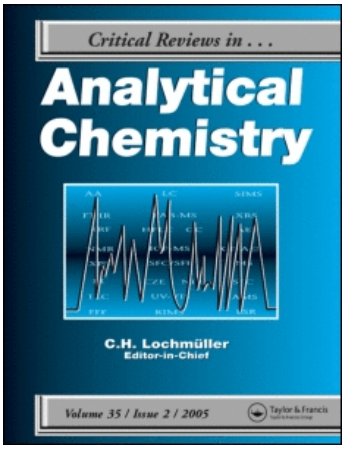


Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Recent Developments in Complexometric Titrimetry

R. Přibil; A. J. Barnard Jr; J. T. Baker

To cite this Article Přibil, R. , Barnard Jr, A. J. and Baker, J. T.(1973) 'Recent Developments in Complexometric Titrimetry', Critical Reviews in Analytical Chemistry, 3: 2, 113 — 146
To link to this Article: DOI: 10.1080/10408347308542659
URL: http://dx.doi.org/10.1080/10408347308542659

RECENT DEVELOPMENTS IN COMPLEXOMETRIC TITRIMETRY

Author: **R. Přibil**
Laboratory of Analytical Chemistry
Czechoslovak Academy of Science
Prague, Czechoslovakia

Referee: A. J. Barnard, Jr.
J. T. Baker Chemical Co.
Phillipsburg, Pa.

TABLE OF CONTENTS

INTRODUCTION

Attempts to utilize complexation reactions in analytical chemistry are almost as old as this science itself. As early as 1832, Marozeau used mercury(II) chloride for the volumetric determination of iodide as HgI_4^{2-}. Similarly, Liebig, in 1851, first described the determination of potassium cyanide by titration with silver nitrate. A number of additional volumetric determinations based on the formation of slightly dissociated complexes were proposed, but attained relatively little use or importance.

Complex-forming reagents were used, however, to a much greater extent as masking agents to suppress interferences by adventitious elements, mainly in qualitative spot tests introduced by Feigl 40 years ago. Much more attention has been devoted to organic chelate-forming reagents in gravimetric and colorimetric analysis. Since the introduction of dimethylglyoxime, hundreds of organic reagents have been described, some of which form insoluble chelates suitable for gravimetry, while others form soluble and intensely colored chelates, most of which are extractable into organic solvents and are suitable for colorimetric trace analysis. None of these reagents ever attained the imaginary ideal of being absolutely specific for a single element. The effort to discover new compounds which are precipitating or colorimetric reagents still continues. Every successive issue of *Chemical Abstracts* records new ones, but rarely any with anything new to recommend them.

Volumetric analysis based on the formation of stable soluble complexes or chelates remained, however, on the same low level as a hundred years ago. In 1945, Professor Schwarzenbach from Zurich, in his lecture before the Swiss Chemical Society, called attention to the fact that metallic

cations could be titrated as Lewis acids with the sodium salt of nitrilotriacetic acid (NTA) or ethylenediaminetetraacetic acid (EDTA).

The introduction of EDTA and, later on, other multidentate ligands able to form 1:1 complexes in "one step" has revolutionized the whole of volumetric analysis. From its beginning just over two decades ago, complexometric titrimetry (complexometry, chelatometry) has developed more quickly than any other method of chemical analysis. By the introduction of very sensitive metallochromic indicators and powerful masking agents, complexometry became very popular with professional analysts because of its simplicity and accuracy. As the last noninstrumental method developed in this century for the determination of macro amounts of almost all metals in the periodic table, it is now indispensable for routine analysis. Physical-chemical methods of end-point detection also make possible the complexometric determination of semimicro or micro amounts of metals.

Complexometric titrations, so simple in their performance, are well founded with very detailed theoretical treatment. Professors Schwarzenbach and Ringbom are the main contributors to the "theory of complexometry." It is beyond the scope of this review to go into detail and compare the theoretical treatments of both authors; these were published in their excellent monographs.[1,2] It can only be said that Ringbom has more understanding for analytical chemists and attempts to present the "theory" to them as simply as possible. Terms such as apparent constants (Schwarzenbach) or conditional constants (Kolthoff, Ringbom), alpha coefficients of side reactions, transition points of indicators, etc. help very much for the deeper understanding of reaction mechanism of complexometric titrations. As is almost every theory, the theory of complexation reactions is, more or less, far from the real conditions we meet in the solutions of practical samples such as ores, alloys, and so on. Ringbom's theory is very useful but, often to the harm of analysts, not much used in common practice.

REFERENCES

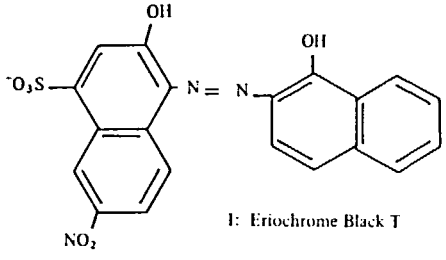
1. Schwarzenbach, G., *Die Komplexometrische Titration*, 5th ed., Ferdinand Enke, Stuttgart, 1965.
2. Ringbom, A., *Complexation in Analytical Chemistry*, Interscience, New York, 1963.

COMPLEXOMETRIC INDICATORS

Introduction

The sudden "disappearance" of the metallic ion at the end point of a titration can be followed by physical instrumental methods but also, and more simply, with so-called complexometric indicators. Although analytical chemists have available a large number of very sensitive reagents that permit the detection of almost any individual metal ion, special requirements pose difficulties in selecting indicators. Therefore, for a long time only a few well-known inorganic and organic compounds were used for the detection of the titration end point. Schwarzenbach called these compounds "weak-colored" indicators; they include potassium thiocyanate for the titration of iron and cobalt, potassium iodide for the titration of bismuth, and so on. Their value in complexometry is now negligible. The so-called "metallochromic indicators" are most important for complexometry. All are complex-forming compounds capable of forming relatively stable complexes with metals and undergoing easily detectable color changes when they do so. The first indicators of this type, murexide and Eriochrome® Black T, were proposed by Schwarzenbach. The possibility of discovering new complexometric indicators became very attractive for analytical chemists and remains so to this day. During the last two decades more than a hundred indicators have been proposed for complexometry. The first attempts to identify new indicators were rather empirical and primitive. A solution of a "new compound" was added to one of a cation (usually calcium) ion, the color change under optimal conditions (pH, buffers) was observed, and the consumption of EDTA was compared with the theoretical value. The end point was described subjectively as very sharp, satisfactorily sharp, distinct, and so on. The greatest attention has been paid to organic azo dyes marketed under various names and

synonyms. Only a few were newly prepared just for complexometric purposes. Not too much was known about the purities of commercial dyes, and sometimes even their true structures were uncertain. The same thing is true of a great many indicators that have been prepared and recommended by a single author. Impure materials are, of course, unsuitable for detailed research: for the determination of dissociation constants, stability constants of individual metal complexes, etc. In some cases it was even impossible to determine the stoichiometric compositions of the complexes, and many confusing results were published. For example, the composition of the magnesium complex of Schwarzenbach's classical indicator, Eriochrome Black T (I), was determined as 1:1.[1]



I: Eriochrome Black T

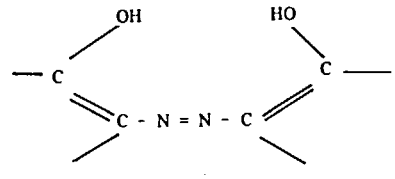
Harvey et al.[2] reported a 2:1 complex at pH 10.1, while Young and Sweet[3] reported complexes of 1:1, 2:1, and 3:1, according to the pH of the solution. Finally, Diehl and Lindstrom[4] found that only a 1:1 complex is formed, as had originally been reported by Schwarzenbach and Biedermann.[1] Difficulties with the purities of indicators still persist. For example, the very useful indicator xylenol orange (XO) is marketed by various firms, not in reagent-grade quality, but as a mixture of the di- and tri-sodium salts containing water and traces of starting material (iminodiacetic acid), as well as the half-condensed product semi-xylenol orange (SXO) (see III). The latter was isolated from commercial xylenol orange by paper chromatography by Olson and Margerum.[5] A detailed study of the separation of XO and SXO by cellulose chromatography was published by Murakami and co-workers.[6] Chromatographically pure xylenol orange was recently prepared from its barium salt.[7] Uncertainty regarding the structure of an indicator also leads to confusing statements, as in the cases of calcion IREA and calcichrome. Calcion was proposed as an excellent indicator for calcium by Lukin and co-workers,[8] and was considered to be 7-(3',6'-disulfo-8'-hydroxynaphthylazo)-3,6-disulfo-8-hydroxynaphthylazo chromotropic acid (Structure IV). Close and West[9] published the synthesis of calcichrome as cyclo-tris-7-(1-azo-8-hydroxynaphthalene-3,6-disulfonic acid (Structure V). Because of the great similarity between the two syntheses, there was a suspicion that the compounds have identical compositions. Indeed, by spectrophotometric studies of their calcium complexes, it has been almost definitely proved[10] that both reagents have Structure IV. The identity of both reagents was also proved by Mendes-Bezerra and Stephen.[11] Their polarographic data also favor Structure IV more than the cyclic one.

Classification of Indicators

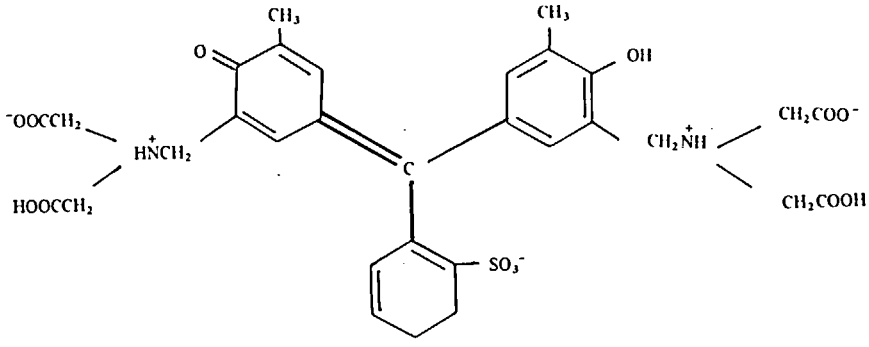
Attempts have been made to divide all complexometric indicators into a few groups. Usually they are classified on the basis of their structure by considering the chromophoric group responsible for the color. The most important classes are azo dyes and their derivatives and triphenylmethane dyes, which can be subdivided into phenolic compounds, phthaleins and sulfonephthaleins, and miscellaneous compounds that cannot be easily classified. On the basis of the reaction indicating the end point, West[50] divided all important indicators into the following: metallochromic, fluorescent, redox, and chemiluminescent. It is beyond the scope of this review to describe the two last classes of indicators, which are seldom used.

Azo Dye Indicators

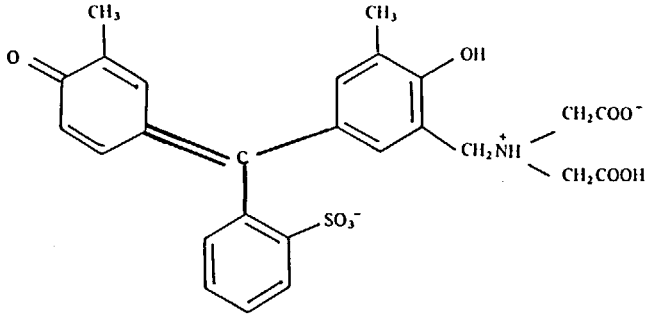
As has been mentioned, the first metallochromic indicator of this type was Eriochrome Black T (Solochrome® Black T, C.I. 14645) (see Structure I) proposed by Schwarzenbach and Biedermann[1] in the earlier stage of complexometry. It belongs chemically to the *o,o'*-dihydroxyazo dyes with the characteristic chelate-forming group:



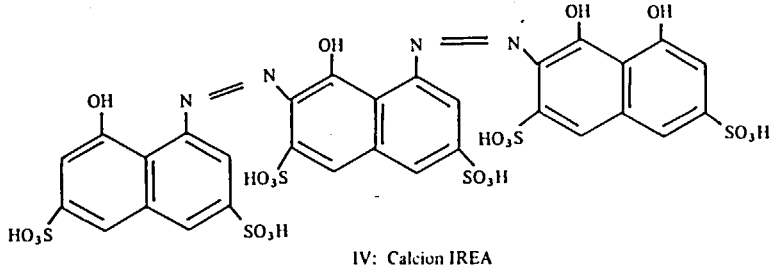
It is a very sensitive indicator for magnesium, zinc, and manganese in ammoniacal buffers, but it is



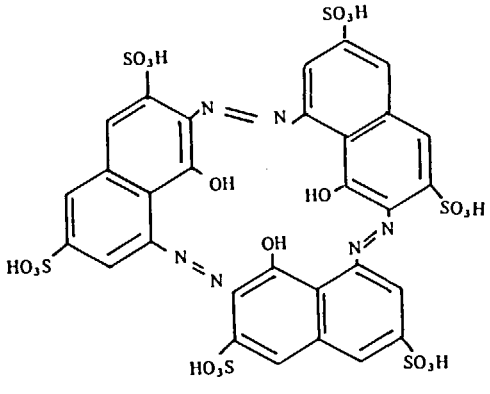
II: Xylenol orange



III: Semi-xylenol orange



IV: Calcion IREA



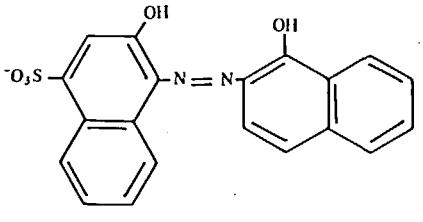
V: Calcichrome

practically useless for the determination of calcium when no trace of magnesium is present. Traces of iron, aluminum, copper, nickel, and cobalt block the indicator. The color change from wine-red to "steel-blue" is sufficiently sharp for the determination of calcium and magnesium together, usually in the presence of masking agents for trace elements (such as BAL for heavy metals). It cannot be used in the presence of iron even if this is masked with triethanolamine. It is still used in spite of the fact that its solutions are not stable over long periods of time. Therefore, mixtures with solid potassium nitrate (1:100) are normally used.

It was obvious that other derivatives of Eriochrome Black T would function as metallochromic indicators, at least in alkaline media, for magnesium (calcium) and zinc or manganese. Many such compounds were "discovered" or synthesized. The magnitude of the effort to find the best possible indicator for calcium and magnesium was inspired by the fact that there were no known good and fast volumetric methods for both that could be applied to the analysis of complex materials. In addition, the possibility of determining micro amounts of calcium (in, for example, blood serum and other biological fluids) by simple titration was very attractive. All these indicators may now be considered useful only for determinations of the alkaline earths and manganese; in titrations of other metals they have been superseded by indicators, which function in acidic media. For this reason, only a few will be mentioned here with regard to determinations of calcium and magnesium.

Solochrome Black 6 B (C.I. 14640)

This indicator, 1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulfonic acid (Eriochrome Blue Black B or Erio B) (VI), differs from Eriochrome Black T only by the absence of a nitro group in the 6-position.

