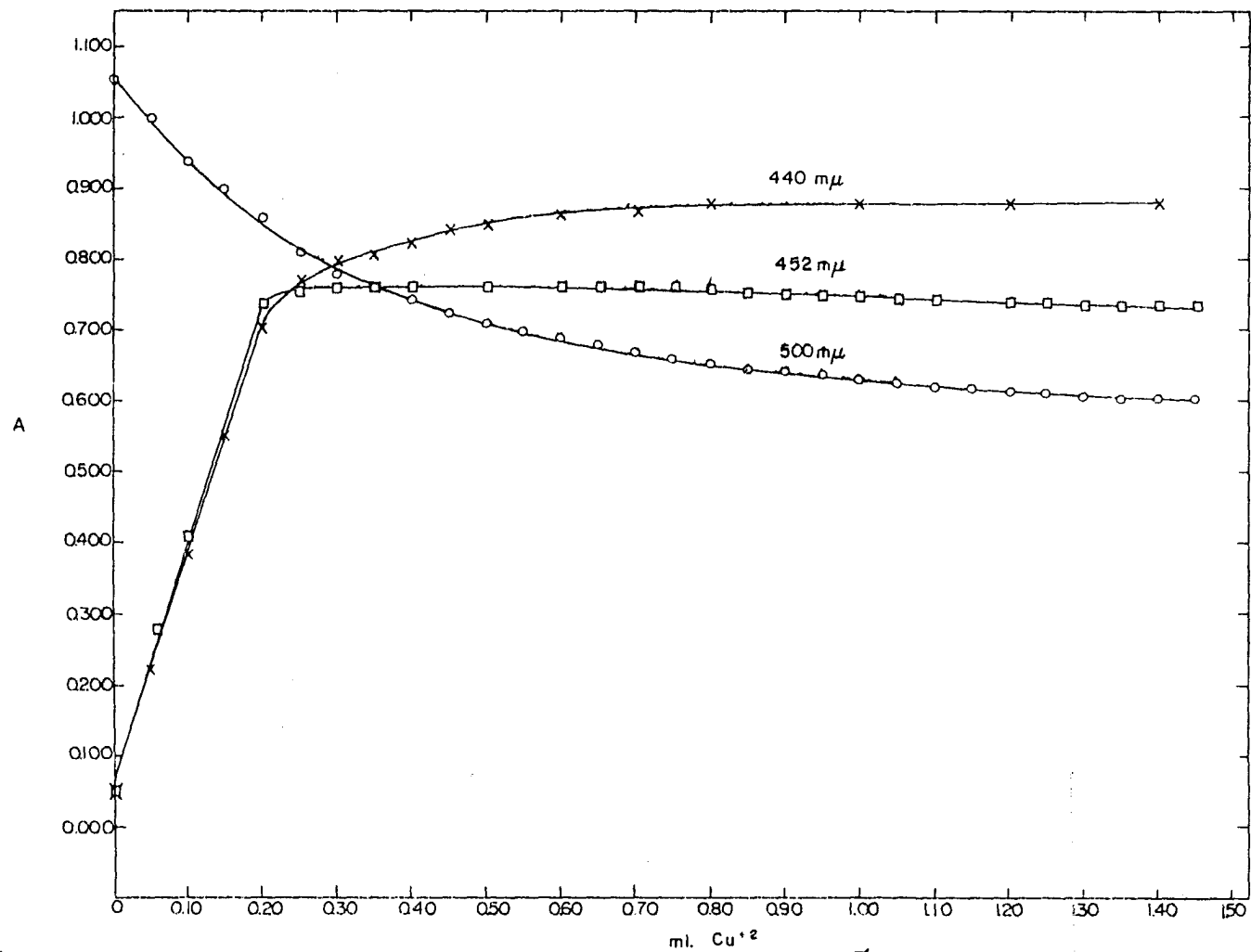


Figure 5. Photometric titrations of 100 ml. 3.0×10^{-5} M Naphthyl Azoxine with 4.9×10^{-3} M copper

dissociation, was calculated to be 0.0238 by

$$\alpha = \frac{A_{3'} - A_2}{A_{3'}} = \frac{0.714 - 0.697}{0.714} = 0.0238 \quad (2.1)$$

after the absorbances were corrected for differences in concentration. The concentration, c , of the complex was 0.976×10^{-5} M. For a 1:2 complex, the formation constant can be written:

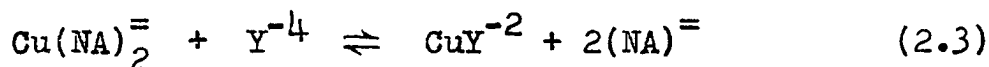
$$K_f = \frac{c(1-a)}{4a^3c^3} = \frac{(1-a)}{4a^3c^2} \quad (2.2)$$

Substituting values, K_f at pH 6 was calculated to be 1.9×10^{15} . The only assumptions made were that the reagent was 100% pure and that the copper or Naphthyl Azoxine present in the lower amount would determine the concentration of the complex. Errors in these assumptions would be small and tend to be compensating.

Discussion

When copper was added to the solutions in the titrations of cations such as lanthanum, the copper-Naphthyl Azoxine complex was formed in preference to displacing lanthanum from its EDTA complex. In the titration with EDTA, the

reactions are:



The equilibrium constant for the copper reaction may be written:

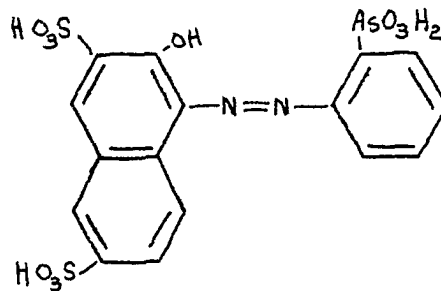
$$K = \frac{K_{\text{CuY}}}{K_{\text{Cu}(\text{NA})}} = \frac{10^{18.8}}{10^{14.7}} = 10^{4.1} \quad (2.5)$$

while that for the lanthanum reaction is $10^{15.5}$. The difference between these constants is great enough to drive the equilibria as suggested. Lanthanum and copper-EDTA complexes would be influenced equally by pH effects, while hydrolysis of lanthanum at pH 5 to 6 should be minor. The pH effect on copper-Naphthyl Azoxine should be negligible in this range. However, when only a small amount of copper is added, it should be done near the equivalence-point. Otherwise the large excess of other ion would tend to shift the equilibrium in the reverse direction.

2-(2-HYDROXY-3,6-DISULFO-1-NAPHTHYLAZO)-
BENZENEARSONIC ACID; THORIN

Reagent

This indicator compound is 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid. It is here named as a substituted benzenearsonic acid because it is believed that the arsonic acid group provides the compounds' affinity toward higher charged cations. The structural formula is



and can also be designated as 1-(2-arsonophenylazo)-2-naphthol-3,6-disulfonic acid. It has been assigned the trivial name Thorin, adapted from its use as a colorimetric reagent for thorium. Other trivial names include Thoron, Thoronal, Naphthazarin and APANS.

The reagent can be prepared by coupling diazotized 2-amino-benzenearsonic acid with 2-naphthol-3,6-disulfonic acid (or R-acid) (117). It does not act as a pH indicator

although its aqueous solution changes gradually from a bright yellow below pH 3.5 to a yellow orange color at pH 8 and above.

A red complex is formed when Thorin is added to aqueous solutions of the lower rare earths. This complex forms from pH 3 to pH 6 with lanthanum, cerium(III) and neodymium. The color varies from a peach color for dysprosium and erbium to a yellow orange for ytterbium and yttrium in this pH range. Lanthanum in methanol forms a bright red solution with Thorin at pH 1 which fades from pink at pH 3 to tan at pH 8. As water is added to the solution, the pH of the maximum color shifts upward. It is the red complex formed with lanthanum which is used as the indication of equivalence as (ethylenedinitrilo)tetraacetic acid (EDTA) is titrated with lanthanum solution.

Titration of EDTA with Lanthanum

Solution preparation and standardization

Thorin reagent, 0.5%, was made by dissolving about 250 mg. of material in 50 ml. of water. The material used was the trisodium salt prepared by Margerum, et al. of this laboratory (117).

EDTA reagent solutions were made according to the starting material. The disodium salt, dihydrate, of the desired amount was dissolved in water. The tetra acid form was

dissolved by adding ammonia or sodium hydroxide to an aqueous slurry of the acid. The resulting solution was standardized by titration of a known amount of calcium plus magnesium blank or of zinc at pH 10 using Eriochrome Black T indicator.

Standard lanthanum solutions were prepared from weighed amounts of lanthanum oxide which had been ignited to constant weight. The oxide was dissolved in nitric or perchloric acid.

Conditions

Although the pink complex exists from pH 3 to pH 6.5 where lanthanum hydroxide precipitates, the optimum range was found to be pH 5.5 to 6.5. A sharper end-point in fairly clean solutions occurred at pH 6 but higher amounts of diverse ions or the addition of organic solvents required lower pH 5.0 to 5.5 for best color transitions.

Sodium bicarbonate was superior to sodium or ammonium acetate as a buffer and pH adjusting reagent. It has been found generally that carboxylic acids tend to interfere with metal indicator reactions. Possibly an amine buffer might be superior to bicarbonate.

No change in the end-point transition was noted when 0.25 to 0.50 millimoles of EDTA was diluted to 25, 50, or 100 ml. for titration.

Use of 50% non-aqueous solvent had no effect other than requiring the lower apparent pH 5 for the optimum color change.

Solvents tried were methanol, acetone, dimethylformamide and hexamethylphosphoramide.

Procedure

This general procedure for the titration was followed. The desired amount of EDTA was added to water or to the solution of the cation to be determined and diluted to 50-100 ml. solution. Two drops of 0.5% Thorin solution were added. With stirring, about 95% of the amount of lanthanum required was added. The solution was adjusted to pH 6.5 to 7.0 with sodium bicarbonate. The titration was resumed and the equivalence point was taken at the first permanent change from yellow to amber or pinkish orange. Over titration was indicated if enough lanthanum-Thorin complex formed to make a pink or red solution.

Results

The EDTA solution was freshly standardized against zinc to be 0.05082 M and lanthanum solution was 0.04143 M by weight of the oxide dissolved. Aliquots of eight ml. each of EDTA were titrated with the lanthanum as the pH was varied (Table 4). In addition, with reagents diluted to 0.01 M, a titration calculated to require 9.92 ml. took 9.92 and 9.91 ml.

The diverse-ion effect rendered the end-point less sharp at concentrations greater than 0.25 M in NH_4NO_3 . The results of these titrations are also included in Table 4.

Table 4. Lanthanum-EDTA titrations
(9.82 ml. calculated)

ml. observed	Remarks
9.86	pH 6.5, poor change
9.83, 9.83	pH 6.0, good change
9.85, 9.83	pH 5.5, good change
9.83, 9.83	pH 5.0, good change
9.83	pH 4.5, fair change
9.84, 9.84, 9.85, 9.86, 9.85	pH 6.0
9.85, 9.85	250 mg. NH_4NO_3 added, pH 6.0
9.84, 9.85, 9.83	500 mg. NH_4NO_3 added, pH 6.0
9.85	750 mg. NH_4NO_3 added, pH 6.0
9.86, 9.87	1000 mg. NH_4NO_3 added, pH 6.0
9.87, 9.84	1500 mg. NH_4NO_3 added, pH 6.0

Less sharp

This NH_4NO_3 is in addition to the reagents added to adjust the pH. It was determined that a lower pH 5.5 allowed a sharper color transition in the presence of the higher amounts of salt.

Interferences

Cations Most cations interfere with the titration. This was determined by titrating a solution of 4.00 ml. EDTA and five drops of 0.1 M solution of each cation added. The theoretical end-point was 4.91 ml. A titration of about 4.3 ml. would indicate approximately stoichiometric interference. The effects of cations are listed in Table 5.

Thus lithium, silver, barium, magnesium and strontium do not interfere, and calcium causes a slightly low titration. Calcium, of the alkaline earths, seems to be on the border-line of interference. These titrations were done at pH 6.0, a lower pH might eliminate the interference of calcium since interference probably occurs by the forming a complex with the EDTA. The mole ratio of added cation to EDTA was 1:8.