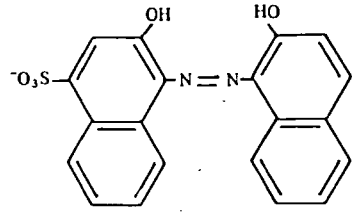


VI: Solochrome Black 6 B

It gives very sharp end points in titrations of magnesium, cadmium, and manganese, but less sharp ones in titrations of zinc and lead. Its advantage is that its solutions are said to be stable for several months.

Solochrome Dark Blue BS (C.I. 15705) – Calcon

Calcon has the same composition as the previous one except for the positions of the naphthalene nuclei (VII).

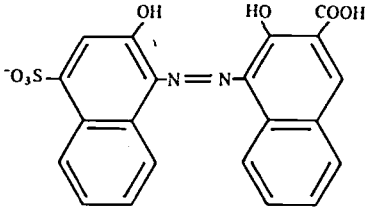


VII: Calcon

It is not a good indicator for calcium in pure solution, but it gives a sharp end point in the presence of magnesium at pH 12. This can be explained by the fact that it functions as an adsorption indicator, covering the surface of the magnesium hydroxide sol and preventing or minimizing the adsorption of calcium. According to Belcher and his co-workers,[12] good results for calcium were obtained at the 10^{-2} *M* level in the presence of equal amounts of magnesium. The authors claimed that calcon was the only indicator that gave satisfactory results under these conditions.

Patton and Reeder's Indicator[13]

This indicator, 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (VII), differs from calcon in that it has an additional carboxyl group:



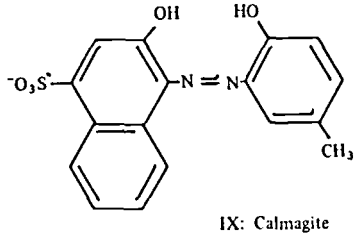
VIII: Patton and Reeder's Indicator

It is a very suitable indicator for the titration of calcium at pH 12 to 14 and for calcium and magnesium at pH 10. The presence of an ionizable carboxyl group in the molecule enables it to

function as an indicator for calcium at such a high pH. It also functions more as an adsorption indicator, because it gives sharper end points for calcium in the presence of precipitated magnesium hydroxide. Its solutions are not stable.

Calmagite

1-(2-Hydroxy-5-methyl-1-phenylazo)-2-naphthol-4-sulfonic acid (IX) was introduced by Lindstrom and Diehl.[14]



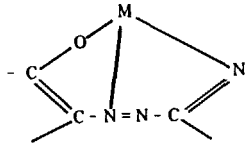
IX: Calmagite

It functions as a very good indicator for calcium, if magnesium is present. Its solutions are stable for prolonged periods.

Many other similar compounds can be described, but they do not offer much advantage for the complexometric determination of calcium and magnesium. Some of them can also be used for the titration of other cations in ammoniacal buffers, but their color changes are inferior to those of the triphenylmethane dye indicators.

Pyridine Derivatives

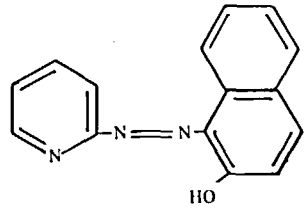
A small but very interesting class of indicators comprises compounds derived from pyridine having an azo group in the neighborhood of a nitrogen atom, which together with a phenolic hydroxyl group is capable of forming chelates with five-membered rings:



In these complexes the metal is bound to two nitrogen atoms and one oxygen atom. Such indicators are more selective than the *o,o'*-azo dyes where two oxygen atoms and one nitrogen atom take part in coordination. Very stable complexes are formed with metals having a tendency to form amine complexes, such as copper, nickel, cobalt, zinc, and cadmium. Less stable are the complexes with lead, bismuth, and manganese. Only two indicators from this group, the so-called PAN and PAR, have found wide application as indicators in slightly acidic media.

PAN

PAN 1-(2-Pyridylazo)-naphthol (X) has been proposed as a complexometric indicator for zinc and other metals by Cheng and Bray.[15]

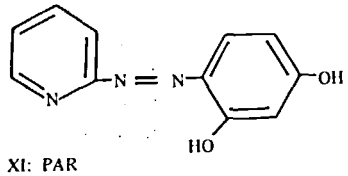


X: PAN

Its main disadvantage is that it is insoluble in water, and its alcoholic solution must be used. Moreover, its complexes are only very poorly soluble in water. According to Flaschka and Abdine,[16] the Cu-PAN complex forms a colloidal suspension and appears to be nearly as stable as the copper(II)-EDTA complex. As a result, the direct titration of copper with this indicator must be performed very slowly. Cheng[17] reported that these difficulties in obtaining good color changes and good results, which are attributable to the insolubility of PAN complexes, can be improved by adding a small amount of ethanol, dioxane, or dimethylformamide to the aqueous solution. Flaschka recommends titrating copper in boiling solutions or in the presence of 50% ethanol or acetone. Because PAN is more effective for copper, many metals could be determined indirectly by back titrating excess EDTA with copper. PAN is by no means the "best indicator" for acidic media, and it can be easily replaced by xylenol orange.

PAR

PAR, 4-(2-Pyridylazo)resorcinol (XI), has been proposed by Sommer and Hniličkova[18] and by Wehber.[19]



XI: PAR

Both the indicator and its complexes are readily soluble in water, due to the presence of an ionizable phenolic group in the 4-position relative to the azo bond. It gives good metallochromic reactions with cadmium, lead, cobalt, copper, etc. in slightly acidic media at pH values between 5 and 7. Bismuth can be titrated even in 0.1 *N* nitric acid. It is considerably superior to PAN and can compete with xylenol orange.

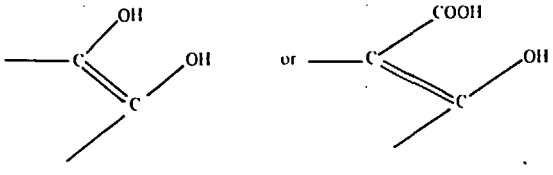
The closely related compounds 4,5-dihydroxy-3-(2-pyridylazo)-2,7-naphthalenedisulfonic acid (PACA), 8-amino-7-(2-pyridylazo)-1-naphthol)-3,6-disulfonic acid (PAHA), and 8-hydroxy-7-(1-naphthylazo)-5-quinolinesulfonic acid (naphthylazoxine) have very similar properties to complexometric indicators.

Thiazolylazophenols also resemble the pyridylazo dyes and can be used similarly to PAN and PAR.

Triphenylmethane Dyes

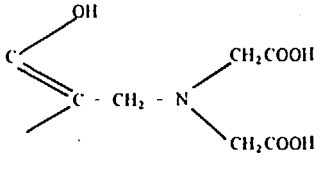
This class includes mostly phthaleins or sulfonephthaleins and can be divided into two subclasses:

a. Phenolic compounds having complex-forming groupings such as



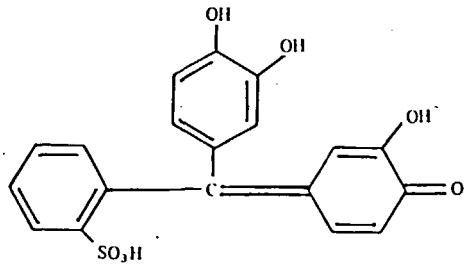
In this class the most important indicators are pyrocatechol violet, pyrogallol red, bromopyrogallol red, eriochrome cyanine RC, and chrome azurol S.

b. Indicators having at least one *N*-(dicarboxymethyl)-amino-methyl group in a position *ortho* to the phenolic group:



To this class belong the most attractive and popular indicators, such as xylenol orange, methylthymol blue, calcein, thymolphthalexon, and many others.

Pyrocatechol Violet

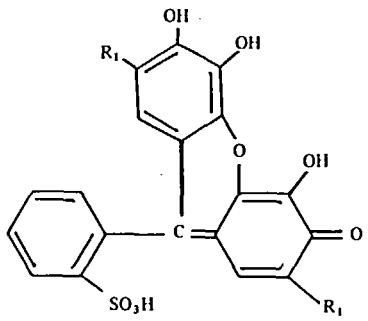


XII: Pyrocatechol violet (PV)

Pyrocatecholsulfonephthalein (XII), originally named pyrocatechol violet, was proposed by Malát, Suk, and Rýba[20] as a complexometric indicator for various cations in acidic media. With catechol violet, complexometry started a new development, the search for indicators which indicate the end point in acidic media, where nearly all elements form EDTA complexes sufficiently stable for titrimetric purposes. Azo compounds, described in a previous paragraph, function almost entirely in alkaline media, where complexometric titrations are absolutely unselective. Suitable color reactions of some of these compounds in acidic media were found only by chance and not too much attention has been paid them. In contrast, pyrocatechol violet is useful for complexometric determinations at pH values between 2 and 6.5, mainly for thorium, bismuth, indium, cadmium, and other bivalent metals. The indicator is not "blocked" by transition metals. Its solutions are stable, and its color change from blue to yellow is normally very sharp. In spite of this, it is not as sensitive as, for example, xylenol orange, which is still very useful in practice.

Pyrogallol Red and Bromopyrogallol Red

Pyrogallol red, *o*-(4,5,6-trihydroxy-3-oxo-3H-xanthen-9-yl)-benzenesulfonic acid and bromopyrogallol red, its 2,7-dibromo derivative, were also described as complexometric indicators by Suk, Malát, and Jeníčková[21-23] for the determination of bismuth at pH 2 to 3, or of lead at pH 4.5 to 5.0. Many indirect determinations based on back titrations with bismuth or lead have been published. Both of these indicators, like the less important chrome azurol S and eriochrome cyanine RC, have now been replaced by the indicators of the next paragraph.



XIII: R_1 = H: Pyrogallol red

o - (4,5,6-trihydroxy-3-oxo-3H-xanthen-9-yl)benzenesulfonic acid

R_1 = Br: Bromopyrogallol red

Indicators with Iminodiacetic Acid Groups

The indicators so far described were mostly known and used for purposes other than those of complexometric titrimetry. The indicators that will be described here were prepared by design in order to get new compounds with the best metallochromic properties. The basic theory of these indicators is well known, and will not be given in detail here. It can, however, be said that all the complexometric indicators so far known function more or less as acid-base indicators. Usually it is their phenolic groups that are responsible for their color changes, which reflect differences of color between their protonated and unprotonated forms. Deprotonation can also accompany complex formation when the molecule contains another atom or group that can participate in the coordination of a metal ion. In all dyes, this is a nitrogen atom, which together with a phenolic oxygen and a metal atom forms five- or six-membered rings. To be useful as a complexometric indicator, an organic molecule must, first of all, have pronounced properties as an acid-base indicator, and in addition it must contain a prominent complex-forming group. The first condition is fulfilled in phthalein and sulfonephthalein acid-base indicators; the second is fulfilled by introducing an iminodiacetic group. The only question was how to prepare such new indicators. The best, and indeed the only, way is by Mannich condensation of the dyes with formaldehyde and iminodiacetic acid. Without going deeply into details, we were able to predict the properties of metallic complexes of new indicators before their synthesis was realized. Because there is no difference between deprotonation and the formation of a complex in which the proton competes with the metallic atom, the deprotonated form of the indicator must have a color similar to that of its metallic complex. For example, xylenol orange is red-violet at pH above 6, and its complexes with bismuth, thorium, and several other metals have nearly the same color at pH 1 to 3.

The first attempt to prepare such compounds was made by Schwarzenbach and his co-workers. They prepared the condensation product of *o*-cresolphthalein with formaldehyde and iminodiacetic acid and named it phthalein complexone.[24] This indicator is also known as metalphthalein or phthalein purple. Unfortunately, the authors started with the less suitable "parent compound" *o*-cresolphthalein, which because of its lactone form can function only in alkaline media as an indicator for calcium, barium, etc. As starting materials for the new metallochromic indicators, the most promising were the well-known sulfonephthalein acid-base indicators, such as cresol red and thymol blue, among others. With the introduction of the previously described indicators, the effort to prepare the best possible complexometric indicators reached its climax.

Xylenol Orange[25-27]

Xylenol orange (XO), 3,3′-bis-*N*,*N*-di(carboxymethyl)-aminomethyl-*o*-cresolsulfonephthalein (see Structure II), functions only in acidic media (pH 0 to 5.8), forming intense red or red-violet complexes with at least 20 common cations and with all the rare earths. The indicator itself is lemon-yellow in acidic media, and it is stable for a very long period of time. Normally, a few drops of its 0.5% aqueous solution are used. The complexes of this indicator differ very much in their stabilities. The complex with zirconium is formed even in 1 *N* nitric acid, and other complexes of tervalent and quadrivalent elements exist between pH 1 to 3. At pH values between 4 and 5.8, bivalent heavy metals react with the indicator. This makes it possible to perform a great number of stepwise determinations of two or three metals, such as of bismuth and lead, of zirconium, thorium, titanium, etc. Some metals, such as copper, nickel, aluminum, and gallium, block the indicator and can be determined only indirectly by back titration with lead or zinc solutions.

Xylenol orange became very popular and is probably the best and the most frequently used indicator of all those described in the literature. Several hundred articles have been published about its application in the analysis of ores, minerals,

alloys, and so on.[28] The very sensitive reactions of xylenol orange (detection limit less than 1 μg/ml) have also been utilized for colorimetric determinations of traces of at least 20 metals.[29]

More recently, it has been found that some of these XO complexes can be smoothly extracted into long-chain amines, while some others are not extracted.[30] The new possibilities for the detection and determination of traces of titanium in thorium or indium in gallium, etc. are still open.[31]

Methylthymol Blue

Methylthymol blue (MTB) (XIV), 3,3′-bis [*N*,*N*-di(carboxymethyl)aminomethyl] thymolsulfonephthalein, has been prepared similarly by Mannich condensation of thymolsulfonephthalein with formaldehyde and iminodiacetic acid.[32] As a complexometric indicator it can be used over a wide range of pH values, both in acidic media (pH 0 to 6.5) and in alkaline media (pH 10 to 12.5). All of its complexes are intensely blue, and the color change at the end point in acidic media is very sharp from blue to yellow. In alkaline media, however, it is from intense blue to colorless or smoky gray. Its solutions are not stable enough for long storage, and mixtures of it with potassium nitrate are generally used. It is also more sensitive than xylenol orange toward oxidation and can be easily destroyed by boiling with very dilute nitric acid. Nevertheless, methylthymol blue is undoubtedly one of the most useful indicators, not only for the same titrations as xylenol orange in acidic media, but also for determinations of alkaline earths in solutions containing ammonia or sodium hydroxide. Like xylenol orange, methylthymol blue is now widely used, and is marketed by various firms under this originally proposed trivial name.[32]

Semi-xylenol Orange

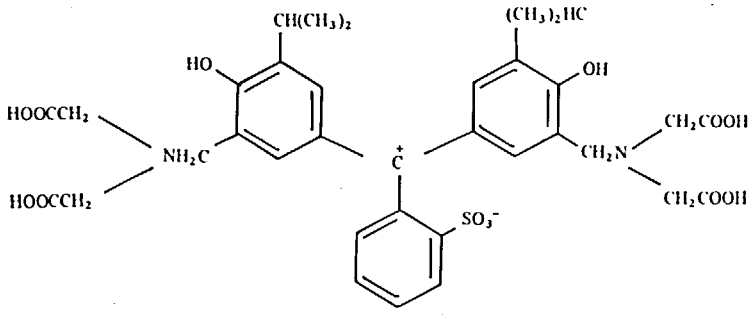
This mono-condensation product (see Structure III) is actually not used as an indicator, being isolated from xylenol orange as an impurity. It has been claimed that SXO gives more sensitive reactions than xylenol orange. This indicator probably forms only 1:1 complexes.

Glycinethymol Blue

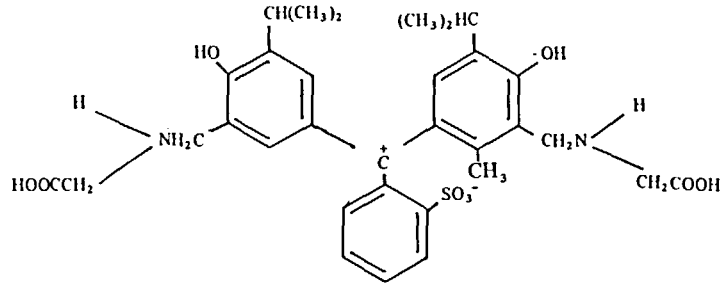
Glycinethymol blue, 3,3′-di(*N*-carboxymethylaminomethyl)thymolsulfonephthalein (XVV), was prepared by the Mannich condensation of thymol blue with formaldehyde and glycine instead of iminodiacetic acid.[33] As expected, it functions as a copper-selective indicator. A very dilute solution of copper can be titrated at pH 6 with a very sharp color change from intense blue to yellow. At higher pH values, the indicator begins to turn blue and produces intense colors with bivalent nickel, cobalt, and several other cations. All of these elements can be determined indirectly by adding a small measured excess of EDTA and back titrating with a standard solution of copper(II). In the presence of a high concentration of copper(II), the color change is from blue to emerald-green. A very sensitive determination of copper in the presence of appreciable concentrations of magnesium, alkaline earths, cadmium, manganese, lead, and even equimolar amounts of nickel was described by Sanderson and West,[34] who used ethylenediaminetetrapropionic acid (EDTP) as titrant.

Phthaleincomplexone

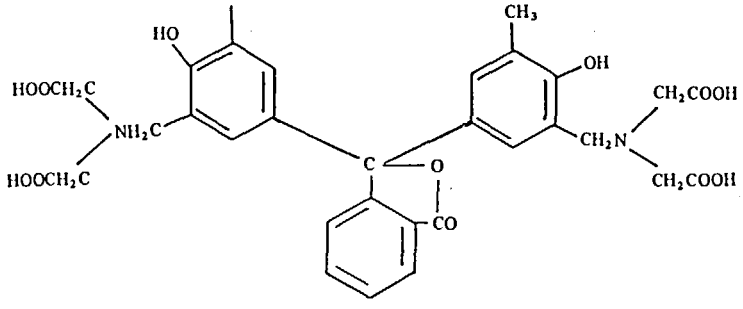
It was mentioned previously that phthaleincomplexone was the first indicator to be prepared from a triphenylmethane dye by condensing *o*-cresolphthalein with formaldehyde and iminodiacetic acid (XVI).



XIV: Methylthymol blue (MTB)



XV: Glycinethymol blue (GTB)



This has been proposed as an indicator for calcium, barium, strontium, magnesium, manganese, and cadmium. In alkaline media at pH 10 to 11, the indicator is intense pink, while at higher pH values it assumes an intense pink or red color. Its complexes at pH 10 are intensely red in color, so that color changes from intense red to pale pink may be obtained.[24] The color of the metal-free indicator may be suppressed by the addition of 20 to 50% ethanol.

We have to expect that other cations may react with the indicator to form complexes that may not be intensely colored. We have found, for example, that zinc either as an amino-complex or as zincate "blocks" the indicator forming an almost colorless complex. This effect has been utilized in a method for the indirect determination of cadmium in the presence of a large amount of zinc. As an indicator for calcium, phthalein-complexone has been replaced by other phthalein indicators to be described below, but it has its historical value.

Glycinecresol Red

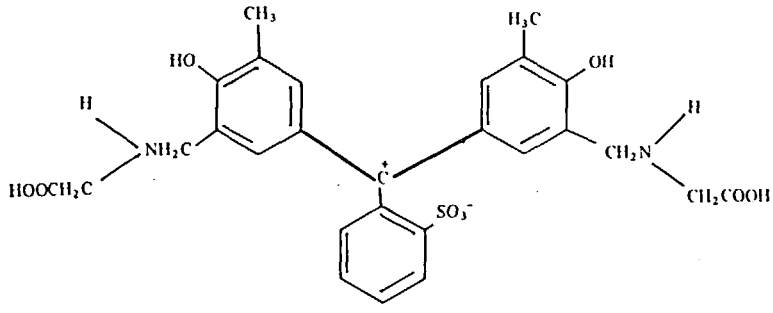
Glycinecresol red, 3,3'-di(*N*-carboxylamino-methyl)-*o*-cresolsulfonephthalein (XVII), has indicator properties similar to those of glycine-thymol blue, and is used for the determination of copper in acidic media. The dye is more sensitive than glycinethymol blue, and forms intense red chelates with various metals.[35]

Thymolphthalexon

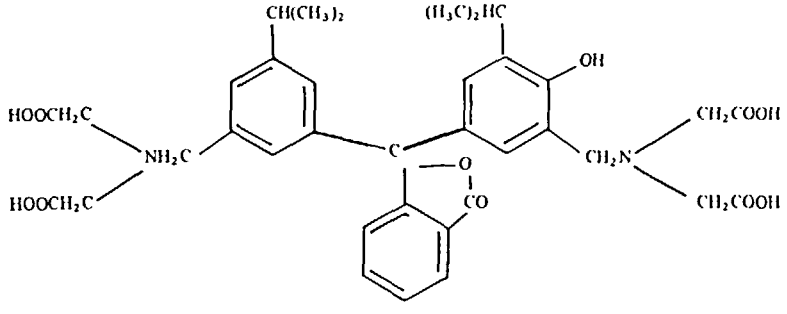
Thymolphthalexon, 3,3'-bis[*N*,*N*-di(carboxy-methyl)aminomethyl]thymolphthalein (XVIII), forms intense blue chelates with alkaline earths in strongly alkaline media and was recommended for their complexometric determination.[36] Unlike azoic dye indicators, it has the advantage of being useful in alkaline solutions containing the triethanolamine-iron complex. The determination of calcium and magnesium together in the presence of iron, aluminum, and traces of manganese is consequently very easily feasible. In the presence of hydroxylamine or ascorbic acid, manganese can be determined directly, and gives a very sharp color change from intense blue to gray or colorless end point.[37] Thymolphthalexon is superior to phthaleincomplexone, and is generally used in the form of a 1:1000 mixture with solid potassium nitrate.

Calcein (Fluorexon)

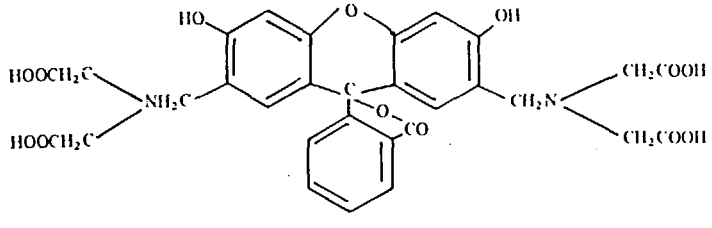
Calcein, *N*,*N*-di(carboxymethyl)aminomethyl-fluorescein (XIX), was first prepared in a rather impure form by Diehl and Ellingboe,[38] by a



XVII: Glycinecresol red



XVIII: Thymolphthalexon

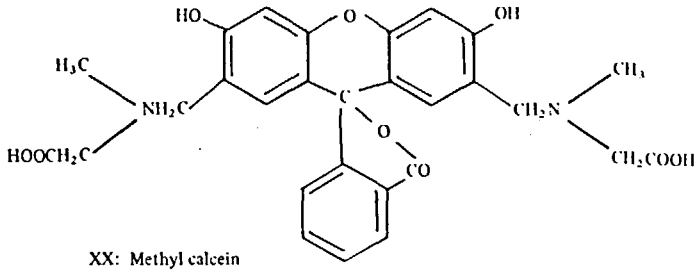


XIX: Calcein (fluorexon)

Mannich condensation of fluorescein, iminodiacetic acid, and formaldehyde. They utilized calcein as a visual indicator for calcium at pH 12, obtaining a color change from yellow-green to brown at the end point. They did not observe fluorescence of either the dye or its calcium complex. It has been found that the pure fluorescein-complexone (fluorexone), in contrast to commercial calcein, shows only a small residual fluorescence in alkaline media, while its calcium complex is strongly fluorescent.[39] This small residual fluorescence is more pronounced in the presence of sodium hydroxide than in that of potassium hydroxide.[40] In a less alkaline media (pH 11) and also in acidic solutions, the indicator alone fluoresces, and the addition of cadmium and zinc intensifies this fluorescence, whereas many other elements extinguish the fluorescence. Only copper at pH 4 to 10 and manganese at pH 8 to 10 can be reliably determined in this way.[41]

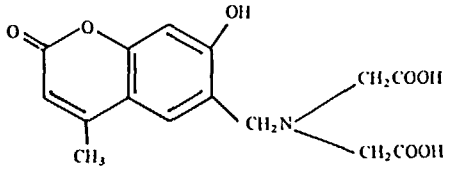
Methyl Calcein

Methyl calcein has been prepared by Wilkins[42] by condensing fluorescein with *N*-methylglycine (XX). It has properties similar to those of fluorexone, and can also be used for the determination of manganese at pH 9.5. The end point is indicated by the appearance of a blue fluores-

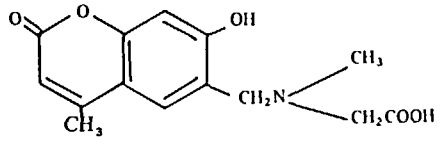


XX: Methyl calcein

cence due to the liberated indicator. Calcein blue (XXI) and methyl calcein blue (XXII) were proposed by Wilkins[43,44] as metallofluorescent indicators.



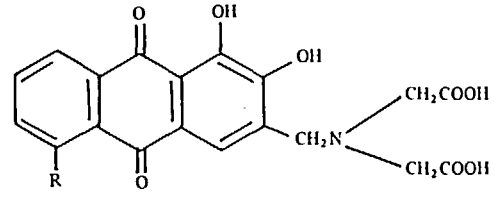
XXI: Calcein blue



XXII: Methyl calcein blue

The latter is more useful, since it has a brighter fluorescence than methyl calcein.

Two additional indicators have been prepared by Belcher and his co-workers.[45] They condensed two dihydroxyanthraquinones with iminodiacetic acid. The condensation led, as could be expected, to new products having only one $-N(CH_2COOH)_2$ group in the molecule. Alizarin complexone (XXIII) has been recommended for the determination of molybdenum(VI) by addition of excess EDTA and with a standard zinc(II) solution back titration at pH 4.3.



XXIII: R = H. Alizarin complexone
XXIV: R = OH. Alizarin bordeaux complexone

At this pH, xylenol orange is unsatisfactory. Alizarin bordeaux complexone (XXIV), prepared by the same authors, probably has similar metallochromic properties.

Belcher's school of chemists has prepared a very interesting group of metallofluorescent indicators derived from benzidine or diaminostilbene.[46-48] All have bright blue fluorescences, in various pH ranges depending on their compositions, which are extinguished by the addition of copper(II). Some of them can also be used in alkaline media for the determination of calcium. Many other metals can be determined indirectly by back titration of excess EDTA with copper solution. All of these indicators are bis(iminodiacetates) (XXV – XXVII, see next page).

The enumeration of more indicators, all of them less important and some of them uncritically overestimated by their users, could be almost endless and is beyond the scope of this short review. The main question is how to evaluate and compare the individual indicators. This will be discussed in the next paragraph.

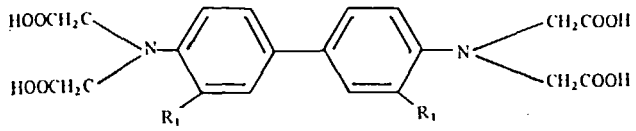
Accuracy of End-point Detection

Complexometric indicators are usually evaluated quantitatively on the basis of their adherence to the following requirements:

1. The indicator itself must be soluble in water, and so must its metal products (complexes). It must be stable enough to withstand reasonable periods of storage and to resist oxidation by air or by oxidizing agents in the solutions in which it is used.

2. The color reaction must be sensitive enough to detect the small traces of metal ions present in a solution just before the end point of a titration with EDTA.

3. The colors of the metal-indicator complex and the free indicator must be sufficiently different to be easily distinguishable by the human



XXV: $R_1 = OCH_3$: *o,o'*-dianisidine-*N,N,N',N'*-tetraacetic acid
XXVI: $R_1 = COOH$: 3,3'-dicarboxybenzidine-*N,N,N',N'*-tetraacetic acid
XXVII: $R_1 = OH$: 3,3'-dihydroxybenzidine-*N,N,N',N'*-tetraacetic acid
XXVIII: $R_1 = H$: 4,4'-Diaminostilbenetetraacetic acid

eye. For example, methylthymol blue gives a very sharp color change at the end point, from intense blue to yellow in acidic media.

4. Although the metal-indicator complex must be sufficiently stable to produce a sharp end point, it must be less stable than the corresponding EDTA-complex; otherwise, the EDTA will be unable to remove the metal from the indicator complex at the end point.

5. The reaction between the indicator complex and EDTA must be rapid to permit easy and precise detection of the end point. If the reaction is slow, the results will tend to be high because of overtitration. Very slow reactions are unsuitable and lead to the "blocking" of the indicator.

All of these requirements must be satisfied in any individual titrations, and they may all be evaluated experimentally. The evaluation of accuracy, i.e., of titration error, is theoretically a more complicated problem, which can be solved only with the aid of a sophisticated theory of indicators, such as the one developed by Ringbom.[49] In a very simple way, Ringbom's considerations can be explained as follows:

1. The stability of the metal-EDTA complex ML is given by its stability constant:

$$K = \frac{[ML]}{[M]\,[L]}$$

2. The stability of this complex depends on the acidity of the solution and also on the extent of other side reactions of the metal with other complex-forming compounds present in the solution (ammonia in the buffer, other complex-forming anions, hydrolysis of the metal, etc.). Under these conditions, the effective stability of the complex is considerably lower than is implied by the value of K, and is best described by the "conditional constant" K':

$$K' = \frac{[ML]}{[M']\,[L']}$$

At the end point of the titration $[M']_{eq} = [L']$ and, because the complex is very little dissociated, [ML] is equal to the total concentration of the metal C_M. Therefore, we can write

$$[M']_{eq} = \left(\frac{[C_M]}{K'}\right)^{1/2}$$

3. The metal-indicator complexes behave similarly and are always present at the end of the titration. Assuming that only a 1:1 complex MI is formed, we get a similar equation for its conditional stability constant:

$$K'_{MI} = \frac{[MI]}{[M']\,[I']}$$

or in logarithmic form:

$$\log K'_{MI} = \log ([MI]/[I']) + pM'$$

where $-\log [M'] = pM'$.