Anion In contrast to the many cation interferences, only a few anions interfere in the titration of EDTA with lanthanum. Anion interference was checked in a manner similar to that for cations - a 2.00 ml. aliquot of EDTA containing 5 drops of 0.1 M anion solution was titrated with lanthanum. Only citrate, oxalate, and phosphate interfered with this titration. Results are included in Table 6. A supplementary test of several anions was conducted by adding 10 drops of the anion to a lanthanum solution, then adding a measured excess of EDTA and titrating the excess with

Table 5. Cation interference^a
(4.91 ml. calculated)

Ml. observed			Ml. observed	
No foreign ion	4.92, 4.93, 4.93,	Li ⁺¹	4.92	
	4.93, 4.93, 4.93,		Mg ⁺²	4.91, 4.94, 4.92, 4.93, 4.93
	4.92, 4.93, 4.91,			
	4.90, 4.90, 4.92,			
	4.92, 4.91, 4.92,			
4.91				
Ag ⁺¹	4.92, 4.92	Mo ₇ O ₂₄ ⁻⁶	No e.p.	
Al ⁺³	4.3	Nb ⁺³ (as F ⁻)	No e.p.	
Ba ⁺²	4.93	Ni ⁺²	4.22	
Be ⁺²	4.8 at pH 3	Pb ⁺²	4.37	
Bi ⁺³	3.60	Sn ⁺²	4.70	
Ca ⁺²	4.89, 4.87, 4.89,	Sn ⁺⁴	4.85, 4.85	
	4.88, 4.89			
Cd ⁺²	4.49	Sr ⁺²	4.94, 4.92	
Ce ⁺³	4.35	Ta ⁺⁵ (as F ⁻)	No e.p.	
Co ⁺²	4.32	Ti ⁺⁴	4.50	
Cr ⁺³	4.72	TiO ⁺² (as KOx)	No e.p.	
Cu ⁺¹	4.7	UO ₂ ⁺²	No e.p.	
Cu ⁺²	4.36	V ₂ O ₂ ⁺⁴	4.3-4.4	
Fe ⁺²	4.30	VO ₃ ⁻	4.89	
Fe ⁺³	4.28	WO ₄ ⁻²	4.94	
HfO ⁺²	4.36	Zn ⁺²	4.33	
Hg ⁺²	4.35	ZrO ⁺²	4.75	

^aSalts added mostly as perchlorates, some as chlorides or nitrates, except as noted.

lanthanum. In this test only fluoride ion interfered; cyanide, sulfate and succinate did not. The results are given in Table 7.

Table 6. Anion interference
(2.48 ml. calculated)

Anion	Ml. observed	Anion	Ml. observed
None	2.48, 2.49	Phosphate	2.8
Benzoate	2.48	Phthalate	2.45
Bromate	2.50	Picrate	2.46
Chromate	2.48	Succinate	2.47
Citrate	2.8	Sulfate	2.50
Cyanide	2.48	Tartrate	2.52
Fluoride	2.47	Tartrate (10 drops)	2.52
Fluoride (10 drops)	2.47	Thiocyanate	2.49
Formate	2.46	Thiosulfate	2.49
Iodide	2.48	8-Hydroxyquinoline	2.50
Oxalate	No e.p.	Dimethylglyoxime	2.50

Table 7. Anion interference
(0.48 ml. calculated)

Anion	ml. observed
Cyanide	0.50
Sulfate	0.48
Tartrate	0.49 (poor end point)
Fluoride	0.82
Succinate	0.48

Determination of Metals

Rare earths

Only the lower rare earths form pink complexes with Thorin, but back titration of the excess EDTA with lanthanum has been successfully applied to the determination of other rare earths. Although it is not a necessity, the formation constant of lanthanum-EDTA being the lowest of all the rare earths makes the reaction more direct.

Rare earth solutions were prepared as standard from column-purified oxides at least 99.9% pure by spectrographic analysis. The oxides were ignited to constant weight to eliminate carbonate as well as water before being dissolved in perchloric acid. Solutions were prepared of lanthanum,

neodymium, dysprosium, erbium, ytterbium and yttrium. The EDTA solution was prepared by dissolving the sodium salt of (ethylenedinitrilo)tetraacetic acid in water and was standardized by titration with standard calcium solution using a magnesium blank and Eriochrome Black T indicator. The results are given in Table 8.

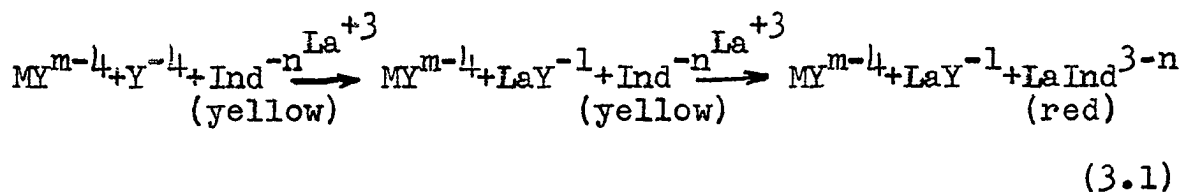
Table 8. Determinations of rare earths

Metal	Mg. taken	Mg. found
Nd	68.14	68.05, 68.18, 68.18, 68.18
Dy	73.69	73.61, 73.81, 73.74, 73.68
Er	75.84	75.89, 75.89, 76.04, 75.96
Yb	77.80	78.04, 78.20, 78.11, 78.11
Y	43.71	43.75, 43.71, 43.71

Other metals

The lanthanum titration of an excess EDTA was successfully applied to the determination of bismuth, cadmium, cobalt, copper, nickel, lead, thorium, and zinc. Titrations could not be obtained for chromic, gallic, ferric, manganous, mercuric or stannic ions. Aliquots of standardized solutions

of the cations were taken so that 10 ml. of 0.05 M EDTA would be in slight excess. The titration can be written



in which M^{+m} is the cation to be determined, Y^{-4} is EDTA ion, and Ind^{-n} is the indicator ion.

Bismuth Although bismuth reacts with Thorin at low pH's, the usual procedure was applied to the determination of bismuth. Some variation of pH and amount of Thorin was tried to get the best results. Two drops of Thorin and titration in the range of pH 5.5 to 6.0 provided the sharpest end-point and best stoichiometry. Findings are given in Table 9. Since bismuth hydrolysed readily, some care in its manipulation was required. When the EDTA was added to the bismuth solution, a white precipitate formed which dissolved with stirring at pH 1. A higher pH brought about solution faster. Then raising the pH with sodium bicarbonate caused no further precipitation. The bismuth solution was made up by weight of the metal as 100% bismuth. With bismuth in excess, Thorin formed a bright red soluble complex between pH 1 and pH 2. When the mole ratio approached unity, a voluminous flocculent red-orange precipitate formed in this

Table 9. Bismuth determinations
(104.35 mg. bismuth taken)

Mg. found	Remarks
103.48	pH 5, 1 drop Thorin, poor end-point
103.68	pH 4.2, 1 drop Thorin, poor end-point
104.02	pH 4.2, 2 drops Thorin, poor end-point
104.12, 104.02	pH 5.5 to 6.0, 2 drops Thorin, good end-point

pH range which left a clear, colorless supernatant when it settled.

Cadmium Cadmium does not form a colored complex with Thorin. The lanthanum back titration was applied with only fair results. Two variations improved the end-point which was not as sharp as for some other metals. Fifty percent alcohol and a higher pH in the range 6.0 to 6.5 provided the best color transition. The cadmium was standardized by titrating with EDTA using Eriochrome Black T indicator with a zinc blank. Results are given in Table 10.

It was found that trace of zinc did not improve the end-points of this titration. The optimum amount of indicator is a personal choice. One drop provides a change from light yellow to pale pink, while two provides a deep yellow color changing to orange at the end-point and on to red-orange. The author's preference was for the use of two drops.

Table 10. Cadmium determinations
(54.06 mg. cadmium taken)

Mg. found	Remarks
54.05	50 ml. H ₂ O, pH 6.5, not sharp
53.90	50 ml. H ₂ O, pH 6.2, not sharp
53.99	50 ml. 50% MeOH, pH 6.4
53.90	50 ml. acetone, turbid, clearing
54.19	50 ml. water, pH 6.3, 1 drop Thorin
53.84, 53.89	50 ml. 50% MeOH, pH 6.4, 1 drop Thorin
53.84, 53.95	50 ml. 75% MeOH, same conditions
53.99	50 ml. 25
53.84	50 ml. 50% MeOH, pH 6.4, 2 drops Thorin

Cobalt The back titration of aliquots of an unstandardized cobalt solution showed good precision. Ten ml. of 0.05 M EDTA were added to each sample of 9.50 ml. of 0.05 M cobalt in about 50 ml. of water. The lanthanum back titrations were 0.80, 0.80, 0.76, 0.79 and 0.80 ml. The pink color of the cobalt altered the end-point transition to a change from yellow-orange to orange. The color change was sharp, however, but not of great contrast. Little difference was noted between the use of 1 or 2 drops of 0.5% Thorin.

Copper The deep blue color of the copper-EDTA complex nearly masks the end-point of the titration of 0.5 millimole

or 32 mg. of copper. However two-fold dilution or use of a sample size of 0.25 millimole or less would minimize the blue color. Copper evidently forms a colorless Thorin complex which is stronger than that of lanthanum since the addition of a small amount of copper solution to the red lanthanum-Thorin complex abstracts the color at pH 5 to 6. Thus the excess EDTA should be added to the copper prior to the indicator to minimize any copper indicator reaction.

Two drops of 0.5% Thorin gave the best end-point. This turns the blue copper-EDTA solution green. Near the end-point the temporary formation of lanthanum-Thorin causes blue flashes; the increment turning the solution blue-green is taken as the equivalence point. One drop of indicator is not enough to provide a color change. More than three drops makes the solution too green. A visible change from green to darker olive-green was observed with 0.5 ml. of Thorin. The copper solution was standardized by EDTA titration using murexide, or ammonium purpurate, indicator at pH 9.5. The results are listed in Table 11.

Nickel Nickel poses a similar color problem as does copper, forming a blue EDTA complex, apparently forming a weakly colored complex with Thorin, but does not displace lanthanum from the lanthanum-Thorin complex. One drop 0.5% Thorin gave the sharpest end-point from green to light purple, while more indicator seemed only to darken

Table 11. Copper determinations
(31.39 mg. copper taken)

Mg. found	Remarks
no e.p.	1 drop Thorin, pH 5.5, 100 ml.
31.34	2 drops Thorin, pH 5.5, 100 ml.
31.28	3 drops Thorin, pH 5.5, 100 ml.
31.26	3 drops Thorin, pH 4.5 to 5.0, 60°
31.34	3 drops Thorin, pH 5.0 to 5.5, 60°
31.19	3 drops Thorin, pH 5.5 to 6.0, 40°
31.34	10 drops Thorin, pH 5.5

Table 12. Nickel determinations

Mg. taken	Mg. found	Remarks
53.64	53.78	5 drops Thorin
26.82	26.77, 26.80, 26.92, 26.92, 27.10	3 drops Thorin
21.46	21.56	
13.41	13.53	1 drop Thorin
2.68	2.74	1 drop Thorin, sharp e.p.

the color. The optimum pH is 5.5 or a little above. Results are given in Table 12.

Lead The titration of lead presented no difficulties and gave reproducible but high results. The average of seven determinations was 95.37 mg. with an average deviation of 0.14 mg. The calculated titration was 95.15 mg. The lead solution was made with the oven-dried reagent-grade lead nitrate. The titer was determined by the weight of the salt taken and its dilution.

Table 13. Lead determinations
(95.15 mg. lead taken)

Mg. found	Remarks
95.32, 95.32	50 ml. soln, 2 drops Thorin
95.23, 95.50	50 ml. soln, 1 drop Thorin
95.12, 95.50	25 ml. soln, 1 drop Thorin
95.59	75 ml. soln, 1 drop Thorin

Thorium Satisfactory determinations of thorium were difficult to achieve. Several procedures were tested to obtain a satisfactory titration for thorium and to help explain the reasons for its behavior. These are tabulated in Table

14 with the results and are described below. A first set of ten titrations resulted in the result of 113.2 ± 0.2 mg. thorium found when 112.5 mg. were taken. The difference of 0.6% was unsatisfactory but the precision of only 0.2 mg. or 0.2% was acceptable. The error cannot be readily explained since the thorium was standardized with excellent precision, by EDTA titration using the Alizarin Red S procedure of Fritz and Ford (60). Therefore, these two reagents should be correct relative to one another at least. Deviation of the lanthanum reagent should not be significant since in this type of back titration, a 1% error in the concentration of the titrant would cause only about 0.1% in the final results if the back titration was less than 1 ml. when the total EDTA was ten ml. of a similar concentration.

However, these titrations demonstrated that pH 4.5 to 5.0 provided a better color transition than at higher pH's. In addition several attempts to titrate thorium directly with EDTA using Thorin did not provide sufficiently sharp end-points. Titrations were made at pH 2.0 to 2.5 and pH 3 with just thorium originally present, and at pH 4.5 to 5.0 and pH 2.0 with 0.50 ml. lanthanum added for the end-point reaction.

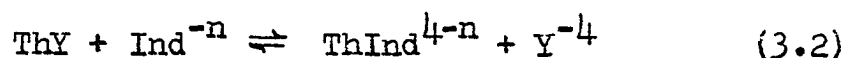
A second series of thorium titrations with more freshly prepared EDTA and lanthanum solutions produced better results. The initial slight pink color was present even when Thorin was added to the solution of thorium and excess EDTA.

Table 14. Thorium determinations
(112.5 mg. thorium taken)

Mg. found	Remarks
113.2, 112.9, 112.7	Thorin added before EDTA
112.9, 112.9, 112.9, 112.7	Thorin added after EDTA 25°, 60°, 55°, 40°, respectively

The end points were poor under all conditions tried (Table 14). The last titration was of a larger excess of EDTA.