The indicator changes color when $[I'] = [MI]$, so that

$$\log K'_{MI} = pM'_{trans}$$

The transition is centered around the point at which pM' equals the logarithm of the conditional stability constant of the metal-indicator complex. To evaluate the accuracy we need the values of $[M']_{trans}$ and $[M']_{eq}$. The lower the difference between these two values, the better is the accuracy of the titration. Techniques for evaluating the titration error were also developed by Ringbom and can be found in his book.[49]

Each of these values involves a number of stability constants, which have to be measured very carefully. The effective stability constants of the metal-indicator complexes are especially difficult to describe. All indicators behave as acid-base indicators and function as polybasic acids, so that they exist in a number of anionic forms H_nI, $H_{n-1}I$, ..HI, I (charges are omitted), in addition to forming 1:1 complexes with metal ions. Additional complications may result from the formation of partially protonated metal-indicator complexes such as MHI, MH_2I, etc. Moreover, many indicators are so impure that such measurements and calculations are impossible or devoid of possible practical application. For these reasons, much has to be done in this respect in the future.

Summary

From the practical point of view, for all complexometric titrations we need only a very limited number of indicators that function in the whole range of pH. Five or six indicators suffice for all complexometric determinations. The question as to which are the best can be answered: only those that became popular during the last 20 years and are produced commercially. According to my personal opinion and experience, these are the ones derived from triphenylmethane dyes.

REFERENCES

1. Schwarzenbach, G. and Biedermann, W., *Helv. Chim. Acta*, 31, 678 (1948).
2. Harvey, A. E., Komary, J. M., and Wyatt, G., *Anal. Chem.*, 25, 498 (1953).
3. Young, A. and Sweet, T. R., *Anal. Chem.*, 27, 418 (1955).
4. Diehl, H. and Lindstrom, F., *Anal. Chem.*, 31, 414 (1959).
5. Olson, D. C. and Margerum, D. W., *Anal. Chem.*, 34, 1299 (1962).
6. Murakami, M., Yoshino, T., and Harasawa, S., *Talanta*, 14, 1293 (1967).
7. Emr, A. and Přibil, R., Czech. Patent, 140,865, April 15, 1971; British Patent, 1,213,533, November 25, 1970; U.S. Patent, 3,669,988, June 13, 1972.
8. Lukin, A. M., Smirnova, K. A., and Zavarichina, G. B., *Zh. Anal. Khim.*, 18, 444 (1963); see also *C.A.*, 52, 1346 (1958) and U.S.S.R. Patent, 110,996, March 3, 1957.
9. Close, R. A. and West, T. S., *Talanta*, 5, 221 (1960).
10. Bezděkova, A. and Buděšínský, B., *Collect. Czech. Chem. Commun.*, 30, 811 (1965).
11. Mendes-Bezerra, A. E. and Stephen, W. I., *Analyst*, 94, 1117 (1969).
12. Belcher, R., Close, R. A., and West, T. S., *Talanta*, 1, 238 (1958).
13. Patton, J. and Reeder, W., *Anal. Chem.*, 28, 1026 (1956).
14. Lindstrom, F. and Diehl, H., *Anal. Chem.*, 32, 1123 (1960).
15. Cheng, K. L. and Bray, R. H., *Anal. Chem.*, 27, 782 (1955).
16. Flaschka, H. and Abdine, H., *Chem. Anal.*, 45, 2 (1956).
17. Cheng, K. L., *Anal. Chem.*, 30, 243 (1958).
18. Sommer, L. and Hniličkova, M., *Naturwissenschaften*, 45, 544 (1958).
19. Wehber, P., *Z. Anal. Chem.*, 166, 186 (1959).
20. Malát, M., Suk, V., and Rýba, O., *Collect. Czech. Chem. Commun.*, 19, 258 (1954).
21. Suk, V., Malát, M., and Jeníčková, A., *Collect. Czech. Chem. Commun.*, 21, 418 (1956).
22. Jeníčková, A., Malát, M., and Suk, V., *Collect. Czech. Chem. Commun.*, 21, 1599 (1956).
23. Jeníčková, A., Malát, M., and Suk, V., *Collect. Czech. Chem. Commun.*, 21, 1257 (1956).
24. Anderegg, G., Flaschka, H., Sallmann, R., and Schwarzenbach, G., *Helv. Chim. Acta*, 37, 113 (1954).
25. Körbl, J., Přibil, R., and Emr, A., *Collect. Czech. Chem. Commun.*, 22, 961 (1957).
26. Körbl, J. and Přibil, R., *Chem. Anal.*, 45, 102 (1956).
27. Körbl, J. and Přibil, R., *Chem. Listy*, 50, 1440 (1956); *Collect. Czech. Chem. Commun.*, 22, 961 (1957).
28. Přibil, R., *Komplexometrie*, Vols. 1 – 4 German ed., VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1960 – 1966.
29. Přibil, R., *EDTA and Related Compounds in Analytical Chemistry*, Pergamon Press, Oxford, 1972.
30. Přibil, R. and Veselý, V., *Talanta*, 17, 801 (1970).
31. Přibil, R. and Adam, J., unpublished results.
32. Körbl, J. and Přibil, R., *Collect. Czech. Chem. Commun.*, 23, 873 (1958).
33. Körbl, J., Kraus, E., and Přibil, R., *Collect. Czech. Chem. Commun.*, 23, 1219 (1958).
34. Sanderson, I. P. and West, T. S., *Talanta*, 10, 247 (1963).
35. Körbl, J., Svobada, V., Terzijská, D., and Přibil, R., *Chem. Ind.*, 1624 (1957).
36. Körbl, J. and Přibil, R., *Collect. Czech. Chem. Commun.*, 23, 1213 (1958); *Chem. Ind.*, 233 (1957).

37. Přibil, R. and Kopanica, M., *Chem. Anal.*, 48, 35 (1959).
38. Diehl, H. and Ellingboe, J. L., *Anal. Chem.*, 28, 882 (1956).
39. Körbl, J., Přibil, R., and Vydra, F., *Talanta*, 1, 138 (1958).
40. Körbl, J., Vydra, F., and Přibil, R., *Talanta*, 1, 281 (1958).
41. Vydra, F., Přibil, R., and Körbl, J., *Collect. Czech. Chem. Commun.*, 24, 2623 (1959).
42. Wilkins, D. H., *Anal. Chim. Acta*, 23, 309 (1960).
43. Wilkins, D. H., *Talanta*, 4, 182 (1960).
44. Wilkins, D. H., *Anal. Chim. Acta*, 23, 309 (1960).
45. Belcher, R., Leonard, M. A., and West, T. S., *J. Chem. Soc.*, 2390 (1958).
46. Belcher, R., Rees, D. I., and Stephen, W. I., *Talanta*, 4, 78 (1960).
47. Kirkbright, G. F. and Stephen, W. I., *Anal. Chim. Acta*, 28, 327 (1963).
48. Kirkbright, G. F., Rees, D. I., and Stephen, W. I., *Anal. Chim. Acta*, 27, 558 (1962).
49. Ringbom, A., *Complexation in Analytical Chemistry*, Interscience, New York, 1963.
50. Schwarzenbach, H., Senn, H., and Anderegg, G., *Helv. Chim. Acta*, 40, 1886 (1957).

MASKING IN COMPLEXOMETRY

EDTA and its derivatives are very unselective reagents; indeed, they are nearly "universal" volumetric reagents, reacting with almost all the elements with the exception of the inert gases. Long ago, when complexometry was just beginning to be applied, this great disadvantage was overcome by combination with old classical methods. For example, determinations of calcium and magnesium were possible after prior separation of iron and aluminum (manganese) by the usual precipitation with ammonia. Such procedures were still tedious and drawn-out. The most simple and elegant way to make complexometric titrations more selective is by the masking of interfering elements. Theoretically, such masking means that the effective (conditional) stability constant for the complexation of an interfering metal ion by EDTA is lowered as far as possible by the addition of another complex-forming compound, which reacts with the interfering ion to form a complex so stable that it does not react with EDTA to any appreciable extent under the conditions of the titration. From a practical point of view, such masking agents must not only yield highly stable complexes but must satisfy many other requirements as well:

1. Their complexes should preferably be colorless or nearly so, and should be soluble in water.
2. The formation of these complexes must be complete and should not involve any side reactions.
3. The masking agent itself must not alter too much the original composition of the solution (for example, its pH).
4. The masking agent must not react with the metal ion that has to be determined.

Other factors, such as the availability, price, and toxicity of a masking agent, are also of some importance.

The first of the four conditions above is more easily satisfied when the cation to be masked is colorless than when it is colored, as are the ions of iron, nickel, cobalt, etc. Unfortunately, complexation is very often accompanied by the formation of intense colors which makes visual titration impossible. For example, although acetylacetone forms very stable complexes with both aluminum and iron, in the titration of zinc with EDTA, acetylacetone can be used only for the masking of aluminum but not for that of iron, because the latter forms an intense red iron-acetylacetonate.

The selectivities of various masking agents are very different. Potassium cyanide masks six cations against EDTA in alkaline media, while triethanolamine masks only iron, aluminum, and tervalent manganese; it also masks copper and cobalt but (very conveniently) much less strongly. Highly selective masking agents are very welcome in complexometry because they can be used to permit highly selective determinations of single elements, usually indirectly by means of suitable back titrations. For example, the mercury(II)-EDTA complex reacts with thiosemicarbazide and the liberated EDTA, the amount of which is equivalent to that of the mercury present, is determined by back titration with lead nitrate, using xylenol orange as the indicator. Such a titration provides an almost specific determination of mercury in the presence of many other metals.

The formation of EDTA complexes itself makes some masking agents more selective. For example,

thioglycolic acid forms a colorless complex with copper and a colored one with nickel, but only the Cu-EDTA complex reacts with thioglycolic acid. This fact makes the successive determination of copper and nickel very simple.

Masking in Alkaline Media

Complexometry in the first years of its development was based only on the use of the "classical" indicators Eriochrome Black T and murexide, both proposed by Schwarzenbach. As they function only in alkaline media, titrations with them were usually performed in Schwarzenbach's buffer (ammoniacal ammonium chloride, pH 10). Murexide was also used in sodium hydroxide media for determinations of calcium. Consequently, only compounds that form stable complexes in solutions having pH values between about 10 and 11 were considered for use as masking agents at that time. Some of these compounds will be briefly discussed in the following paragraphs.

Potassium Cyanide

The use of cyanide to mask copper, silver, mercury, zinc, cobalt, cadmium, etc. was obvious and was proposed very early by Flaschka and Huditz.[1] Demasking of zinc and cadmium from their cyanide complexes with formaldehyde[2] or, more reliably, chloral hydrate[3] was later proposed to make complexometric titrations more selective.

For a very long time the masking of manganese was a very difficult problem in complexometry. The manganese(II)-cyanide complex is not stable enough for masking purposes; on the contrary, manganese can be determined by titration with EDTA even in the presence of a moderate amount of KCN. Only traces of manganese can be masked with a large excess of potassium cyanide. The situation is more favorable with tervalent manganese, which forms the very stable and almost colorless complex $Mn(CN)_6^{3-}$. Such masking can be performed as follows: in strongly alkaline solutions containing triethanolamine, manganese(II) is rapidly oxidized by atmospheric oxygen to an intensely green complex. After adding potassium cyanide and adjusting the pH to 10, this green complex is transformed into colorless or only slightly yellow $Mn(CN)_6^{3-}$.[4] Thus, up to 80 mg of manganese can be masked in the determination of calcium using thymolphthalexon as the indicator. Similarly, the iron-TEA complex reacts with KCN after warming and forms $Fe(CN)_6^{3-}$.

The resolution of mixtures of cobalt and nickel cyanides was described recently. The cobalt(II) cyanide complex is oxidized by hydrogen peroxide to the more stable cobalt(III) complex, which does not react with silver nitrate. Nickel is far more easily displaced from its cyanide and may be determined complexometrically with murexide as the indicator.[5]

Potassium cyanide is a very toxic substance and must be handled with great care. Its replacement in complexometry by other more convenient substances, such as thioglycolic acid, is becoming more and more common.

Ammonium Fluoride

Ammonium fluoride was proposed for the masking of calcium, magnesium, and aluminum.[6] It functions as a precipitating agent for calcium and aluminum and as a true masking agent for titanium, beryllium, thorium, zirconium, the rare earths, niobium, tantalum, antimony, and tin(IV).[7] Fluoride is also very effective for masking in acidic solutions. Fluoborate has also been used as a masking agent, most recently to mask calcium during the determination of aluminum.[8]

Triethanolamine (TEA)

For a long time the masking of iron was a stumbling block in all complexometric methods until triethanolamine (TEA) was introduced in 1954.[9] TEA in strongly alkaline media forms colorless complexes with iron(III) and with aluminum. Manganese(III), as previously mentioned, forms an intense green complex with TEA. This reagent made it possible for the first time to mask iron and aluminum in the determination of nickel in strongly ammoniacal solutions or in the determination of calcium in sodium hydroxide media. Other titrations using Eriochrome Black T were impossible, because the iron(III)-TEA complex oxidizes this indicator and similar compounds. This disadvantage was later overcome by introducing new metallochromic indicators for use in ammoniacal media, including thymolphthalexon and methylthymol blue. A very important application of the masking of iron with TEA arises, for example, in the analysis of ferromanganese,[10] where a simple complexometric determination of manganese has replaced

the 100-year-old Volhard-Wolf method. The analyses of ferrites, slags, minerals, and ores could also be mentioned as practical examples. Aluminum is often reliably masked at room temperature, but it is sometimes preferable to cool the solution to 5°C to avoid blocking of the indicator by traces of aluminum displaced in a back titration.[11] Small amounts of chromium(III) can also be masked with TEA.[12]

2,3-Dimercaptopropan-1-ol (BAL)

Unlike potassium cyanide, whose toxicity is responsible for much of its unpopularity, BAL (British antilewisite, or dimercaprol) is well known to the toxicologist as an effective antidote to arsenic. It forms very stable complexes with heavy metals such as antimony(III), arsenic(III), cadmium, mercury, tin(IV), and zinc. These complexes are colorless and soluble in ammoniacal solutions. The complexes of bismuth and lead are faintly yellow.[13] All these elements are reliably masked in ammoniacal media for determinations of calcium or magnesium. BAL can also be used to resolve a copper-nickel mixture, for it will displace copper from its EDTA complex but will not displace nickel. BAL is a powerful but somewhat underestimated masking agent. It is especially useful for masking traces of heavy metals (present, for example, as impurities in the reagents used) and often improves the clarity and sharpness of the color change of an indicator.

Thioglycollic Acid

Thiogylcollic acid (TGA, mercaptoacetic acid) was proposed by Přibil and Vesely[16] for the masking of lead, zinc, cadmium, copper, silver, mercury, and indium. Bismuth is also masked in acidic media. Iron forms an intensely red complex with TGA in ammoniacal media and makes many titrations impossible. This problem can be circumvented by first masking iron with triethanolamine in a strongly alkaline medium, where TGA does not react and the solution remains colorless.

Other Mercapto Compounds

Several other compounds, including 3-mercaptopropionic acid, mercaptosuccinic acid, 2,3-dimercaptopropane-1-sulfonic acid, and sodium diethyldithiocarbamate, have been suggested for masking heavy metal ions. All these compounds behave similarly to BAL and TGA.

Masking in Acidic Media

With the discovery of very sensitive indicators suitable for use in acidic media, such as xylenol orange, methylthymol blue, and catechol violet, complexometry has reached the peak of its development. The stability constants of various metal-EDTA complexes differ very much, ranging from the low value for the barium-EDTA complex (log $K_{BAL} = 7.8$) to the high values of 23, 25, and 36 of log K for the EDTA complexes of thorium, iron or indium, and cobalt(III), respectively. The influence of pH on the stability of complexes is well known and has been the subject of detailed theoretical study. The more stable the complex, the lower the pH required to cause its essentially complete dissociation. In other words, hydrogen ion competes with metal ions, yielding protonated forms of EDTA that are more or less dissociated, depending on the pH. In practice we can use complexometry over the whole range of pH values. It is no problem, for example, to determine bismuth in the presence of lead or zinc or to determine zinc in the presence of magnesium. Such step wise titrations are very often used in analyzing various alloys.

To make titrations more selective, special masking agents are still desirable. Using organic ligands as masking agents, we again have to consider competition between hydrogen ions (protonation) and metal ions (complex formation). This means that many masking agents are highly efficacious in alkaline media but nearly worthless or, at best, very weak in acidic media. On the other hand, there are a few inorganic anions, such as fluoride, iodide, thiocyanate, thiosulfate, and sulfate, that function as highly specific masking agents.

Sodium Sulfate

Sodium sulfate (or potassium sulfate), when used in large concentration, masks thorium at pH values below 2, and has been used for this purpose in determinations of zirconium[14,15] and of titanium as the Ti-H_2O_2-EDTA complex.[16] Both determinations are performed indirectly by back titrating excess EDTA with bismuth nitrate, using xylenol orange as the indicator. The masking of thorium by sulfate is effective only at very low pH values; at pH 4 to 5, thorium is demasked and can be determined, for example, with TTHA.

Ammonium Fluoride

As mentioned previously, ammonium fluoride is very effective for the masking of aluminum, titanium, and many others. In acidic media it is most used for masking aluminum, especially in analyses of iron-aluminum mixtures. The sum of iron and aluminum is usually determined at pH 5 to 5.5 by adding excess EDTA and back titrating with zinc chloride. After adding fluoride and boiling the solution, the liberated EDTA is determined by further titration with zinc using xylenol orange as the indicator. Under certain conditions, iron(III) may be precipitated as potassium hexafluoroferrate(III), K_3FeF_6, from solutions treated with ammonium fluoride and potassium carbonate. This precipitate does not react with EDTA or CyDTA and does not adsorb other metal ions present. This provides an easy and frequently useful way of masking iron.[22]

Potassium Iodide and Thiosemicarbazide

Both these compounds are highly selective masking agents for mercury. The first was proposed by Schwarzenbach and Biedermann,[17] the second one by Körbl and Přibil.[18] Uncomplexed lead and copper also react with iodide, but their EDTA complexes do not. The reverse masking of mercury is, therefore, possible with both reagents. After the determination of the sum of mercury and lead or copper, the mercury-EDTA complex is destroyed by adding one of the reagents, and the liberated EDTA is titrated with zinc(II), using xylenol orange as the indicator. Such procedures can be considered to be specific for mercury determination and can be widely applied. For example, a small amount of nickel can be extracted as the diethyldithiocarbamate with ethyl acetate, then displaced into an aqueous phase by treatment with mercury(II) chloride, after which excess mercury may be masked with potassium iodide, and the nickel determined by titration with EDTA. Indium has been determined in the same way, and nickel may be determined selectively in the presence of indium by masking the latter with thioglycolic acid before the carbamate extraction. These procedures were used in analyses of special gold-plating baths.[19] Potassium iodide was also proposed for masking cadmium in the determination of zinc, but an enormous amount of iodide is needed to mask a small amount of cadmium.

Thiourea

Thiourea is an excellent masking agent for copper, reacting with it in slightly acidic media to form colorless solutions or a slight white precipitate at high concentrations of copper. This is the basis for several methods for the determination of other divalent metals in the presence of copper. A small amount of iron can be determined in the presence of a large amount of copper after masking copper with thiourea in the presence of ammonium fluoride to prevent reaction of the iron with thiourea.[20]

Ascorbic Acid

Ascorbic acid is usually used as a reducing agent. For example, it keeps manganese in the divalent state in ammoniacal solutions containing triethanolamine, and it reduces copper(II) and thallium(III) to lower oxidation states, in which they do not interfere in titrations with EDTA of other elements such as bismuth and thorium. The masking of chromium(III) with ascorbic acid is remarkable;[21] after a slightly acidic solution of chromium(III) has been boiled with 1 to 2 g of ascorbic acid for a sufficient time, a complex of chromium(III) seems to be formed and is stable enough to prevent precipitation of chromium(III) on addition of ammonia. The complex is bluish-green in color but not intensely so; therefore, even 10 mg of chromium in 200 ml has no influence on the color change of the indicator. This has been applied in determinations of calcium, manganese, or nickel in the presence of chromium.[22] Combining ascorbic acid with triethanolamine or potassium cyanide gives rise to other obvious possibilities.

1,10-Phenanthroline

1,10-Phenanthroline (phen) forms very stable complexes with many bivalent heavy metals, but not with lead(II), and has been proposed for the masking of copper, zinc, cadmium, cobalt, and manganese(II) when only lead has to be determined. Stepwise determinations of lead and copper or of nickel and cobalt are also possible.[23] Aluminum or indium can be determined similarly.[24] Masking with phenanthroline has been applied to analyses of low-melting alloys containing bismuth, lead, tin, and cadmium.[25]

It is well known that most transition metals form substitution-inert complexes with metallochromic indicators and cannot be determined

directly by titration with EDTA. For example, even traces of copper block Eriochrome Black T in alkaline media or xylenol orange in acidic media. It has been found that a very small amount of phenanthroline (e.g., 0.5 ml of an 0.001 *M* solution) overcomes such blocking, so that copper can be determined by titration with EDTA using xylenol orange as indicator.[26] This can be explained as follows: near the end point most or all of the unreacted copper is bound as a phenanthroline complex which reacts smoothly with EDTA:

$$Cu(phen)_3^{2+} + H_2Y^{2-} = CuY^{2-} + 2\,H^+ + 3\,phen$$

The liberated phenanthroline then reacts immediately with the copper-indicator complex:

$$\underset{\text{red-violet}}{Cu(XO)^{n-}} + 3\,phen = \underset{\text{yellow}}{Cu(phen)_3^{2+}} + XO^{-(n+2)}$$

Perhaps the main disadvantage of phenanthroline for routine analysis is its high price, although this is now dropping steadily.

Summary

From a practical point of view, we do not need too many masking agents. In analyses of silicates, ores, and concentrates, triethanolamine is most useful for the masking of iron and aluminum and traces of manganese, as is ammonium fluoride for masking aluminum and titanium. Potassium cyanide is dangerous, but can usually be replaced by thioglycolic acid or by the more expensive BAL. For masking copper in acidic media, thiourea is more attractive than ascorbic acid, although the latter is very useful for masking iron(III) and thallium(III). Hydrogen peroxide has an exceptional position in complexometry, because it forms an almost colorless complex with titanium(IV) in alkaline media.[27] On the other hand, in acidic media it reacts with titanium(IV) and EDTA to yield a very stable peroxo complex, Ti-EDTA-H_2O_2, which makes it possible to determine titanium in relatively acidic media by back titration with bismuth nitrate, using xylenol orange as the indicator.[28]

REFERENCES

1. Flaschka, H. and Huditz, F., *Z. Anal. Chem.*, 137, 172 (1952).
2. Flaschka, H., *Z. Anal. Chem.*, 138, 332 (1953).
3. Přibil, R., *Collect. Czech. Chem. Commun.*, 18, 783 (1953).
4. Povondra, P. and Přibil, R., *Collect. Czech. Chem. Commun.*, 26, 2164 (1961).
5. Přibil, R. and Veselý, V., *Talanta*, 13, 515 (1966).
6. Přibil, R., *Collect. Czech. Chem. Commun.*, 19, 64 (1954).
7. Dubský, J., *Collect. Czech. Chem. Commun.*, 24, 4045 (1959).
8. Přibil, R. and Veselý, V., *Chem. Listy*, 63, 1217 (1969).
9. Přibil, R., *Collect. Czech. Chem. Commun.*, 19, 58 (1954).
10. Přibil, R. and Kopanica, M., *Chem. Anal.*, 48, 35 (1959).
11. Ritchie, I. A., *Analyst*, 80, 402 (1955).
12. Přibil, R. and Veselý, V., *Talanta*, 8, 565 (1955).
13. Přibil, R. and Roubal, Z., *Collect. Czech. Chem. Commun.*, 22, 1771 (1954).
14. Milner, G. W. C. and Edwards, J. W., *Anal. Chim. Acta*, 20, 31 (1959).
15. Přibil, R. and Burger, K., *Talanta*, 4, 8 (1960).
16. Přibil, R. and Veselý, V., *Talanta*, 11, 1197 (1964).
17. Schwarzenbach, G. and Biedermann, W., *Chimia*, 2, 56 (1948).
18. Körbl, J. and Přibil, R., *Collect. Czech. Chem. Commun.*, 22, 1771 (1957).
19. Přibil, R. and Veselý, V., *Talanta*, in press.
20. Přibil, R. and Veselý, V., *Talanta*, 8, 743 (1961).
21. Přibil, R. and Veselý, V., *Talanta*, 8, 565 (1961).
22. Přibil, R. and Veselý, V., *Chem. Anal.*, 50, 100 (1961).
23. Přibil, R. and Vydra, F., *Collect. Czech. Chem. Commun.*, 24, 3103 (1959).
24. Kopanica, M. and Přibil, R., *Collect. Czech. Chem. Commun.*, 25, 2230 (1959).
25. Přibil, R. and Kopanica, M., *Chem. Anal.*, 48, 87 (1959).
26. Přibil, R., *Talanta*, 3, 91 (1960).
27. Wehber, P., *Z. Anal. Chem.*, 154, 182 (1957).
28. Bieber, B. and Večeřa, Z., *Collect. Czech. Chem. Commun.*, 26, 2081 (1961).

VOLUMETRIC REAGENTS IN COMPLEXOMETRY

EDTA is by far the most widely used volumetric reagent in complexometric analysis. We accept the general opinion that EDTA is the best reagent because it forms sterically regular complexes, in which the metal ion becomes a part of at least three five-membered rings, and because it is capable of acting as a hexadentate ligand and can therefore form coordination-saturated complexes with most metal ions. During the last 2 decades, more than 50 congeners of EDTA have been prepared and investigated. West, in his recent book,[1] systematically describes a great number of such compounds, which are chiefly interesting to the coordination chemist. In chemical analysis, however, they are mostly worthless since they form complexes less stable than those of EDTA. Fortunately, there are a few exceptions, which are useful in cases where EDTA more or less fails or cannot be used at all. These reagents, to which more and more attention is now being paid, will be described in this chapter.

Ethyleneglycol-bis(2-aminoethylether)tetraacetic acid (EGTA)

The complex forming properties of EGTA (I) were investigated by Schwarzenbach and his co-workers.[2] Most metal ions form complexes with EGTA that are less stable than those with EDTA, although the calcium-EGTA complex is more stable than the calcium-EDTA complex. It is also remarkable that the stabilities of the EDTA complexes of cadmium and zinc are much more nearly equal than those of the corresponding EGTA complexes, as is indicated by Table 1.

Determination of Calcium and Magnesium

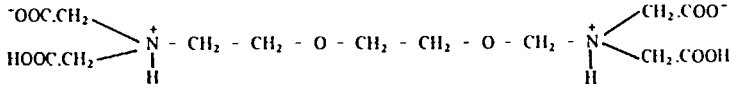
The stability constants of the complexes of magnesium and calcium with EGTA are sufficiently different to be very promising for the direct determination of calcium in the presence of magnesium or even for the stepwise titration of both. As yet there is no sensitive indicator for calcium alone, but this problem has been solved by Ringbom[3] and Sadek[4] with their co-workers. Both these groups have used zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene) to indicate the end point. Zincon does not give a color reaction with calcium and magnesium, but it does form a blue complex with zinc. If we add small amounts of the zinc-EGTA complex to a calcium-magnesium solution and zincon, calcium displaces zinc from its EGTA complex and the solution becomes blue.

$$\underset{\text{orange-yellow}}{Ca^{2+} + HIn^{3-}} + ZnL^{2-} = CaL^{2-} + \underset{\text{blue}}{ZnIn^{2-}} + H^{+}$$

At the end point of the titration with EGTA the last trace of zinc is bound, and the solution turns orange-yellow again. Such titrations are reliable only under certain conditions, e.g., in the presence of a suitable buffer. Ringbom used a special buffer of pH 9.5 to 10 containing borax, ammonium chloride, and sodium hydroxide. Reilley used a triethanolamine buffer. Unfortunately, other conditions which have to be maintained in the solution are very inconvenient for routine analysis. For example, Ringbom claimed that the concentration of zinc-EGTA added has to be one tenth that of the calcium present, and that the concentration of ammonium salts is also critical. The latter requirement poses difficulties whenever the titration has to be performed after separating iron with ammonia. According to Reilley, the method gives good results as long as the ratio Mg: Ca does not exceed 20:1, but as the concentration of magnesium increases above this limit the color change becomes less satisfactory.

In a short communication, Nakagawa, Wada, and Tanaka[5] recommended PAN as the indicator instead of zincon. Their method is based on a back titration of excess EGTA in the presence of Zn-EGTA with a calcium solution. They claimed that the presence of as much as about 100 mg of magnesium can be tolerated when the end point of the titration is located photometrically, but gave no results in their paper.

Flaschka and Ganschoff[6] simplified the method by using murexide as the indicator, following the



I = EGTA

titration of calcium with EGTA photometrically. They reported that a 100-fold excess of magnesium does not influence the calcium determination. Burg and Conaghan[7] proposed masking magnesium with tartaric acid in the direct titration of calcium with calcon as indicator. It is well known that such a titration improves as the concentration of magnesium increases,[8] and the authors therefore recommend the addition of a magnesium solution before titrating to samples containing less magnesium than calcium. Their method has been reproduced by Date and Toei,[9] who used Patton-Reeder indicator and obtained very good results.

Combined Determination of Mg with CyDTA and Ca with EGTA[10]

This method, allowing first the determination of magnesium and then that of calcium, is based on the following principles.