These results averaged 112.9 mg. thorium found, which was 0.35% higher than calculated. The high experimental findings can be explained by the reaction



to form a colored thorium-Thorin complex before all the excess EDTA is titrated. The faint pink color of a thorium plus excess EDTA solution to which Thorin has been added would indicate a premature end-point and high results. This would require K_f of thorium-Thorin to be somewhat near the magnitude to K_f of Thorin-EDTA. Byrd (30, p. 64) has found evidence of a strong thorium-Thorin complex having the ratio 2:3, and calculated the $\log K_f$ to be 22. The $\log K_f$ of thorium-

EDTA is 23. Byrd also calculated $\log K_f$'s of 12 and 6 for 1:2 and 1:1 complexes respectively.

Zinc Zinc does not form a colored complex with Thorin. The end-point color change in the lanthanum back titration is less sharp than for some other metals. The titration results varied, but the average of six agreed with amount of zinc taken (Table 15). The use of 50% alcohol solvent and slightly higher pH provided the best end-point transition. The zinc was standardized by EDTA titration using Eriochrome Black T indicator.

Table 15. Zinc determinations
(29.8 mg. Zn taken)

Mg. found	Remarks
29.7	1 drop Thorin, pH 5.8 to 6.0
29.9, 29.7, 29.8, 29.9	2 drops Thorin, pH 5.8 to 6.0
29.7	2 drops Thorin, 1:1 methanol, pH 6.0 to 6.2, better end-point

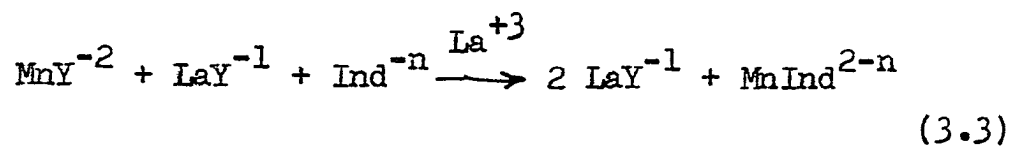
Unsuccessful applications No titration was obtained for chromium(III), gallium, iron(III), manganese(II), mercury(II), and tin(IV).

Chromium forms the EDTA complex very slowly at room temperature, but quickly at elevated temperatures. When formed the color is so deeply purple that no Thorin color change could be visible.

The end-point in the iron titration were either very poor and over-titrated or indeterminate. The color of iron-EDTA probably masks the color change. Two-fold dilution did not help the end-point visibility.

A sufficiently sharp and accurate end-point was not obtained for the titration of gallium. This element forms only a tan-colored solution with Thorin at pH 3-5, but it apparently does not allow the lanthanum-Thorin end-point reaction to occur sharply. A number of titrations produced deepening of the solution color in a range of 0.05 to 0.10 ml. about the calculated end-point. The range was shortest with 50% methanol.

Manganous ion did not form a colored complex with Thorin. In the titrations tried, no color transition occurred. The reason may be that lanthanum displaced manganese from the EDTA complex as the lanthanum-EDTA formation constant exceeds the manganese-EDTA constant. Therefore the final reaction would be



Mercuric ion did not form a colored complex with Thorin. No end-point was observed in its back titration.

Stannic ion plus EDTA precipitated which prevented any lanthanum back titration. Tin was added to the EDTA and vice versa; the solutions were varied from pH 0 with HCl to pH 9. A forward titration attempt of tin plus lanthanum with EDTA also was unsuccessful.

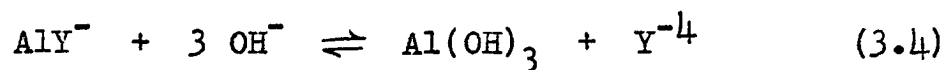
Determination of aluminum

Because of the scarcity of simple volumetric methods a special effort was made to obtain a good volumetric determination of aluminum by the lanthanum back titration of excess EDTA. Some chemical similarities of aluminum and lanthanum suggest that there may be advantages to such a method. The tendency of aluminum to hydrolyse is probably a significant cause of difficulty. The hydrolysis reaction would compete with the chelating reaction of EDTA. The quantitative evaluation of this is subject to correct identification of the chemical species and the availability of the pertinent data. Latimer and Hildebrand (106) and Moeller (133) state that aluminum probably precipitates as a gel forming $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or $\text{AlO}(\text{OH})$, and ages to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or $\text{Al}(\text{OH})_3$. In 1955, Szabó, Csányi and Kávai (184) noted the solubility product constants for aluminum hydroxide given in the literature ranged from 10^{-14} to 10^{-33} . By using data from titrations of aluminum solutions with sodium hydroxide, they determined

K_{SP} to be 1.25×10^{-33} at 20° and 1.92×10^{-32} at 30° .

They also calculated the acid dissociation constant to be 180×10^{-13} at 20° and 1.34×10^{-13} at 30° . The low values for K_{SP} would appear to be reasonable. In addition, ter Haar and Bazen (72) report the species $Al(OH)HY^-$ formed at pH 4.5 and $Al(OH)Y^{-2}$ at pH 8.5 as postulated by Biederman.

A simplified reaction, however, may be written and analyzed with interesting results.



A constant for this hydrolysis reaction can be written

$$K_h = \frac{[H_n Y^{n-4}] \beta}{[AlY^-] [OH^-]^3} = \frac{\beta}{K_f \cdot K_{SP}} \quad (3.5)$$

in which β is the function of pH which converts the total concentration of all uncomplexed protonated EDTA species to the completely dissociated Y^{-4} ion. The value of β at pH 6 is $10^{-4.6}$; K_f for aluminum is $10^{16.2}$ at 25° . From the solubility product constants at 20° and 30° of Szabo, Csanyi and Kawai (184), the molar solubilities were calculated. A linear extrapolation provided a molar solubility at 25° from which K_{SP} at 25° was calculated to be 6.17×10^{-33} or $10^{-32.21}$. Therefore, K_h at 25° and pH 6 is $10^{11.4}$. Using

this value, the ratio, R, of $[AlY^-]$ to $[Y^{-4}]$ may be calculated. Since $[Y^{-4}] = Al(OH)_3$ in the equation as written, this ratio R is the ratio of aluminum complexed to aluminum hydrolysed.

$$K_h = \frac{1}{R} \cdot \frac{\beta}{[OH^-]^3}, \quad \text{or} \quad R = \frac{\beta}{K_h [OH^-]^3} \quad (3.6)$$

at pH 6, $R = 10^{8.0}$. At pH 7, $R = 10^{5.0}$. It can be seen that for every increase of pH by one unit, R will decrease by 10^3 . From equation 3.2, the ratio $[AlY^-] / [Y^{-4}]$ can be calculated as a function of K_f , K_{SP} , and $[OH^-]$.

$$R = \frac{[AlY^-]}{[Y^{-4}]} = \frac{K_f \cdot K_{SP}}{[OH^-]^3} = \frac{10^{-16}}{[OH^-]^3} \quad (3.7)$$

In this equation, $[OH^-]$ raised to the third power is the only independent variable.

These findings indicate that aluminum is complexed by EDTA at pH's less than 8. The reaction apparently is slow at room temperature but is faster at elevated temperatures. Ter Haar and Bazen (72) found they needed to titrate the excess EDTA which was added to aluminum, with thorium ion at pH 3.5 at room temperature or at pH 4.3 at 100°. They made their titrations under the former conditions but

obtained results consistently low by 1%. Wänninen and Ringbom (197), using zinc as a back titrant, dithizone indicator, 50% alcohol and pH 4.5 to 4.6, had errors of only 0.1%.

The best results for a number of samples by the procedure incorporating lanthanum as a back titrant and Thorin indicator required heating and were accurate to $\pm 0.5\%$ for a 13 mg. sample of aluminum. Findings tended to be higher than the calculated value rather than lower. Preliminary determinations had varied by as much as 2% from the calculated amounts of aluminum taken. Variations in pH, temperature, and order of addition of reagents were tested with mixed results. It became apparent that heating of the aluminum-EDTA solution was beneficial. The aluminum solution from which the final series of determinations was made was standardized by evaporation of four 50 ml. aliquots in platinum dishes, followed by ignition to the oxide. The value 0.05322 M was determined for the concentration of the aluminum solution. Aliquots of 9 ml. containing 12.92 mg. were taken for determination; ten ml. 0.0582 M EDTA were added and back titrations were made with 0.04143 M $\text{La}(\text{ClO}_4)_4$ solution.

Several titrations at room temperature gave low aluminum recovery, which confirmed that all the aluminum was not being chelated by the EDTA. Different procedures which included heating of the aluminum-EDTA solutions were then

tried. Of 59 determinations, 37 fell within 0.13 mg. of 12.92 mg. taken, or with 1%. However, only 16 results were within 0.06 mg. or 0.5%. There were 18 determinations falling within +0.5% to +1% deviation while only 3 deviated between -0.5% and -1.0%. This skewness of distribution is also reflected in the results from the procedure which provided the closest agreement with the samples taken. In this procedure the aluminum sample plus excess EDTA was diluted to about 50 ml. and adjusted to pH 5.5 to 6.0 with NaHCO_3 . This solution was heated at about 60° for a few minutes and then cooled on an ice bath to room temperature. The pH was adjusted if necessary as the temperature approached 25° and the titration as made while the temperature was between 23° and 27°. The results are listed in Table 16.

Additional work on smaller amounts of aluminum was conducted in connection with some aluminum-vanadium alloys. Samples containing 2.87 mg. aluminum were treated with an excess EDTA and back titrated with 0.01036 M $\text{La}(\text{ClO}_4)_3$. Regular and elevated temperature procedures gave low results, but addition of non-aqueous solvents and lower pH provided fair values (Table 17).

These results demonstrate the difficulty of making an accurate determination of aluminum in aqueous solution. If the principle reason is a strong tendency for aluminum to hydrolyse, a possible solution would be to raise the pH

Table 16. Aluminum determinations
(12.92 mg. aluminum taken)

Number	Al found %	Deviation %	Number in range	Deviation mg.
1	13.10	+1	2	.18
1	13.06			.14
2	13.04	+0.5 to +1.0	9	.12
1	13.02			.11
1	13.03			.10
5	12.99			.07
1	12.97	±0.5	15	.05
4	12.93			.01
1	12.92			.00
2	12.91			.01
2	12.90			.02
5	12.87	.05		
1	12.84	-0.5 to -1.0	2	.08
1	12.82			.10
1	12.59	-1.0	2	.33
1	12.51			.41
Average	12.92			0.081

Table 17. Aluminum determinations
(2.87 mg. aluminum taken)

Mg. found	Remarks
2.88	50% Methanol, pH 4.0 to 5.0
2.88, 2.87, 2.88, 2.88	50% Acetone, pH 4.0 to 5.0
2.89, 2.89, 2.89, 2.89	68% Acetone, pH 4.0 to 5.0
2.87	50% Dimethylformamide, pH 4.0 to 5.0

homogeneously in the presence of the desired excess of EDTA as by urea hydrolysis at an elevated temperature. A larger excess of EDTA might bring about an improvement in accuracy and precision of results.

Determination of Fluoride Ion

Thorin was used as the indicator in the EDTA titration of excess lanthanum or cerium(III) after precipitation of the rare earth fluoride. Reproducible analyses were obtained for 1 to 10 mg. fluoride. Silver and sulfate ions caused only moderate interference.

Procedure

The precipitation of the rare earth fluoride was patterned after the procedure described by Popov and Knudson (143). These men determined fluoride indirectly by precipitation of lanthanum fluoride from an acetate buffered solution. The precipitate was coagulated on heating in the presence of acetate ion. After separation, they precipitated the excess lanthanum with cupferron and weighed the oxide after ignition.

While the insolubility of rare earth fluorides is attributed to high lattice energies (133, p. 426), acetate ion seems to be necessary to obtain a coagulated precipitate from solution. Meyer and Schulz (127) in 1925 investigated lanthanum as a precipitant for fluoride. They found that lanthanum

fluoride redissolved in the presence of an excess of lanthanum nitrate or chloride but not with lanthanum acetate.

Their procedure incorporated precipitation from strong acetic acid solution to obtain a $\text{LaF}_3 \cdot \text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$ precipitate which was dried and weighed, then ignited to the oxyfluoride and weighed. Good results were reported from the difference in weights for 1 to 140 mg. fluoride. Fisher (50) in 1930 tried to use the method of Meyer and Schulz but could not reproduce their results. Fisher claimed also that acetate ion was required to obtain a filterable precipitate. However, Giammarino (63) claimed the mixed precipitate formed was $2 \text{LaF}_3 \cdot \text{LaAc}$ and based a nephelometric determination of fluoride on this reaction.