1. A small amount of free EGTA does not disturb the direct titration of calcium with CyDTA using methylthymol blue as the indicator. That is why the difference between the stability constants of the complexes of magnesium with CyDTA (log K = 10.3) and EGTA (log K = 5.2) is sufficiently large for such a titration, and the indicator used is sufficiently sensitive for the detection of magnesium even if it is bound with EGTA. The proper amount of EGTA needed to mask calcium can be determined by titrating the calcium separately with EGTA, using calcein (fluorexone) as the indicator. The procedure described below will make this principle clearer.

2. The approximate determination of calcium can be obtained by the following procedure. To the nearly neutral solution of calcium and magnesium add one tenth its volume of 1 *M* potassium hydroxide (to bring the pH to 12 to 13) and a small amount of indicator. Titrate slowly with 0.05 *M* EGTA to the point where the green fluorescence vanishes, the solution will become yellow or pink, depending on the concentration of the indicator. The consumption of EGTA corresponds to the amount of calcium only if the amount of magnesium present is small; otherwise, the results are a little low due to the adsorption of calcium onto the precipitated magnesium hydroxide.

The Determination of Magnesium

To the second aliquot of the solution add the same amount of 0.05 *M* EGTA as in (2) and then 1 to 2 ml more, then add 20 ml of buffer (3 g NH_4Cl dissolved in 100 ml of concentrated ammonia) and a small amount of methylthymol blue, and titrate the intense blue solution slowly with 0.05 *M* CyDTA to smoky gray. The amount of CyDTA consumed directly gives the amount of magnesium with sufficient accuracy, providing that this amount does not exceed 25 to 30 mg. At the end point of this titration, the solution contains a small excess of EGTA, which can be titrated with 0.05 *M* calcium solution to an intense blue. Because the initial amount of added EGTA is known, we can then easily calculate the concentration of calcium. This method gives very good results, which are more accurate than common methods in which two aliquots are used for separate determinations of (1) calcium (in the presence of precipitated magnesium hydroxide) and (2) the sum of calcium and magnesium. It fails only when very small amounts, less than 2 to 3 mg, of calcium are present. In this case, it is better to determine magnesium alone with CyDTA, as described above, and then the sum of calcium and magnesium by another procedure, e.g., with CyDTA in ammonia buffer. The method has another important advantage: it can be used in the presence of aluminum, iron, and other metals after the interfering elements are appropriately masked. Up to now, the method has been applied to the determination of magnesium and calcium in calciferous materials and silicates.[11]

Determination of Cadmium and Zinc

The stability constants of the complexes of EGTA with cadmium and zinc are too nearly equal (see Table 1) to permit normal visual stepwise titrations of both metals. However, with the aid of

TABLE 1

	$\log K_{CaL}$	$\log K_{MgL}$	Δ	$\log K_{CdL}$	$\log K_{ZnL}$	Δ
EDTA complexes	10.7	8.7	2.0	16.5	16.5	0.0
EGTA complexes	11.0	5.2	5.8	15.6	12.8	2.8

a special phototitrator, Flaschka and Carley[12] carried out consecutive titrations of cadmium and zinc using excess murexide as the indicator. Because both metals form colored complexes in ammoniacal solutions, in this case the indicator functions as a "slope indicator" and not as a "step indicator." The "disappearance" of the colored cadmium-murexide complex and then of the zinc-murexide complex (measured at 470 nm) give rise to two breaks on the titration curve, indicating the successive consumptions of EGTA in the reactions with cadmium and zinc. Such titrations, performed on a microscale, often require that special precautions be taken to maintain the necessary conditions and have as yet found but little use in routine analytical laboratories.

Fabregas et al.[13] have used an interesting reaction for masking cadmium. It is based on the displacement reaction between cadmium ion and the lead-EGTA complex according to the equation:

$$Cd^{2+} + Pb\text{-}EGTA^{2-} + SO_4^{2-} = Cd\text{-}EGTA^{2-} + PbSO_4$$

Zinc does not react with the lead-EGTA complex. After filtering off the precipitated lead sulfate, the determination of zinc can be performed either at pH 5.5 with xylenol orange or at pH 10 with Eriochrome Black T as the indicator. The method is limited to samples in which the weight of zinc does not exceed 1/17 of the weight of cadmium.

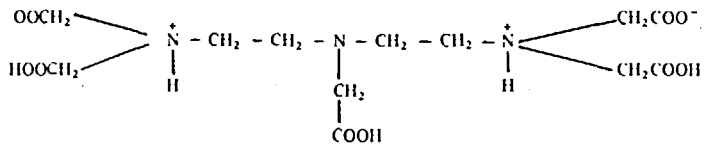
A third method for the analysis of zinc-cadmium mixtures, developed by Přibil and Veselý,[14] can be used even when the amounts of these elements are very different. It is based on the facts that the cadmium-EGTA complex does not react with sodium hydroxide, whereas the zinc-EGTA complex reacts quantitatively to yield tetrahydroxozincate. The zinc-EDTA complex reacts similarly, but slowly and incompletely. This difference between the behaviors of the EGTA complexes has been used for the determination of cadmium in the presence of zinc, e.g., by back titration of excess EGTA with calcium. Not many indicators can be used for such titrations; methylthymol blue and thymolphthalexon are unsuitable because the solution titrated must be very alkaline, while calcein (fluorexone) reacts with tetrahydroxozincate to give a highly fluorescent complex. Only cresolphthalexon (metalphthalein) can be used as the indicator. The end point is indicated by a color change from pink (zinc indicator complex) to intense blue (calcium indicator complex). As much as 300 mg of zinc can be tolerated. If this method is used in combination with thiourea precipitation, a small amount of cadmium can be determined in the presence of as much as 5 g of zinc. The method is superior to previous ones, because a moderate amount of lead is also masked as the hydroxo-complex anion, while iron and aluminum can be masked simultaneously by the addition of triethanolamine. By the same procedure, we can also determine a small amount of zinc in cadmium.

Diethylenetriaminepentaacetic Acid (DTPA)

DTPA (II), an octadentate ligand, has a structure that is very favorable to the formation of highly stable complexes. It behaves as a pentabasic acid, and its acid-base properties were studied by Kroll and his co-workers,[15] Wänninen,[16] Frost,[17] Durham,[18] and Ryskiewich and Anderegg, et al.[19] By titrating DTPA with potassium hydroxide, we obtain only one well-defined inflection point on the titration curve; it corresponds to the consumption of three moles of sodium hydroxide by each mole of DTPA.

DTPA generally forms complexes that are more stable than those of EDTA, but a little less stable than those of CyDTA. In addition, according to Wänninen,[20] DTPA tends to form binuclear complexes, M_2L, which might interfere in complexometric determinations; unfortunately, he gave no experimental data regarding the stabilities of these binuclear complexes. From the stability constants of DTPA complexes, we can expect that DTPA would be a more effective titrant than EDTA. This is true only for titrations performed in alkaline media. In acidic media all DTPA complexes are less stable than the corresponding EDTA complexes because of the greater basicity of DTPA.

Little attention has been paid heretofore to DTPA as a volumetric reagent. Wänninen[21] proposed the use of DTPA for the complexometric determination of barium and the indirect determination of sulfate. This is based on the fact that the barium-DTPA complex is a little more stable ($\log K_{BaL} = 8.8$) than the barium-EDTA complex ($\log K_{BaL} = 7.8$). His method for barium was reexamined by Olsen and Novak.[22] Wänninen's procedure for the consecutive determination of calcium and magnesium is more interesting.[20] It is based on the titration of calcium with EGTA, using the Zn-EGTA-zincon system as the indicator.



H = DTPA

After masking zinc with potassium cyanide, magnesium is determined in the same solution with DTPA, using Eriochrome Black T as the indicator. Further examples of DTPA titrations are most interesting because similar procedures cannot be performed either with EDTA or CyDTA.

Determination of Thorium and the Rare Earths

The stability constants of the EDTA complexes of thorium (log K = 23.2) and the rare earths would lead us to expect that successive determinations of thorium and then, at least, the light rare earths (for which the values of log K range between about 16 and 18) could easily be performed. Unfortunately, this expectation has been impossible to confirm in practice. The rare earths do not interfere in the titration of thorium at pH 2.5 to 3, using xylenol orange as the indicator, but the subsequent titration of the rare earths at pH 5 to 6 cannot be carried out because of the color reaction of the thorium-EDTA complex with xylenol orange. Similar reactions occur with methylthymol blue or pyrocatechol violet. On increasing the pH, a hydroxo complex of thorium is formed, which dissociates sufficiently to undergo a sensitive color reaction with the indicator. The resulting coloration makes any further titrations impossible. For the same reason, CyDTA also cannot be used. Thorium forms a more stable complex with DTPA than with EDTA or CyDTA, even at the higher pH which is suitable for the titration of rare earths. No coloration appears when the pH is increased after the titration of thorium is completed.[23] Due to the high practical importance of such a determination, the whole procedure will be given here.

Procedure

Dilute an acidic solution containing 10 to 200 mg of thorium and "light lanthanides" to 150 to 200 ml. Adjust the pH to 2.5 to 3 with dilute ammonia or nitric acid. Add a few drops of xylenol orange and titrate slowly with 0.05 *M* DTPA solution to a clear yellow end point. Add more DTPA (more than enough to complex the remaining elements), adjust the pH to 5 to 5.5 with solid urotropine, and back titrate the excess DTPA with 0.05 *M* lead nitrate solution until the yellow coloration of the solution turns to red-violet. In the original paper various mixtures of thorium with lanthanum, cerium, praseodymium, and neodymium were analyzed, because other rare earths were not available at that time. Gupta and Powell[24] later extended the procedure to include all of the lanthanides from samarium to lutetium with very good results. In addition, they improved the method by replacing the back titration of the rare earths with a direct titration of them with HEDTA (*N*-hydroxyethylethylenediaminetriacetic acid).

It may be remarked that the reactions of the EDTA and CyDTA complexes of thorium with xylenol orange at pH values above 4 have been used to distinguish between EDTA and CyDTA on the one hand and DTPA on the other in a systematic qualitative procedure for the identification of various "complexones."[25]

Determination of Iron in the Presence of Aluminum

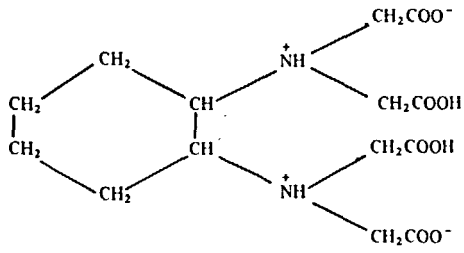
The difficulties that occur in determining iron in the presence of very large amounts of aluminum are well known, and this problem has been the subject of many publications. Although the stability constant of the aluminum-DTPA complex is not known, while log K for the iron-DTPA complex is 27.5, attempts have been made to determine iron with the DTPA in the presence of aluminum. It has been found that in relatively acidic solutions (pH 1 to 2), aluminum is more easily displaced from its DTPA complex than from its EDTA complex.[26] Indirect potentiometric back titration of excess DTPA with iron solution, originally described by Přibil et al.,[27] was used. Very good results for iron were obtained up to an Al:Fe ratio of 70, at which good results cannot be reached by visual titration. In addition, not many elements interfere.

Procedure

To a slightly acidic solution of the sample add 5 ml of buffer (pH 1.6) and dilute to 100 ml. Titrate with 0.05 *M* DTPA using a platinum electrode until the potential break is reached. The amount of DTPA used corresponds to the amount of iron present. If aluminum must also be determined, add to the same solution a known amount of CyDTA (more than equivalent to the aluminum present), and 15 ml of buffer solution (pH 5), and titrate the excess CyDTA with iron(III) chloride potentiometrically. If a large amount of aluminum is present, a smaller aliquot has to be taken, because the titration gives good results only if not more than 25 mg of aluminum are present.

Trans-1,2-diaminocyclohexanetetraacetic acid, CyDTA

CyDTA (III)



III = DCTA (CDTA or CyDTA)

was first investigated by Schwarzenbach and Ackermann.[28] The stability constants of almost all CyDTA complexes exceed those of the corresponding EDTA complexes by two to three orders of magnitude. For the complexes of barium, thorium, lanthanum, and vanadium(IV) (VO^{2+}), however, the differences are much smaller, less than one order of magnitude. CyDTA is a more effective titrant than EDTA, in spite of the fact that the formation of complexes with CyDTA is often somewhat slow, so that direct titrations have to be performed more carefully than they do with EDTA. Only a few examples of complexometric determinations, which cannot be performed with other reagents, will be given here.

Determination of Calcium in the Presence of Barium

According to Close and West,[29] the difference between the stability constants of the calcium-CyDTA complex (log K = 12.5) and the barium-CyDTA complex (log K = 8.0) is sufficiently large to permit determination of calcium in the presence of barium, provided that a very selective indicator for calcium, calcichrome [cyclotris-7-(1-azo-8-hydroxynaphthalene-3,6-disulfonic acid)], is used. The authors determined calcium in a strongly alkaline medium by titrating with 0.02 *M* CyDTA to the point at which the color changed from pink to blue. When the barium is present in large excess, the end point is near the equivalence point, sluggish but still sharp. By very slow titration (one drop each 10 sec) very good results were obtained up to a barium:calcium ratio of 12:1.

Determination of Calcium in the Presence of Strontium

The strontium-CyDTA complex (log K = 10.0) is slightly less stable than the calcium-CyDTA complex, but the difference is not large enough to permit a selective determination of calcium. Strontium can be precipitated with ammonium sulfate from hot solution; after slow cooling, calcium can be titrated directly in the presence of acetone, the color changing sluggishly from pink to blue at the end point. The authors consider this method to be good "when the time factor is more important than accuracy."

Determination of Nickel in the Presence of Copper[30]

The nickel-CyDTA complex is very stable and, in ammoniacal buffer, is inert toward potassium cyanide. On the other hand, other CyDTA complexes, such as those of copper, zinc, cadmium, and mercury, react instantaneously giving very stable $M(CN)_4^{2-}$ complexes. A procedure for the indirect consecutive determination of nickel and copper is based on this fact. A sufficient excess of CyDTA is added to the solution of copper and nickel. It is then made alkaline with ammoniacal ammonium chloride buffer and back titrated with magnesium solution, using Eriochrome Black T;

	log K_{BaL}	log K_{ThL}	log K_{LaL}	log K_{VOL}
CyDTA complexes	8.0	23.2	16.3	19.4
EDTA complexes	7.8	23.2	15.4	18.8

the color changes from blue to wine-red at the end point. After adding potassium cyanide, the liberated CyDTA, whose amount corresponds to the amount of copper, is again titrated with magnesium solution. Many other combinations, such as nickel-manganese-copper, nickel-cobalt-copper, and nickel-copper-cobalt-manganese, were also analyzed.