Acetate ions were found necessary in this application, but the 1:3 lanthanum-fluoride ratio held for the calculations. The procedure found to give the best results utilized a minimum of reagents because of the unfavorable effect of higher ionic strength on the titration color change. The sample of 1 to 10 mg. fluoride was diluted to 20 to 100 ml. depending on whether centrifuging or filtration was to be employed. With low volumes, the reactions could be carried out in the centrifuge tubes. About 1 gram of ammonium nitrate was added and the solution was made just acid to methyl orange. The lanthanum solution was added, and the solution was heated to near boiling. The hot solution was readjusted to be just acid to methyl orange after addition of 2 to 4 drops of

glacial acetic acid. The precipitate would then coagulate. It was centrifuged or filtered, and washed with 2.5% ammonium nitrate. The filtrate and washings was then titrated with EDTA at pH 7. Back titration of an excess of EDTA was also used and either method was satisfactory.

Determination

According to concentrations of the solutions as standardized, the method provided a straight line relation of fluoride found to fluoride taken with a slope of 1.025. Samples taken from three sources of fluoride could not be distinguished over this range. Results are given in Table 18. These three sources of fluoride were analytical grade sodium fluoride used in the developmental work, a new bottle of analytical grade sodium fluoride, and sodium fluoride prepared by the reaction of hydrofluoric acid and sodium hydroxide. This preparation was carried out by adding 48% hydrofluoric acid slowly to a stirred solution of sodium hydroxide in a polyethylene beaker in an ice bath. The product was filtered on a medium sintered glass filter, washed with ethanol, and transferred into a watch glass to be dried in an oven.

One to two percent high results were obtained in the presence of silver, and up to 10% high with sulfate in fairly high proportions. It is suggested that these ions might be used to precipitate other interfering ions. These effects are shown in Table 19 and Table 20.

Table 18. Fluoride determination

Mg. F taken	Mg. F found	Average deviation	Number of determinations	Comparison with slope of 1.025
0.00	0.015	0.00	4	0.00
2.00	2.06	0.026	6	2.05
4.00	4.09	0.021	6	4.10
6.00	6.17	0.012	5	6.15
8.00	8.21	0.012	5	8.20
10.00	10.25	0.030	4	10.25

Table 19. Effect of silver ion
(10.00 mg. fluoride taken, 10.25 mg. expected)

Mg. Ag	Mg. F found	Remarks
12	10.38	
24	10.2-10.5	Poor end-point
48	10.41, 10.29	
96	10.4-10.8	Turbid solution

Table 20. Effect of sulfate ion
(10.00 mg. fluoride taken; 10.25 mg. expected)

Mg. SO_4	Mg. F found
0	10.35, 10.50
10	10.91, 10.94
40	11.15, 11.15
80	11.28, 11.40

It was considered to try to determine 0.1 to 1.0 mg. fluoride by a similar titration with more dilute solutions, but without requiring separation of the precipitate. However the end-points with 0.01 M EDTA were poor, and strongly affected by added salt.

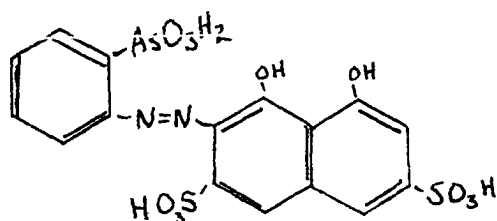
2-(1,8-DIHYDROXY-3,6-DISULFO-2-NAPHTHYLAZO)-
BENZENEARSONIC ACID; ARSENAZO

The reagent Arsenazo has been applied to the determination of small amounts of rare earths by spectrophotometric determination of the end-point of EDTA titrations. Successively more dilute titrations were accurately performed down to the titration of 100 ml. of 7.5×10^{-7} M neodymium with 1.0×10^{-5} M EDTA. Phototitration of rare earths were made in the presence of a tenfold molar excess of uranium with the use of diethyldithiocarbamate as a masking agent. A procedure for the purification of the commercial indicator was devised. Spectra were obtained for Arsenazo and its rare earth and uranyl complexes. It was determined that 1:1 complexes were formed with rare earths. The lanthanum-Arsenazo complex formation constant was calculated to be 2.7×10^8 .

Reagent and Complexes

Reagent

This compound, 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-benzenearsonic acid, was first prepared as one of a series by Kuznetsov (91) in 1941. Its structural formula is



He noted that it formed a colored product with thorium, uranium and the rare earths. In 1952, Kuznetsov (92-95) described conditions for the qualitative detection of rare earths. With associates, he (96-99) applied the reagent to the quantitative determination of aluminum, beryllium and zirconium. Emi and Hayami (48) determined fluoride by the bleaching of the thorium-Arsenazo complex.

Arsenazo is related to Thorin, and would be expected to have similar affinity for tri- and tetravalent cations. Arsenazo is a more sensitive reagent for the rare earths, and it forms a colored complex with all of the elements of the series which were investigated. This paper describes its use as a sensitive indicator in EDTA titrations of rare earths as dilute as 10^{-6} molar.

Arsenazo may be prepared by coupling diazotized o-arsanilic acid with chromotropic acid. It is also sold by the Synthetic Chemicals Division of Eastman Kodak Company under the catalogue number 7302. The reagent is quite

soluble in water and alcohols, fairly soluble in acetone and dimethylformamide, very slightly soluble in acetonitrile, and insoluble in pyridine and ether.

Purification

The indicator used in this investigation was purchased from Eastman Kodak Company. It was a dark brown solid claimed to be the dihydrate of the trisodium salt. On this basis it reacted as 60% pure indicator. The material may be used as received as a reagent for visual titrations and colorimetric determinations. For characterization of the reagent and its complexes, a purer product was desired.

A recrystallization procedure was devised from which a product equivalent to nearly 100% tetraacid dihydrate was obtained. This bright orange material precipitated when a concentrated aqueous solution of the salt was added slowly with stirring to concentrated hydrochloric acid. If too much indicator solution was added so that the acid was diluted a dark purple product was obtained instead. This has not been characterized, but its equivalent weight corresponds to 97% pure trisodium salt dihydrate, or to lower purity di- or monosodium salts. If obtained, this may be redissolved in water, concentrated and reprecipitated.

The orange product was filtered, washed with acetonitrile and dried at 110°. Excessive drying darkened it, but apparently did not adversely affect it, since this material

showed higher absorbance per gram than any precipitated by other methods. Calculated as the acid, its molar extinction coefficient was 30,600, at 500 m μ , pH 6.

Recrystallization of either the purified or the original sodium salt from alcohol was not successful. A red-violet product was obtained but its absorptivity was comparatively low. Extraction from acidic solution into iso-amyl alcohol was tried using a continuous ether-extraction apparatus. Apparently efficient extraction occurred but a product was not obtained from the extract.

Spectra

The absorption spectra of Arsenazo and its complexes were taken to determine the optimum wave length and pH for photometric titrations and spectrophotometric determination. The indicator spectra for several pH's are given in Figure 6. Within this range there was little pH effect. Other spectra have shown that there was no change from pH 4 to pH 3, but that a twenty percent drop in absorbance occurred between pH 8 and pH 9. The absorption peak remained at 500 m μ .

Spectra of the purple lanthanum and ytterbium complexes are given in Figure 7 and Figure 8. They show that the complexes dissociated below pH 6. The lanthanum complex was the only rare earth complex whose peak is slightly lower than 560 m μ . The uranyl complex (Figure 9) was blue between pH 4

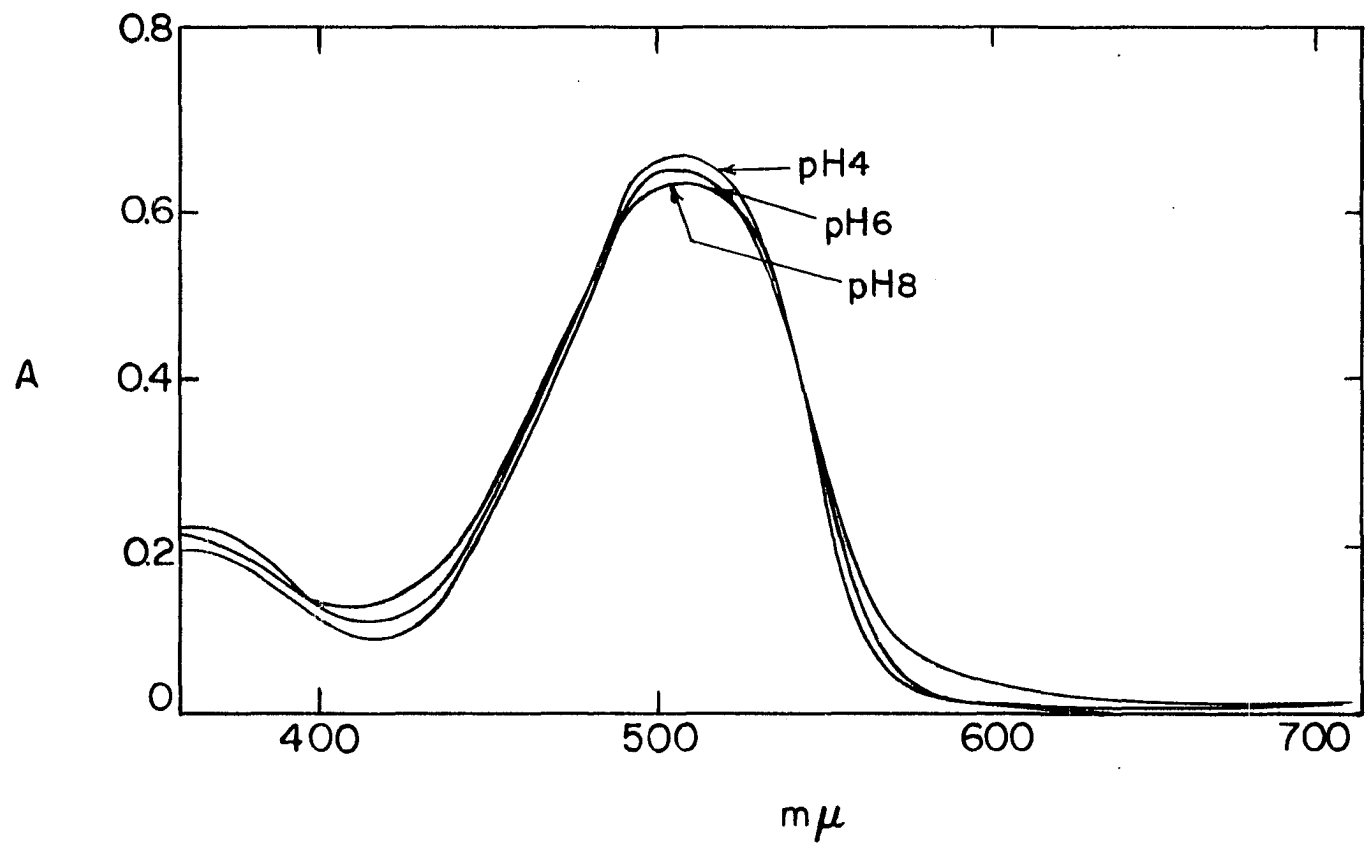


Figure 6. Spectra of Arsenazo at pH 4, pH 6 and pH 8, 1.14×10^{-5} M, 2.01 cm. cells

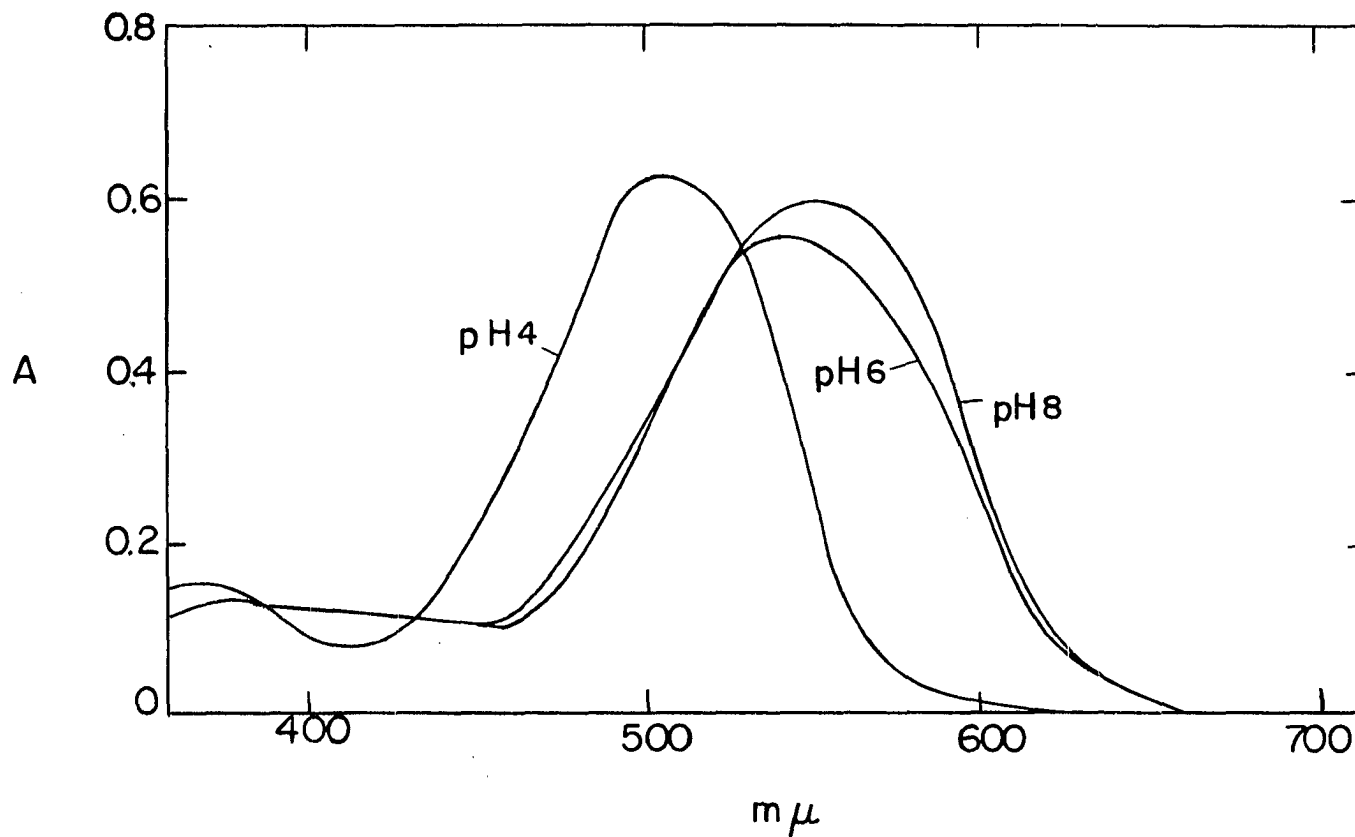


Figure 7. Spectra of lanthanum-Arsenazo complex at pH 4, pH 6 and pH 8, 2.03×10^{-5} M, 1.00 cm. cells

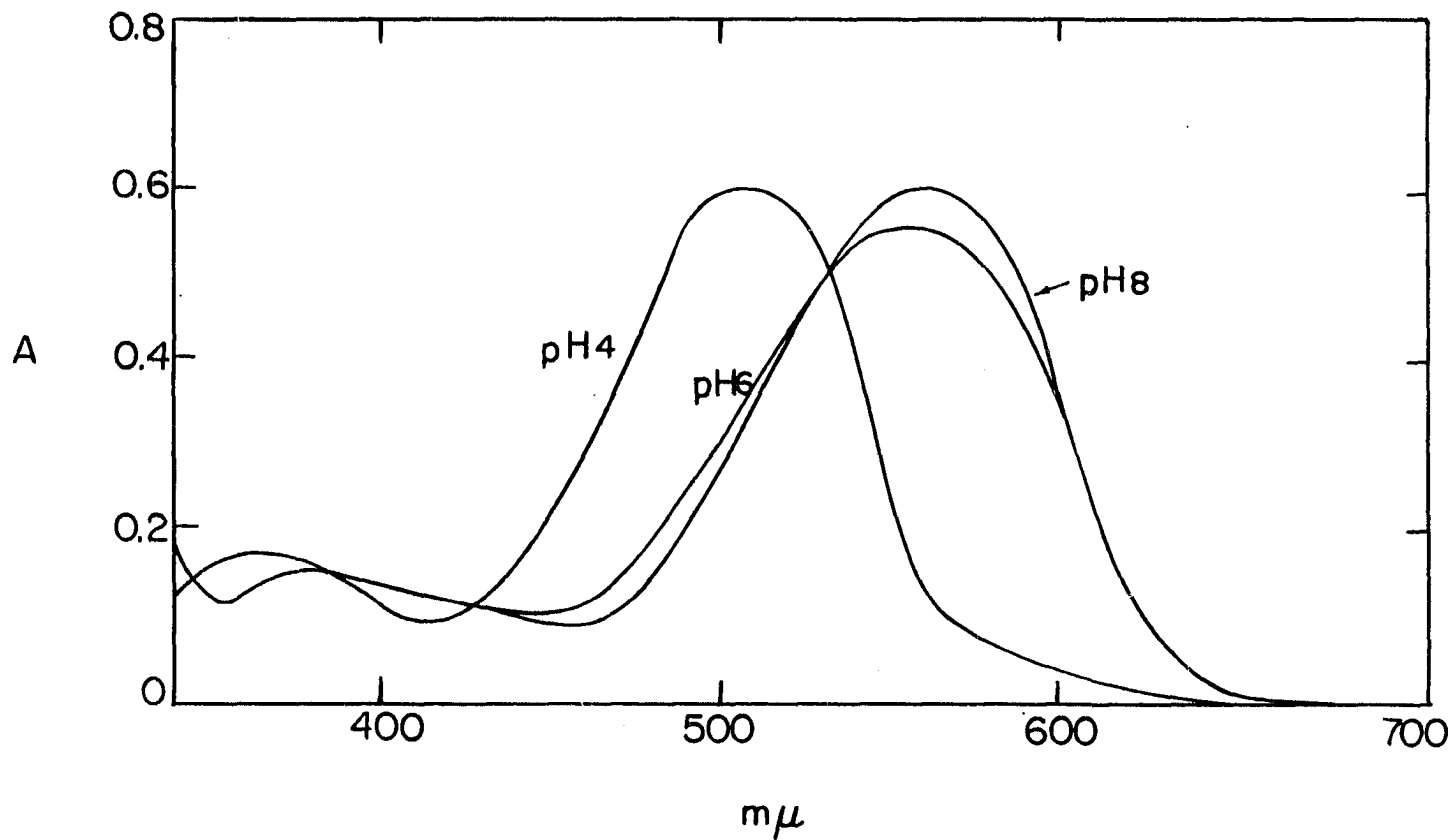


Figure 8. Spectra of ytterbium-Arsenazo complex at pH 4, pH 6 and pH 8, 2.22×10^{-5} M, 1.00 cm. cells

and 8. At both higher and lower pH's the solution became purple, although with different shades. The indicator peak was evident in the pH 3 spectrum, while a different spectral shift occurred at pH 9.

These spectra show that pH 6 to 8 and a wave length of 570 μ would provide the greatest absorbance change between the rare earth complexes and the free indicator. For visual titrations, pH 5.5 was satisfactory. The pH 6 obtained with pyridine buffer was most satisfactory for the photometric titrations.

Using the data from these spectra, the molar extinction coefficients were calculated. They are given in Table 21.

Table 21. Molar extinction coefficients

Species	pH 6	pH 8	Wave length, μ
Arsenazo	28,000	27,000	500
Lanthanum complex	24,800 23,700	28,000 27,400	560 570
Ytterbium complex	24,800 25,800	26,600 26,800	560 570
Uranyl complex	19,300	20,100	600

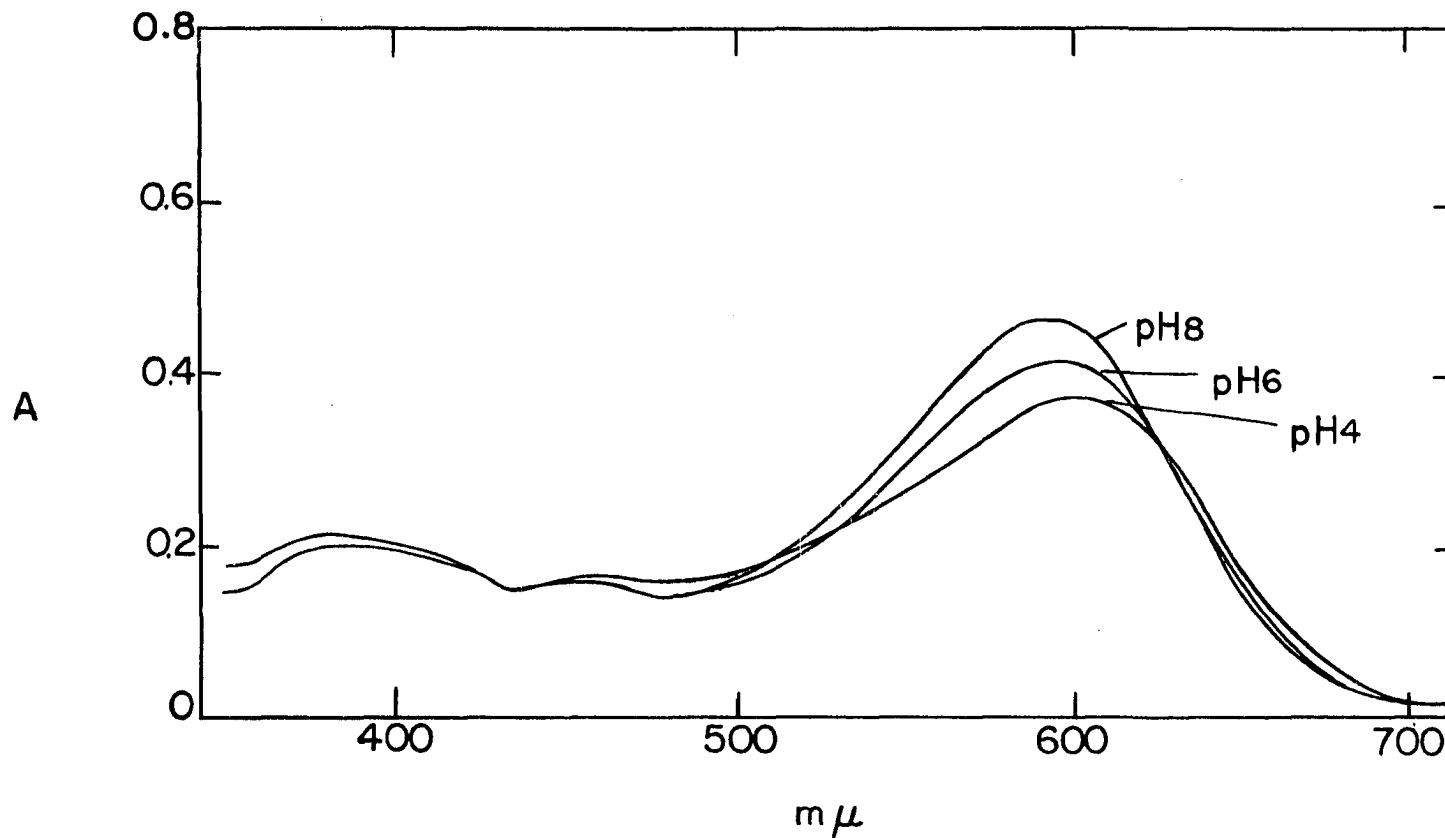


Figure 9. Spectra of uranyl-Arsenazo complex at pH 4, pH 6 and pH 8, 2.12×10^{-5} M, 1.00 cm. cells

Slopes of Beer's Law plots at 570 m μ and pH 8 gave extinction coefficients of 27,000 to 28,000 for lanthanum, cerium(III), praseodymium, neodymium, samarium, dysprosium, erbium, ytterbium, lutecium and yttrium.

Rare earth-Arsenazo complex

Mole-ratio phototitrations, such as reproduced in Figure 10, and absorption spectra of various ratios of indicator to cation have provided evidence that Arsenazo forms 1:1 complexes with the rare earths. The absorption peak shifting and enhancement when higher ratios of the reagent are added have consistently equalled the sum of absorption due to the 1:1 complex plus excess indicator.

The mole-ratio titration of Figure 10 produced a straight line to the extrapolated end-point of 2.02 ml. The calculated equivalence point for a 1:1 complex was 1.97 ml. One half, or 0.99 ml., is the 1:2 complex equivalence point. The purity of the arsenazo which was obtained by acid precipitation was calculated from these data to be 102.5% pure as the acid dihydrate.

The formation constant for the lanthanum-Arsenazo complex was calculated according to the method of Harvey and Manning (73a) from data of the mole-ratio titration. From the experimental and extrapolated equivalence point absorbances, the degree of dissociation at pH 7 was calculated by equation 4.1.