Determination of Aluminum with CyDTA[31]

The formation of the aluminum complex proceeds slowly at normal temperature, is not quantitative unless the solution is boiled, and is hindered by large concentrations of neutral salts. Contrary to all expectations, it has been found that the aluminum-CyDTA complex is formed rapidly in cold solutions even in the presence of large concentrations of sodium and potassium salts (10 g NaCl or $NaNO_3$ in 150 ml). This makes it possible to determine aluminum very simply by mixing the solution with excess DCTA and back titrating with lead nitrate at pH 5 to 5.5, using xylenol orange as indicator. Up to 40 mg of aluminum in 150 to 200 ml solution can be determined with high accuracy.

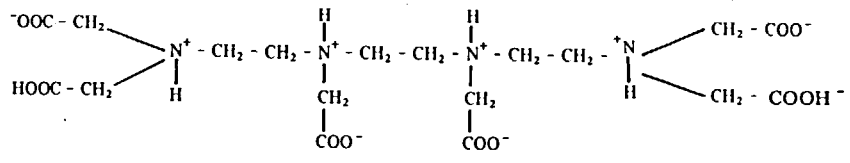
A further advantage of this method is that it can be used for the determination of aluminum in the presence of chromium, which reacts with CyDTA only in hot solutions or in the presence of "catalysts." Because CyDTA in slightly acidic media is not attacked by chromate, even in hot solutions, it is possible to use CyDTA for the successive determination of aluminum and chromium(III) in chromate solutions.[32] This method for the determination of aluminum has also been applied by various authors to the analysis of aluminum alloys and silicates. Iron(III) can also be determined in the same way, and by masking aluminum with ammonium fluoride, both elements are very easily determined.[31]

Triethylenetetraminehexaacetic Acid (TTHA)

This decadentate chelating agent (IV) was first mentioned by Frost,[17] who prepared it by the reaction of triethylenetetramine with sodium cyanide and formaldehyde in an alkaline medium according to Bersworth's patent.[33] The free acid was separated from the alkaline reaction product by an ion-exchange resin. Frost was also the first to measure the dissociation constants of the acid (Table 2). TTHA behaves as a hexabasic acid, H_6L. According to Frost, its neutralization occurs in two steps. The first weak inflection occurs on the addition of three moles of potassium hydroxide per mole of TTHA (formation of H_3L^{3-}), and is followed by a second well-defined inflection corresponding to the formation of the tetraanion H_2L^{4-}. The titration curves were reexamined by Grimes, Huggard, and Wilford[34] and by Bohigian and Martell.[35] The values of the dissociation constants obtained by these authors are also summarized in Table 2.

TTHA has ten coordinating groups and can, therefore, be expected to form very stable 1:1 complexes with metals of high coordination number and binuclear or higher complexes with metals of low charge and low coordination number.

The formation of stable 1:1 complexes with some metals, and the formation of 2:1 complexes with others, seemed very promising for complexometry. The first titrations of metal ions with standard 0.05 *M* solutions of TTHA were performed by Přibil and Veselý.[36] At that time (1962) no stability constants of 1:1 and 2:1 complexes were known. Fortunately, the authors had available very suitable metallochromic indicators for carrying out such titrations, such as xylenol orange for acidic media and thymolphthalexon, fluorexon (calcein), or murexide for alkaline sulutions. From the qualities of the color change and the accuracies of the results, they were able to decide empirically whether either 1:1 or 2:1 complexes were formed exclusively under the conditions employed. Their results and observations are included in Table 3. From these observations we can see that under the proper conditions TTHA forms binuclear complexes of the type M_2L^{2-} with the majority of bivalent



IV = TTHA

TABLE 2

Dissociation Constants of TTHA

	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	Remarks
Frost[17]	–	2.64	4.08	6.26	9.67	10.82	1 *M* KNO_3, 25°C
Grimes et al.[34]	2.46	2.52	4.00	5.98	9.35	10.33	30 ± 0.02°C
Bohigian and Martell[15]	2.42	2.95	4.16	6.16	9.40	10.19	1 *M* KNO_3, 20°C

TABLE 3

Titrations of Various Metals with TTHA

Metal	pH of the solution	Indicator	Back titration with	Composition of complex	Remarks
Bi	1–2	XO	Direct	1:1	
	3–4	XO	Th	1:1	
Th	3–4	XO	Direct	1:1	
Tl(III)	3–3.5	XO	Direct	1:1	At 50 to 60°
	3–3.5	XO	Th	1:1	
	5–5.5	XO	Pb	1:1	
Zr	3–4	XO	Th	1:1	Slight displacement at the end point, then indicator blocking
Ti(IV)	5–5.5	XO	Pb	2:1	As peroxocomplex
Ga	3–4	XO	Th	2:1	
	5–5.5	XO	Pb	2:1	
In	3–5	XO	Direct	1:1	In hot solutions
	5–5.5	XO	Pb	1:1	
	9.5	Erio T	Direct	1:1	Sluggish end point in the presence of tartaric acid
Sn(II)	3–4	XO	Th	2:1	
Sn(IV)	3–4	XO	Th	1:1	Slight displacement
Al	5–5.5	XO	Pb	2:1	After boiling with TTHA
Cr(III)	5–5.5	XO	Pb	2:1	After boiling with TTHA
	10–11	FRX	Ca	–	displaced
La	5.5	XO	Direct	1:1	
Pb	5.5	XO	Direct	2:1	
Zn	5.5	XO	Direct	2:1	
	9–10	Erio T	Direct	2:1	
Cd(II)					
Cu(II)					
Co(II)					
Ni(II)	5.5	XO	Pb	2:1	
Co(II)					
Ni(II)	10–12	THFX	Ca	2:1	
		FRX			
Ni	10–11	Mur	Direct	2:1	
Hg(II)	5.5	XO	Direct	2:1	
Mn(II)	10–11	THFX	Direct	1:1	
	10–12	FRX	Ca	1:1	

Table 3 (continued)

Ca	10–12	THFX	Direct	1:1	
	10–12	FRX	Direct	1:1	
Mg	9	THFX	Direct	2:1	In TEA solution free of salts and in the presence of alcohol

XO = Xylenol Orange, THFX = Thymolphthalexon, FRX = Fluorexon
Erio T = Eriochrome Black T, Mur = Murexide, TEA = Triethanolamine

cations, with the exception of manganese and calcium, which form 1:1 complexes in alkaline media. It seems that under limited conditions magnesium can form a 2:1 complex. Tervalent elements also form binuclear complexes, ML°, except for thallium(III), indium, bismuth, and lanthanum, which form 1:1 complexes. As expected, quadrivalent elements form 1:1 complexes. The only exception is titanium, which forms a 2:1 peroxo complex in the presence of H_2O_2. The existence of a similar zirconyl-peroxo complex has not been proved with certainty. Various examples of analytical procedures, entirely new in complexometry, will be described later.

The remarkable properties of TTHA in complex formation have been investigated thoroughly by various authors.[34,35,37-39] From a theoretical point of view, we have to presuppose that besides ML and M_2L complexes, other hydrogen or hydroxo complexes, such as MHL, MH_2L, M_2HL, M_2H_2L, and $M_2(OH)_2L$, will be formed (see Table 4). We can expect that only the 1:1 and 2:1 complexes will be of analytical importance. As discussed previously, the first complexometric determinations with TTHA[36] were based on practical experiences, and hence the obtained results need much theoretical treatment. In their first paper, Harju and Ringbom[40] have applied the general theory of Ringbom[41] to the treatment of competition between 1:1 and 2:1 complexes formed during the titration. Usually, we use a chelating agent as a titrant; in the case of TTHA, we have to consider schematically written reactions:

$$2M + L = M_2L \text{ and } M_2L + L = 2ML \quad (1)$$

Conversely, in the titration of TTHA with a metal solution, two equivalence points also have to be expected:

$$L + M = ML \text{ and } ML + M = M_2L \quad (2)$$

Which system of reactions takes place in the solution depends not only on the respective stability constants and the pH of the solution, but also on the method of end-point detection. Harju and Ringbom[40] presented a very interesting example of copper titration without an indicator; they followed the titration photometrically. At pH 2 to 3.8 copper can be titrated as a 2:1 complex. On the other hand, titration of TTHA at pH 9.2 with a copper solution against solochrome violet leads to a 1:1 complex formation. Harju and Ringbom[38] later calculated conditional constants for various 1:1 and 2:1 complexes over the range of pH values from 2 to 14 and presented these values graphically. In the same manner, they calculated the concentrations (expressed as pM_{eq}) of free metal ions at the end points of the titration and graphically presented the dependences of pM_{eq} on pH. When we compare these values with those of pM_{trans} for the indicators available, we can easily decide to which equivalence point we can titrate each respective element and how accurate such a determination will be. The readers will find more details on the solution of this very interesting problem in complexometry in the literature cited.

Analytical Applications of TTHA

Titrations with TTHA can be performed in various ways, the principles of which will be briefly described.

Stepwise Titrations

It is well known that two metals, M_I and M_{II}, can be determined successively under the following conditions:

i. The difference between the logarithms of conditional constants K'_1 and K'_2 has to be sufficiently large (at least four logarithmic units). The greater this difference, the greater the permissible concentration of the second metal, M_{II},

TABLE 4

Stability Constants of Metal-TTHA Complexes
(μ = 0.1, 25°C)

Metal ion	$\log K_{MY}$	$\log K^{H}_{MHY}$	$\log K^{H}_{MH_2Y}$	$\log K^{M}_{M_2Y}$	$\log \beta_{M_2Y}$	$\log K^{M}_{M_3Y}$	Reference
Ag^{+}	8.67	9.11		5.22	13.89		37
Al^{3+}	19.7	5.85		8.9	28.6		38
Ba^{2+}	8.22[a]	7.66[a]	5.40[a]	3.41[a]	11.63[a]		38
	8.22	5.55[a]		3.41[a]			34
Ca^{2+}	10.06[a]	8.34	3.68	4.10	14.16	4.00	42
Cd^{2+}	19.8						39
Co^{2+}	17.1	8.12		11.7	28.8		38
					28.0		35
	20.4						39
Cu^{2+}	19.2	8.00		13.4	32.6		38
					27.6		35
Er^{3+}	23.19	4.50		11.7	26.92		38
Fe^{3+}	26.8	7.60	2.75	13.7	40.5		38
Hg^{2+}	26.8	6.3		12.3	39.1		38
La^{3+}	22.22	3.30		13.40	25.62		38
	23.1				26.9		34
Mg^{2+}	8.43	9.30		5.95	14.38		38
	8.43	7.55		5.5		5.32	35
	8.47[a]	7.39[a]		5.94[a]			34
Mn^{2+}	14.65	8.74	3.45	6.54	21.19		38
Nd^{3+}	22.82	3.93		3.93	26.75		38
Ni^{2+}	18.1	8.00		14.3	32.4		38
					29.5		35
	19.9						39
Pb^{2+}	17.1	8.20		11.0	28.1		38
	19.5						39
Sr^{2+}	9.26[a]	7.78	4.24	3.44	12.70		38
	29.26[a]	8.07[a]		4.10[a]			34
Sm^{3+}	24.3						39
Th^{4+}	31.9	3.05					38
Zn^{2+}	16.65	8.15		12.05	28.7		38
	20.1						39

[a]: T = 30°C

which can be present without interference with the titration of the first metal, M_I.

ii. The conditional constant K'_I must be of the order of 10^7 for a visual titration of the metal ion M_I using an indicator to succeed.

Many such titrations of two or three metals with EDTA have been described in the last decade. Similar conditions are also valid for TTHA titrations, regardless of whether 1:1 or 2:1 complexes are formed. In this area TTHA has not been fully utilized, as the following examples amply demonstrate.

Determination of Thorium and Lanthanides

Rare earths very often occur in nature together with large amounts of thorium. A rapid method for analyzing such mixtures should be useful, but one cannot be developed with EDTA or CyDTA as the titrant for the reasons discussed previously. It has been found, however, that the thorium-TTHA complex does not undergo a color reaction with xylenol orange at pH 5.5. This can be explained by the high stability of the TTHA complex. The stability constant of this complex was measured very recently by Harju and Ringbom[38] and found to be $10^{31.9}$. Triethylenediaminepentaacetic acid, DTPA, whose complex with thorium has a

stability constant of 10^{27}, behaves similarly, as was mentioned earlier. The stability constants of the complexes of TTHA with all the rare earths, including lutetium, differ very much from that for the thorium-TTHA complex, so that these elements cannot interfere in the determination of thorium; however, the rare earth complexes are sufficiently stable to enable direct determinations of these elements with TTHA at pH 5.5. (For the stability constants of the complexes of La, Nd, and Er see Table 4.)

The procedure is very simple. Dilute the solution containing 10 to 200 mg of thorium and lanthanides to 150 to 200 ml, and adjust the pH to 2.5 to 3 with dilute ammonia or nitric acid. Add xylenol orange indicator and titrate slowly with TTHA to a clear yellow end point. Add more TTHA (more than enough to complex the rare earths), adjust the pH to 5 to 5.5 with solid urotropine, using universal indicator paper, and back titrate the excess TTHA with 0.05 *M* lead nitrate until the yellow color of the solution turns to red-violet.

Titrations Based on 1:1 and 2:1 Complex Formation

When the solution contains two elements, M_I and M_{II}, only one of which forms a 2:1 complex, while the other forms a 1:1 complex under the same conditions, we can determine both without masking and, theoretically, regardless of their concentration ratios, as follows: one aliquot is titrated with a solution of EDTA, with which both elements form 1:1 complexes. The second aliquot is titrated with TTHA. We get two consumptions of titrants T_1 and T_2.

$$\text{The titer } T_1 = [M_I] + [M_{II}]$$

$$T_2 = [M_I] + 1/2\,[M_{II}]$$

and then

$$[M_{II}] = 2(T_1 - T_2)$$

$$[M_I] = 2\,T_2 - T_1$$

Two examples, the determination of bismuth and lead[36] and the determination of gallium and indium,[44] will illustrate this principle.

Bismuth forms only a 1:1 complex with TTHA over a broad range of pH values. Lead could be titrated only as a 2:1 complex at 5 to 5.5. Procedure: To the solution containing lead and bismuth add an excess of 0.05 *M* EDTA solution, adjust the pH to 5 to 5.5 with solid urotropine and back titrate with 0.05 *M* lead nitrate, using a few drops of xylenol orange as the indicator (Titer T_1). Carry out a second titration on another aliquot of the mixture under the same conditions using 0.05 *M* TTHA (Titer T_2).

Gallium and indium cannot be determined with EDTA in their mixtures because they form complexes of about the same stability ($\log K_{InL} = 24.9$, $\log K_{GaL} = 20.3$). With TTHA, however, indium forms a 1:1 complex over the whole range of pH values, while gallium forms only a 2:1 complex (Ga_2L). This can be utilized for determining both over wide ranges of concentration. Indium can be titrated directly with EDTA at pH 3 to 5 in a hot solution, using xylenol orange as indicator; under the same conditions, however, gallium blocks the indicator. The sum of the two metals, can, therefore, only be determined indirectly, e.g., by adding an excess of EDTA at pH 5 to 5.5 and back titrating with zinc solution and xylenol orange. Procedure: To the solution containing gallium and indium, add a sufficient amount of 0.05 *M* EDTA, adjust the pH to 5 to 5.5 with solid urotropine, and heat to nearly boiling. After adding xylenol orange, titrate with 0.05 *M* zinc solution to an intense red color (volume of EDTA - volume of Zn = T_1). To another equal aliquot of the solution add an amount of TTHA equal to the amount of EDTA used above, then carry out the back titration with zinc solution as described above (volume of TTHA - volume of Zn = T_2).