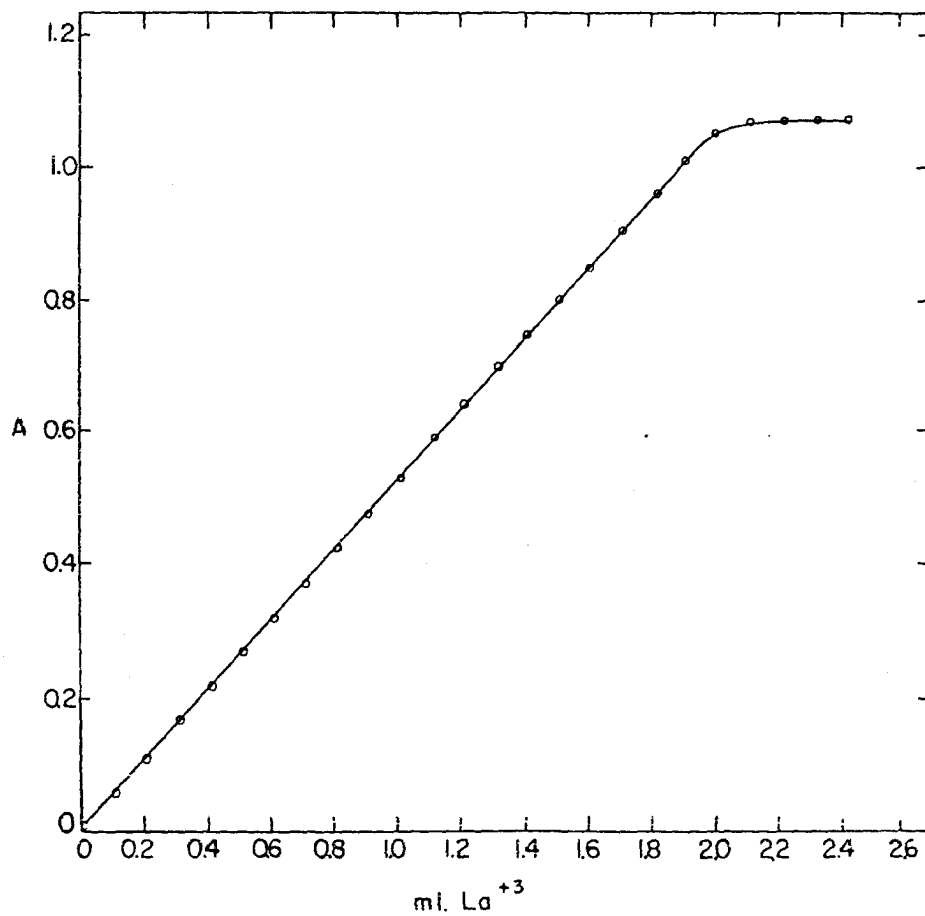


Figure 10. Mole-ratio phototitration of 100 ml. 1.0×10^{-5} M Arsenazo with 5.1×10^{-4} M lanthanum at pH 7

$$\alpha = \frac{1.07 - 1.05}{1.07} = 0.0187 \quad (4.1)$$

The formation constant for the 1:1 complex can be written with α and the molar concentration c .

$$K_f = \frac{c(1-\alpha)}{c^2\alpha^2} = \frac{(1-\alpha)}{c\alpha^2} \quad (4.2)$$

The concentration at the equivalence point was 1.025×10^{-5} M. The constant then is 2.7×10^8 at pH 7.

Photometric Titrations

The photometric titrations were performed on a Beckman Model DU Spectrophotometer adapted by Klingman, Hooker and Banks (88). The titration beakers had a path length slightly more than 4 cm. For titrations with the more dilute solutions, the techniques of instrument scale expansion, as described by Reilley and Crawford (149), were applied. By so adjusting the dark current and sensitivity controls, the scale reading range for a small change in absorbance was multiplied nearly tenfold.

The rare earth solutions were standardized at 0.05 M by gravimetric determination of oxalate precipitations. The EDTA was standardized by titration of standard zinc aliquots.

Dilutions were made using Class A borosilicate volumetric pipets and flasks.

The procedure followed was to add the rare earth aliquot to about 50 ml. of water in the titration beaker. Pyridine or other buffer was added and then the indicator. For the photometric titrations the volume was brought to the 100 ml. mark. The pH was adjusted to the desired value with dilute nitric acid or ammonium hydroxide. The solution was then titrated.

Titration of rare earths

Prior to the photometric titrations, visual macro titrations of the standard solutions were made with good agreement (Table 22).

Table 22. Titrations of rare earths

Ion	Mg. taken	Mg. found	pH
Nd	71.92	71.85 71.85 71.85	5.8
Yb	86.16	86.09 86.09 86.27	5.5 to 7.5

Conditions Photometric titrations required more closely buffered solutions than visual titrations. However, as solutions and titrant were diluted, the pH changes from the titration reaction decreased. Pyridine was excellent in the pH 6 range. Triethanolamine buffered well at pH 7 to 8 but its capacity below pH 7 was limited. Other buffers that were tried reduced the size of the absorbance change and lowered the slope of the Beer's Law plots. The ionic strength up to 0.2 had little effect on the EDTA titrations except at the extreme dilutions. Ionic strength of 0.1 caused a titration of 10 mg. of neodymium to be completely flattened. Tenth molar sodium nitrate also lowered the absorbance of the rare earth-Arsenazo complexes and apparently suppressed the break of a mole-ratio titration. Addition of organic solvents to the titrations caused unfavorable effects. Lower absorbance changes were obtained with dimethylformamide and isopropanol. Acetone and acetonitrile obscured the end-point breaks.

Instrument adjustment When regular absorbance scale readings were desired, the titration solution was placed in the beaker compartment. The instrument was balanced at the desired initial absorbance with the sensitivity and slit-width controls. The dark current then became the only adjustment available once the titration was started. To set the expanded scale for very dilute titrations, solutions approximating the initial and final compositions were used. With the higher absorbing solution in the light path, the

instrument was balanced with the dark current control with the shutter open. A scale reading of 0.5 to 0.8 absorbance was most satisfactory. Then, with the absorbance scale at a low value of 0 to 0.1, the shutter open and the lower absorbing solution in place, the instrument was again balanced with the sensitivity control. Occasionally some juggling of these adjustments were required, but exact settings were not necessary. In addition, the slit width sometimes had to be altered.

Once the instrument controls are set, no corrective adjustments can be made. The titration should be performed as rapidly as convenient to minimize effects of instrument drift.

The practical maximum absorbance change was obtained for the titration of 10^{-5} M rare earth-Arsenazo complex when measured in a titration vessel having a 4 cm. light path length. Therefore no greater relative indicator concentration should be used in titrations of more concentrated rare earth solutions. For lower amounts of rare earth, the Arsenazo should be in slight excess to obtain the maximum absorbance change.

Titrations Photometric titrations of 40 mg. to 10 μ g. of rare earths were successfully performed using EDTA titrant at proportional dilutions. The titration curves are shown in Figures 11 through 16, and the results are collected in Table 23. All titrations described were measured

Table 23. Relative concentrations and analytical results of photometric titrations

Figure	Curve	Mg. taken	Mg. found	<u>M</u> EDTA
11		35.97, Nd	35.97	5.193×10^{-2}
12	1	3.45, Yb	3.45	4.154×10^{-3}
	2	3.60, Yb	3.38	4.154×10^{-3}
	3	3.60, Nd	3.57	4.154×10^{-3}
	4	3.60, Nd	3.60	4.154×10^{-3}
13	1	71.9×10^{-3} , Nd	74.9×10^{-3}	1.039×10^{-4}
	2	71.9×10^{-3} , Nd	74.9×10^{-3}	1.039×10^{-4}
14	1	43.1×10^{-3} , Yb	42.7×10^{-3}	5.195×10^{-5}
	2	36.0×10^{-3} , Nd	36.0×10^{-3}	5.195×10^{-5}
	3	43.1×10^{-3} , Yb	42.7×10^{-3}	5.195×10^{-5}
15	Upper	10.8×10^{-3} , Nd	10.6×10^{-3}	1.039×10^{-5}
	Lower	10.8×10^{-3} , Nd	11.2×10^{-3}	1.039×10^{-5}

at 570 μ where the rare earth complexes were the absorbing species. Other titrations did not produce as large absorbance changes measured at 560 and 550 μ as at 570 μ .

Figures 11 and 12 depict titrations whose end-points could have been detected visually. The curve of Figure 11 is for the titration of 35.97 mg. neodymium with 0.05193 M

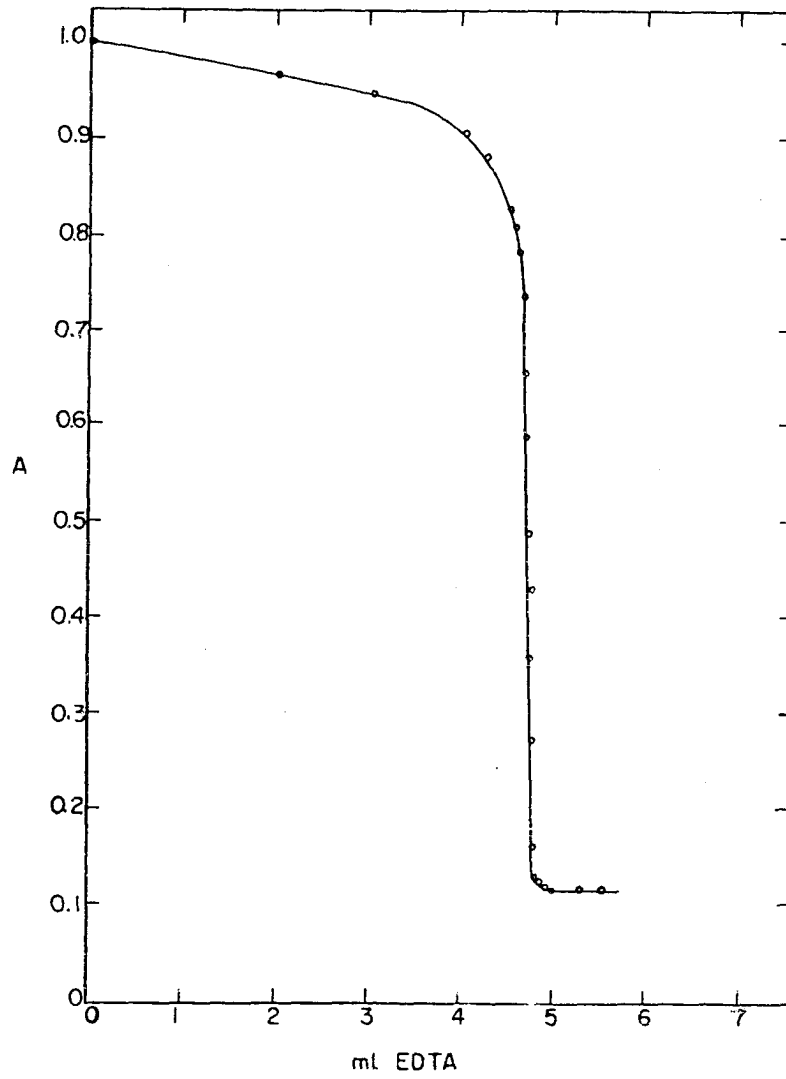


Figure 11. Photometric titrations of 100 ml. 2.5×10^{-3} M neodymium with 5.2×10^{-2} M EDTA at pH 6

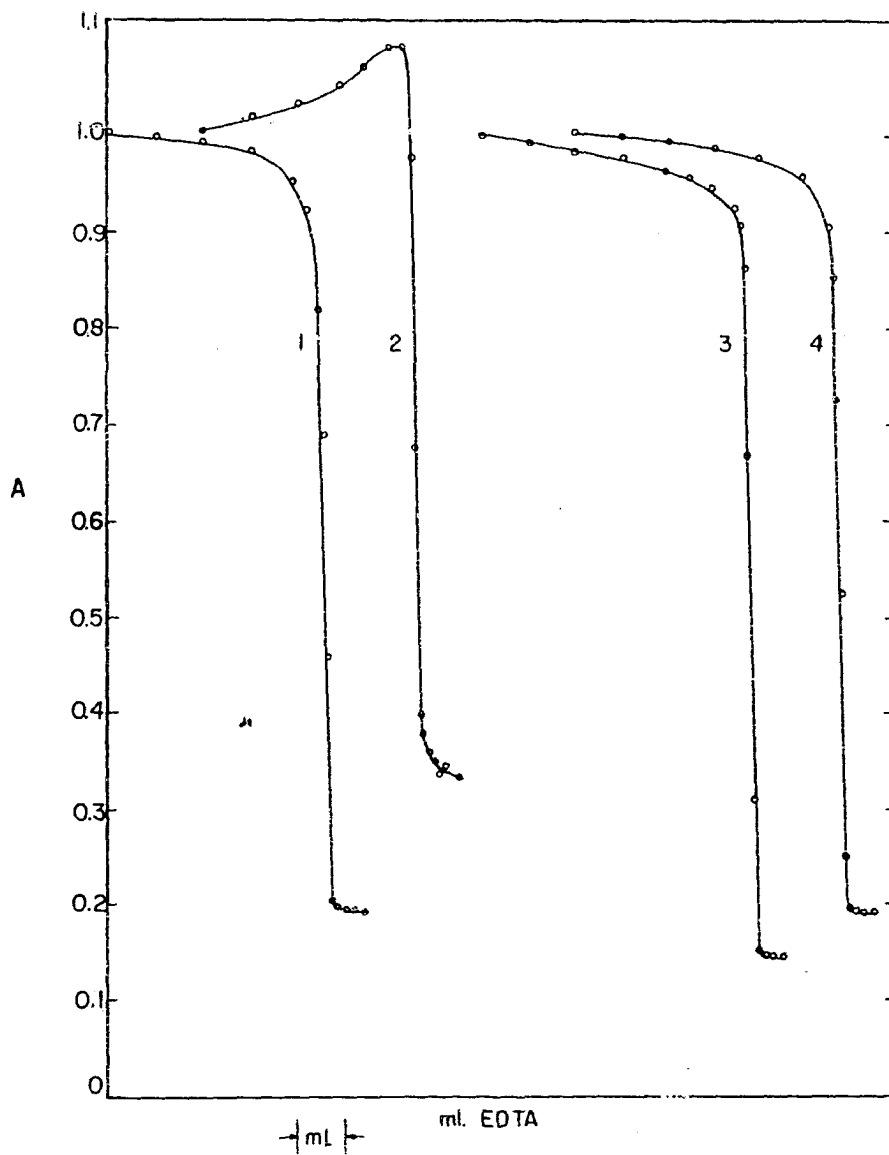


Figure 12. Photometric titrations with 4.2×10^{-3} M EDTA:
 curves 1 and 2, 100 ml. 2.0×10^{-4} M ytterbium;
 curves 3 and 4, 100 ml. 2.5×10^{-4} M neodymium;
 curves 1 and 3, pH 6; curves 2 and 4, pH 7

EDTA, and 35.97 mg. was found. The neodymium was 2.5×10^{-5} M, but the Arsenazo was only 10^{-5} M. The titrations shown in Figure 12 were reduced in concentration one tenth from the one shown in Figure 11, and they represent the probable limit of visible detection. These were titrations of 3.60 mg. of neodymium and 3.45 mg. of ytterbium with 4.15×10^{-3} M EDTA. The amounts found were 3.57 and 3.60 mg. of neodymium and 3.38 and 3.45 mg. of ytterbium. Little difference between pH 6 and pH 7 was detected. Addition of 0.1 M sodium nitrate in solutions 1 and 4 also made little difference. The maximum in the curve for ytterbium at pH 7 was observed a second time and was unexplained. The shape of the curve illustrates the sharpness of the endpoint, which is clearly indicated as the complete disappearance of the complex color. The last six points of the vertical portion were taken at 0.01 ml. increments from 4.75 to 4.80 ml. titrant.

The effect of triethylenetetramine buffer was compared with pyridine in the titrations of Figure 13. It is evident that triethylenetetramine competes slightly with Arsenazo for the rare earth. For both curves, 71.9 μ g. neodymium were titrated with 1.039×10^{-4} M EDTA at pH 6. Both titrations gave the same slightly high results of 74.9 μ g.

The regular and expanded instrument scale titration curves are compared in Figures 14 and 15. The titrations of Figure 14 were of 43.1 μ g. of ytterbium and 36.0 μ g. of

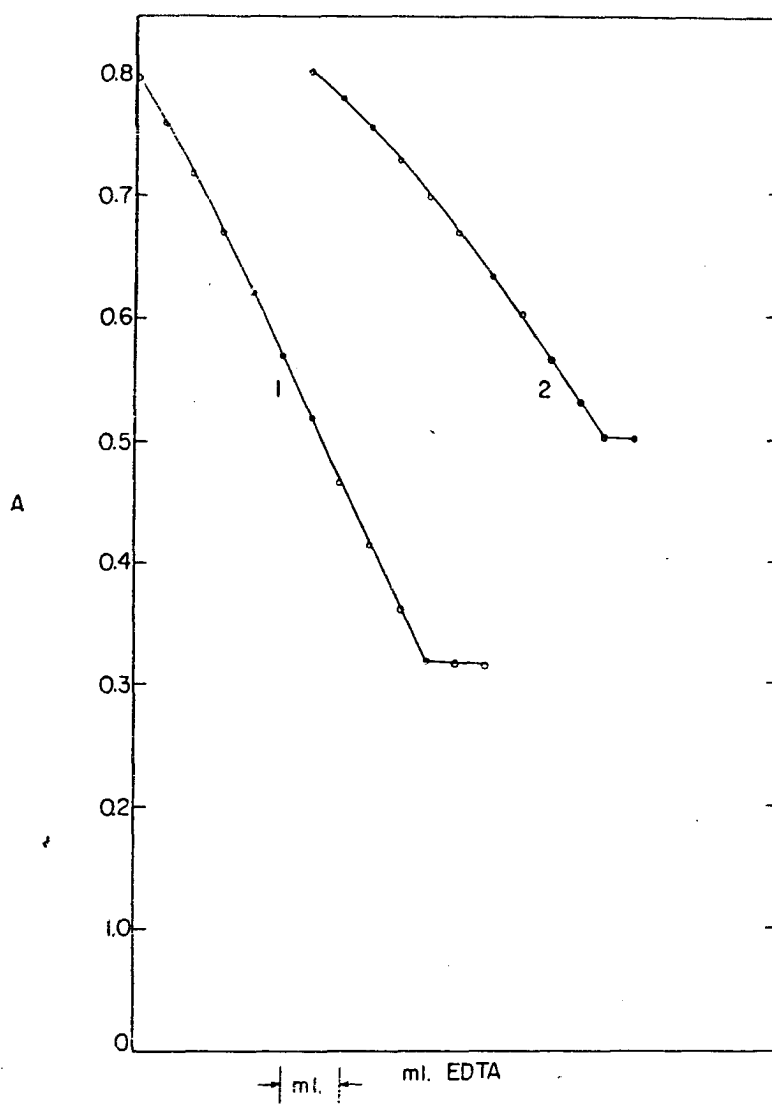


Figure 13. Photometric titrations of 100 ml. 5.0×10^{-6} M neodymium with 1.0×10^{-4} M EDTA: curve 1, pyridine buffer; curve 2, triethylenetetramine buffer

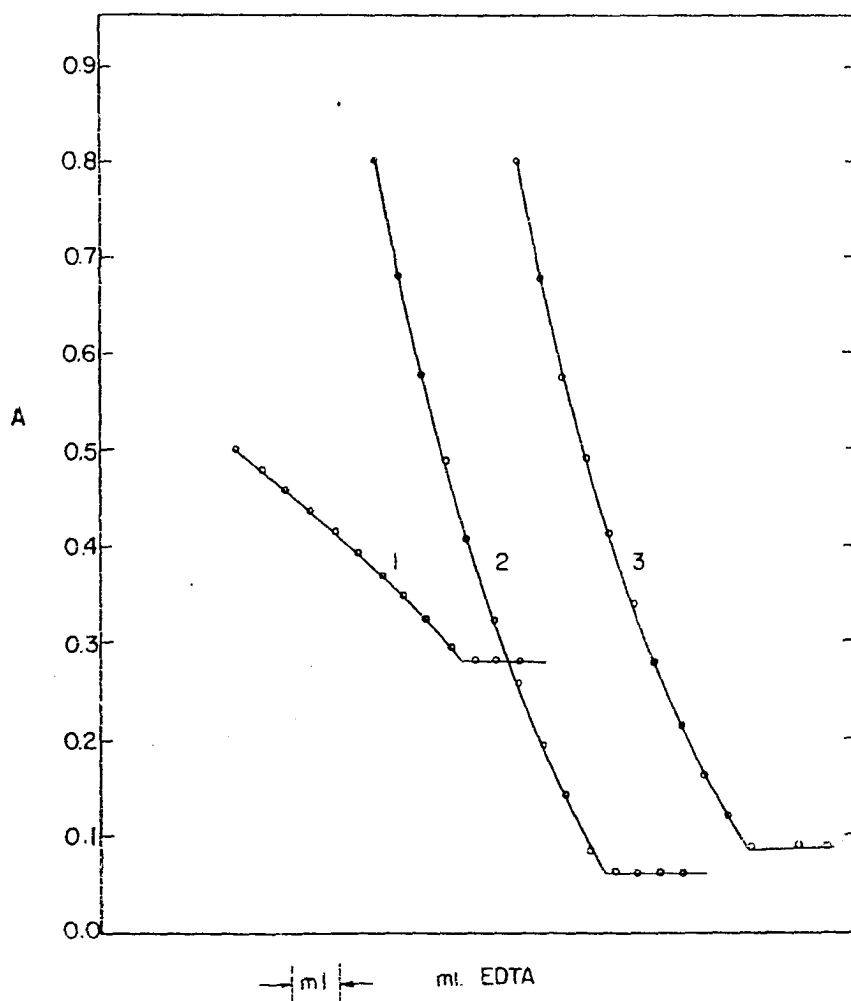


Figure 14. Photometric titrations with $5.2 \times 10^{-5} \text{ M}$ EDTA: curve 1, 100 ml. $2.5 \times 10^{-6} \text{ M}$ neodymium using the regular instrument absorbance scale; curves 2 and 3, 100 ml. $2.5 \times 10^{-6} \text{ M}$ neodymium and ytterbium, respectively, using the expanded instrument absorbance scale

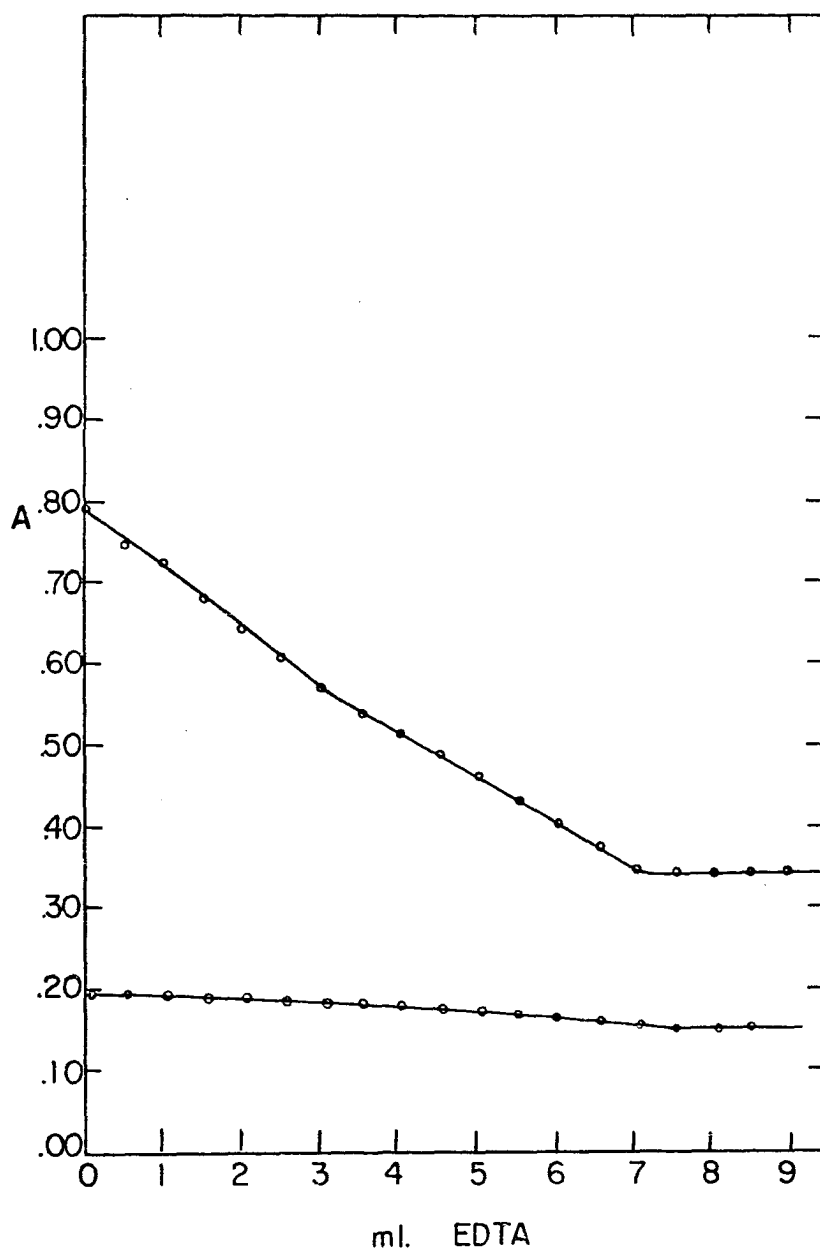


Figure 15. Photometric titrations of 100 ml. 7.5×10^{-7} M neodymium with 1.0×10^{-5} M EDTA: upper curve using the expanded instrument absorbance scale, lower curve using the regular instrument absorbance scale

neodymium using 5.195×10^{-5} M EDTA titrant. The amounts determined by these titrations were 42.7 and 42.7 $\mu\text{g.}$ of ytterbium and 36.0 $\mu\text{g.}$ of neodymium. Scale expansion was not required at this level, but the steeper curves permit more precise equivalence-point extrapolations.

The concentration level of the titrations shown in Figure 15 were sufficiently low that scale expansion was necessary to obtain a useful curve. The solutions were so dilute that the differences in color before and after the titrations were hardly discernable to the eye. The results of these titrations of 10.8 $\mu\text{g.}$ of neodymium were that 10.6 $\mu\text{g.}$ was found from the expanded titration and 11.2 $\mu\text{g.}$ from the other.

Representative curves from the various concentration levels are collected in Figure 16. The restoration of sensitivity by means of scale expansion permits titration end-points to be determined with precision not otherwise possible.

Goddu and Hume (65) recommended that volume corrections be applied if more than 1% dilution occurred in a titration. In these cases where the absorbances were decreasing, the corrections were less than if the curves were rising to the end-point. Corrections were applied to several titrations but only negligible changes in the end-point were obtained.

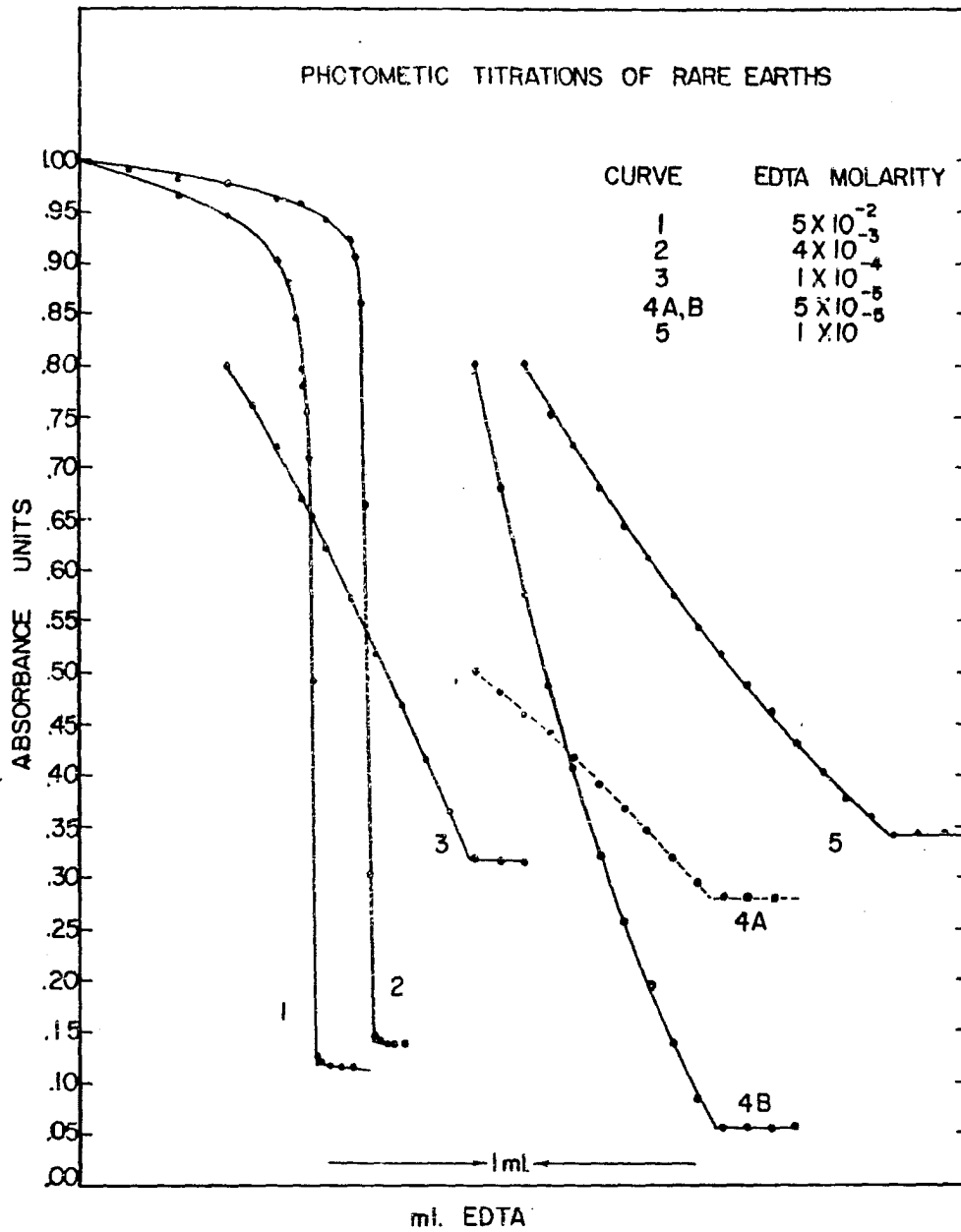


Figure 16. Comparison of photometric titration curves with concentration; curves 1, 2, 3 and 4A using the regular instrument absorbance scale, curves 4B and 5 using the expanded instrument absorbance scale

Titration of rare earths in the presence of uranyl ion

For macro titrations, diethyldithiocarbamate (DDC) has been used successfully to extract the uranyl ion from rare earths into chloroform or 1:1 isoamyl alcohol-benzene solvents. In these concentrations, the small loss of rare earth was insignificant. In concentrations requiring photometric measurement, no losses can be tolerated. Conditions were sought that would allow the titration of rare earths in an aqueous layer without separation of the organic layer containing the extracted uranium. A pH range was not found in which the sulfosalicylate ion retained all the rare earth in the aqueous phase and DDC kept all the uranyl ion in the organic layer for a period of time long enough to perform a titration of the rare earth.

The EDTA titration of rare earths can be followed photometrically in the presence of equal amount of uranyl ion if enough Arsenazo is included to complex all of the uranium and enough of the rare earth to give a measurable color change. The uranyl complex, while not being titrated, would mask the visual detection of the end-point. However, photometric measurements can discern this change. A tenfold excess of uranium in the titration of 5×10^{-6} M rare earth was too deeply colored to obtain a titration curve. The addition of DDC will allow the titration to be carried out.

Figure 17 shows curves of these titrations. Curve 1 is the titration of 100 ml. of 5×10^{-6} M lanthanum in the

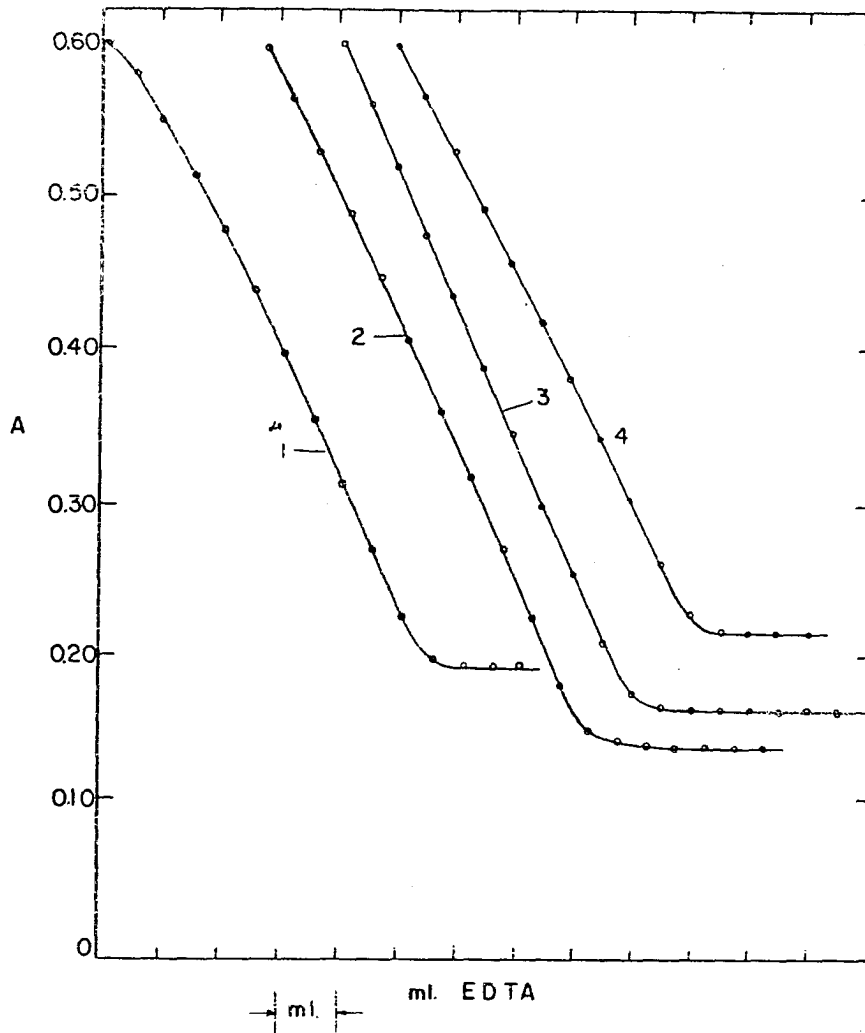


Figure 17. Photometric titrations of 100 ml. 5.1×10^{-6} M lanthanum in the presence of uranyl ion with 1.0×10^{-4} M EDTA: curve 1, 0.1; curve 2, 1.0; curve 4, 10.0 mole ratios of uranium to lanthanum; curves 3 and 4, 1 millimole diethyldithiocarbamate included

presence of 5×10^{-7} M uranyl ion and 5×10^{-4} M Arsenazo. The solution of curve 2 was 5×10^{-6} M in each of lanthanum and uranyl ions and 10^{-5} M in Arsenazo. Curves 3 and 4 are both titrations of 5×10^{-6} M lanthanum in the presence of 10^{-2} M DDC and 5×10^{-5} M Arsenazo. The solution of curve 4 also includes 5×10^{-5} M uranyl ion, or a tenfold ratio of uranium to lanthanum. The DDC evidently interferes somewhat in the lanthanum titration, but the two titrations are nearly equal. The titration volumes of these four trials are 5.37, 5.44, 5.00 and 5.10 ml. Four comparable titrations without uranium or DDC produced good titration curves having end-points at 5.30, 5.37, 5.38 and 5.42 ml.

These solutions were buffered at pH 7 with triethanolamine. Uranyl-DDC precipitated in solution 4. After the titration, this precipitate was dissolved by addition of isopropanol. A comparable titration at pH 6 using 30% isopropanol solvent was titrated to an end-point at 4.90 ml. However the pH 6 titration was evidently too low, since the DDC did not retain the uranyl ion completely. The solution was blue green at the end of the titration, and the absorbance change was decreased about 50%. It was presumed that the 30% isopropanol solution at pH 7 would be more successful. The titration of rare earths in the presence of larger amounts of uranium may be possible without the use of masking agents by greater dilution and utilization of the expanded scale.

CONCLUSION

Summary

Three reagents, Naphthyl Azoxine, Thorin and Arsenazo, which form colored complexes with some metal ions, have been applied to analytical determinations. Some properties of the newer Naphthyl Azoxine and Arsenazo and their complexes have been studied. The technique of photometric titrations was applied both to direct analytical use and to study of the complexes. The combination of phototitrations and expanded instrument scale was shown to have great potential value for low concentration titrations and minimizing color interference.

Naphthyl Azoxine was used as the indicator for direct EDTA titrations of some transition metals, rare earths and thorium. The masking of uranium interference by means of tartrate ion was accomplished in the titration of transition metals but not of rare earths and thorium. Evidence was presented for the formation of a 1:2 copper-Naphthyl Azoxine complex having a formation constant of 1.9×10^{15} at pH 6. Considerations of the end-point mechanism have been discussed.

Thorin was useful as an indicator for direct EDTA titration of only a few lower rare earths. The indirect determination of other rare earths and a number of other metals

has been accomplished by titration of excess EDTA with lanthanum. Fluoride was determined indirectly by titration of the excess lanthanum or cerium after precipitation and separation of the rare earth fluoride.

Arsenazo was used as the indicator for direct EDTA photometric titrations of the rare earths in solutions which were too dilute to detect the end-point visually. Titrations of as little as 10 micrograms were performed with satisfying accuracy. The presence of a tenfold excess of uranium was masked successfully in these titrations. A method for the purification of the indicator was devised. The lanthanum complex was characterized as being 1:1 and possessing a stability constant of 2.7×10^8 . Findings from a survey of the literature of a number of pertinent topics have been presented.

Suggestions for Further Work

In the use of EDTA as a titrant of metal ions and of metal indicators to detect the equivalence point, one weakness lies in obtaining independent standardization checks. An indicator may not signal exact stoichiometry of a cation and EDTA. For example, the EDTA titer obtained by titration of standard zinc using Naphthyl Azoxine may not provide precisely accurate results in titration of rare earths using Arsenazo. However, this particular example may be considered

with confidence. As indicators are improved and their properties are determined, their applicability will become more sure. Empirical standardization is quite satisfactory if several concentrations are determined to confirm a constant proportionality.

The purification of Arsenazo appears to be quite satisfactory. For closer work with Naphthyl Azoxine, a confirmation of purity is desirable. Several batches of material used in this work exhibited considerable variation.

Acetylation of the hydroxy groups of the Thorin and Arsenazo and observation of the reactivity as indicators might demonstrate the role of these groups in the chelate.

Comparison of extinction coefficients of Arsenazo and Naphthyl Azoxine complexes show that the latter might well be applicable to very dilute photometric titrations also.

Arsenazo appears to be a more sensitive reagent for rare earths than Thorin. The use of Arsenazo in the applications demonstrated for Thorin is recommended.

The possibility of titrating rare earths in the presence of a very large amount of uranium might be accomplished by EDTA photometric titration of a highly diluted sample and utilization of the expanded instrument scale technique.

Direct titration of small amounts of fluoride with lanthanum or cerium may be possible without separation if a surface active agent could be found to minimize co-

precipitation and to stabilize the product in a near-colloidal state.

The addition of a pair of small electrodes to the photometric titration apparatus has interesting possibilities in providing both pH and color changes during the course of a titration. Study of pH indicators and of acid constants of any colored species would be greatly facilitated. The adaptation of the titration recording instrument developed in the group to these photometric techniques could be a labor-saving development.

The methods presented are not perfect. Increased selectivity is always desirable and the use of masking agents and separation techniques can always be expanded.

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