A number of other analyses of mixtures of two or three elements can be carried out based on the above mentioned principle, of which the peculiar advantage is that the use of masking agents is not required. The combination of thorium and titanium is very interesting. Thorium forms only a 1:1 complex with each titrant. Titanium, on the other hand, forms a 2:1 peroxocomplex with TTHA. Similarly, tin(II) forms a 2:1 complex, and Sn(IV) a 1:1 complex with TTHA.

Titrations Based on the Mutual Exchange of EDTA and TTHA

The displacement of one ligand L from the complex ML by another ligand L_I

$$ML + L_1 = ML_1 + L \quad (3)$$

has been studied chiefly in connection with measurements of stability constants of various EDTA complexes. In applied complexometry we can bring about such reactions by masking. For example, the EDTA complex of copper(II), unlike that of nickel(II), reacts with thioglycolic acid in alkaline media, and the liberated EDTA may be determined by back titration with calcium chloride solution, using thymolphthalexon as the indicator. In the case of EDTA and TTHA we have to consider very interesting equilibria of the type:

$$M_2X + 2\,Y = 2MY + X \quad (4)$$

$$MX + Y = MY + X \quad (5)$$

where X and Y are the anions of TTHA and EDTA, respectively (charges are omitted). The equilibrium is reached very quickly in the case of substitution-labile complexes. The reaction shifts quantitatively to the right provided that the difference between the stabilities of the complexes M_2X and MY is sufficiently great. In the case of substitution-stable complexes, however, the reactions of M_2X and MX with Y proceed very slowly, often too slowly to be observed at all. Then the cation M is actually blocked or masked by the anion X. Among the substitution-stable complexes of TTHA are the complexes of bismuth, BiX, and of aluminum and nickel, Al_2X and Ni_2X, respectively. On the other hand, the TTHA complexes of lead and iron are substitution-labile and the Reaction 4 proceeds quantitatively. Reaction 4 can be followed very simply by titrating with a solution of a third metal ion which forms only 1:1 complexes with the reagents EDTA and TTHA. An 0.05 *M* solution of lanthanum nitrate is very suitable and was used for back titrations at pH 5 to 5.5 with xylenol orange as the indicator. If Reaction 4 proceeds quantitatively, two ions of Y are substituted for one of X, and the consumption of lanthanum drops to one half. On the other hand, Reaction 5 is followed by the third metal which forms a 2:1 complex with TTHA. For such back titrations 0.05 *M* zinc chloride was used, with xylenol orange as the indicator, at pH 5 to 5.5. If the Reaction 5 proceeds quantitatively to the left, the consumption of zinc solution is double the amount of Y involved in the reaction.

These principles have been utilized in complexometry for the analysis of mixtures of metal ions that cannot be resolved by the usual EDTA titrations, for example, the determination of thorium and scandium.[4,5] With EDTA the elements thorium and scandium form complexes of the same strength (log K_{ThL} = 23.2, log K_{ScL} = 23.1) and their sum can be readily determined by direct titration at pH 2.5 to 4, using xylenol orange as the indicator. Obviously, however, their separate determination in the same solution is impossible unless a highly selective masking agent for one or the other element can be found, and this is unlikely. It has been found that the thorium-EDTA complex reacts very rapidly with TTHA in a hot solution:

$$Th\text{-}EDTA + TTHA = Th\text{-}TTHA + EDTA \quad (6)$$

whereas the scandium-EDTA complex does not take part in such a reaction at all. The excess TTHA and the liberated EDTA are then titrated with a zinc solution:

$$EDTA + Zn = ZnEDTA \quad (7)$$

$$TTHA + 2\,Zn = Zn_2TTHA \quad (8)$$

Because the sum of the amounts of EDTA and TTHA is known, it is very easy to calculate the concentrations of thorium and scandium.

Procedure: Adjust the pH of the solution containing thorium and scandium to 2.5 to 4, and heat it to 50°C. Add xylenol orange and titrate with 0.05 *M* EDTA to a very sharp color change from red-violet to lemon yellow. The warming of the solution is necessary, because the titration of scandium in the cold gives a somewhat sluggish end point. The consumption of EDTA (T_1) corresponds to the sum of the amounts of thorium and scandium. Then add an excess of 0.05 *M* TTHA (T_2) to the hot solution and adjust the pH to 5 to 5.5 with solid urotropine. Let it stand for 5 min, stirring occasionally, and titrate with a 0.05 *M* zinc solution to red-violet. The consumption of zinc is T_3.

Calculation: $2\,T_2 - T_3 = [Th]$

$T_1 - [Th] = [Sc]$

This procedure is reliable even in the presence of a large amount of thorium (250 mg) as long as the thorium-scandium ratio does not exceed 100:1. At

the other extreme, because the atomic weights of thorium and scandium are so disparate, the thorium-scandium ratio should not be smaller than about 1:4. It appears as 1:20 in the consumption of EDTA.

Determination of Thorium, Scandium, and Lanthanides[46]

The stepwise determination of thorium and scandium, and then the sum of the lanthanides, can easily be carried out by titration with TTHA at pH 2.5 to 3.5, and then at pH 5 to 5.5, using xylenol orange in both titrations. However, the determination of thorium and scandium in the presence, not only of each other but of the lanthanides as well, is impossible by the method described in the previous paragraph. When we have the EDTA complexes of thorium and scandium and free lanthanides in the solution used for the determination of thorium according to Reaction 6, we have to boil the solution with an excess of TTHA. In this case, however, the liberated EDTA reacts partly with the lanthanides, and so back titration with zinc according to Reactions 7 and 8 gives bad results. We have found that if CyDTA is used instead of EDTA, it does not react with light lanthanides when it is liberated. For the analysis of the mixture mentioned above, we need two equal aliquots of the solution and proceed as follows:

In both aliquots we determine the sum of thorium and scandium by titrating with 0.05 *M* CyDTA at pH 2.5 to 3 using xylenol orange as indicator:

$$x\,Th + y\,Sc + (x + y)\,CyDTA = x\,ThCyDTA + y\,ScCyDTA$$

Then we add an excess of TTHA to each aliquot, adjust the pH values to 5 to 5.5 with solid urotropine, and boil for 3 min. Only the thorium-CyDTA complex and the free lanthanides react:

$$x\,ThCyDTA + z\,Ln + (x + z)\,TTHA = x\,ThTTHA + z\,LnTTHA + x\,CyDTA$$

After cooling, we titrate one solution with 0.05 *M* lanthanum nitrate to determine the excess TTHA and the liberated DCTA (which corresponds to scandium). Then we titrate the other solution with zinc chloride, using xylenol orange as indicator. The reactions in these two titrations are represented by the equations

$$DCTA + TTHA + 2\,La = LaCyDTA + LaTTHA$$
$$DCTA + TTHA + 3\,Zn = ZnCyDTA + Zn_2TTHA$$

From all these consumptions we can easily calculate the amounts of thorium, scandium, and the sum of the lanthanides, Ln. The reader will find more details in the paper cited.

Masking in Titrations with TTHA

Masking in complexometry, which makes many titrations more selective, is very often used. At least ten masking agents, including potassium cyanide, fluoride, and triethanolamine, are currently applied to the analysis of metal systems. Because TTHA is most valuable as a titrant in acidic media (it is unsuitable for determinations of calcium and magnesium), only a few masking agents are available for use in titrations employing TTHA. Only two examples, the determination of thorium and scandium and the successive determination of zinc and cadmium, will be presented.

Only the stability constant of the thorium-TTHA complex is known ($\log K_{ThL} = 31.9$). Most probably the similar scandium-TTHA complex is substantially less stable. Scandium can be displaced from its TTHA complex by zinc in the presence of phosphate, but the thorium complex is stable toward such treatment. These facts have been used to permit the determination of thorium in the presence of scandium.[47]

Procedure: To the acid solution containing thorium and scandium, add excess 0.05 *M* TTHA, adjust the pH to 5 to 5.5 with solid urotropine, add 10 to 20 ml of 1 *M* Na_2HPO_4, and titrate with 0.05 *M* zinc solution, using xylenol orange as the indicator, until the color changes from yellow to intense red-violet. Before the end point, the zinc solution must be added slowly, because the last traces of scandium are only slowly displaced from its TTHA complex. The final red-violet color is stable, but fades slightly after 5 min. During the titration a precipitate of scandium phosphate appears, but does not affect the sharpness of the end point. Titrate the second aliquot at pH 2.5 to 4 and at a temperature of 50°C with 0.05 *M* CyDTA, using xylenol orange as the indicator. The consumption of CyDTA corresponds to the sum of thorium and scandium.

2-Mercaptopropionic acid, $HSCH_2CH_2COOH$

(MPA), is a very good masking agent for copper and cadmium but not for zinc. It will also mask lead in slightly acidic media as well as iron, bismuth, cobalt, mercury, and copper in alkaline media. The reaction of cadmium with MPA was utilized in a procedure for the determination of zinc in the presence of cadmium.[48] The principle of the determination is as follows. Cadmium is masked with a small excess of MPA and zinc is titrated with TTHA at pH 5 to 5.5 using xylenol orange as the indicator. Good results were obtained up to a cadmium:zinc ratio of 40:1. EDTA is not suitable for the titration of zinc because it yields high results. However, it is possible to determine zinc in the same solution by adding excess CyDTA and back titrating with a standard zinc solution.

Determination of Aluminum in the Presence of Manganese

The stability constants of the EDTA complexes of aluminum and manganese are too nearly equal ($\log K_{AlL} = 16.1$, $\log K_{MnL} = 14.0$) to permit a single complexometric determination of aluminum in the presence of manganese. It has been found that TTHA forms a stable complex with aluminum at room temperature and that manganese does not interfere as long as no more than 20 times as much manganese as aluminum is present. Such a determination is based on the back titration of excess TTHA at pH 5.1 to 5.5 with copper sulfate, using glycinecresol red as the indicator.[49] Even very large amounts of calcium and magnesium do not interfere, although they do in the similar titration with EDTA.

REFERENCES

1. West, T. S., *Complexometry with EDTA and Related Reagents*, 3rd ed., BHG Chemicals Ltd., Poole, 1969.
2. Schwarzenbach, H., Senn, H., and Anderegg, G., *Helv. Chim. Acta*, 40, 1886 (1957).
3. Ringbom, A., Pensar, G., and Wänninen, E., *Anal. Chim. Acta*, 19, 525 (1956).
4. Sadek, F. A., Schmidt, R. W., and Reilley, C. N., *Talanta*, 2, 38 (1959).
5. Nakagawa, G., Wada, H., and Tanaka, M., *Talanta*, 10, 325 (1963); see also *Bull. Chem. Soc. Japan*, 36, 320 (1963).
6. Flaschka, H. and Ganschoff, J., *Bull Chem. Soc. Japan*, 8, 885 (1961).
7. Burg, R. A. and Conaghan, H. F., *Chem. Anal.*, 49, 100 (1960).
8. Belcher, R., Close, R. A., and West, T. S., *Chem. Anal.*, 47, 2 (1958).
9. Date, Y. and Toei, K., *Bull. Chem. Soc. Japan*, 36, 5 (1963).
10. Přibil, R. and Veselý, V., *Talanta*, 13, 233 (1966).
11. Přibil, R. and Veselý, V., *Chem. Anal.*, 55, 82 (1966).
12. Flaschka, H. and Carley, F. B., *Talanta*, 11, 423 (1964).
13. Fabregas, R., Prieto, A., and Garcia, C., *Chem. Anal.*, 51, 77 (1962).
14. Přibil, R. and Veselý, V., *Chem. Anal.*, 55, 4 (1966).
15. Kroll, H., Pinching, G., and Butler, F., Abst. 122nd Am. Chem. Soc. Meeting, Atlantic City, 1952, 6.
16. Wänninen, E., *Suomen Kemistilehti, B*, 28, 146 (1955).
17. Frost, A. E., *Nature* (London), 178, 322 (1956).
18. Durham, E. J. and Ryskiewich, D. P., *J. Am. Chem. Soc.*, 80, 4814 (1958).
19. Anderegg, C., Nägeli, P., Müller, F., and Schwarzenbach, G., *Helv. Chim. Acta*, 42, 827 (1959).
20. Wänninen, E., *Complexometric Titrations with Diethylenetriaminepentaacetic Acid, Acta Academie Aboensis*, Abo Academy, 1960.
21. Wänninen, E., *Suomen Kemistilehti, B*, 29, 184, (1956).
22. Olsen, E. D. and Novak, R. J., *Anal. Chem.*, 38, 152 (1966).
23. Přibil, R. and Veselý, V., *Talanta*, 10, 899 (1963).
24. Gupta, A. K. and Powell, J. E., *Talanta*, 11, 1339 (1964).
25. Přibil, R. and Veselý, V., *Chem. Anal.*, 56, 51 (1967).
26. Přibil, R. and Horáček, J., *Talanta*, 16, 750 (1969).
27. Přibil, R., Koudela, Z., and Matyska, B., *Collect. Czech. Chem. Commun.*, 16, 80 (1951).
28. Schwarzenbach, G. and Ackermann, H., *Helv. Chim. Acta*, 32, 1682 (1949).
29. Close, R. A. and West, T. S., *Talanta*, 5, 221 (1960).
30. Přibil, R., *Collect. Czech. Chem. Commun.*, 20, 162 (1955).
31. Přibil, R. and Veselý, V., *Talanta*, 9, 23 (1962).
32. Přibil, R. and Veselý, V., *Talanta*, 10, 1287 (1963).
33. Bersworth, F. C., U. S. Patent, 2,407,645, September 17, 1946.
34. Grimes, J. H., Huggard, H. J., and Wilford, S. P., *J. Inorg. Nucl. Chem.*, 25, 1225 (1963).

35. Bohigian, T. A., Jr. and Martell, A. E., *J. Inorg. Chem.*, 4, 1264 (1965).
36. Přibil, R. and Veselý, V., *Talanta*, 9, 939 (1962).
37. Wikberg, H. and Ringbom, A., *Suomen Kemistilehti, B*, 41, 177 (1968).
38. Harju, L. and Ringbom, A., *Anal. Chim. Acta*, 49, 221 (1970).
39. Soucek, D. A., Cheng, K. L., and Droll, H. A., *Talanta*, 15, 849 (1968).
40. Harju, L. and Ringbom, A., *Anal. Chim. Acta*, 49, 205 (1970).
41. Ringbom, A., *Complexation in Analytical Chemistry*, Interscience, New York, 1963.
42. Bogucki, R. F. and Martell, A. E., *J. Am. Chem. Soc.*, 80, 4170 (1958).
43. Přibil, R. and Veselý, V., *Talanta*, 10, 899 (1963).
44. Přibil, R. and Veselý, V., *Talanta*, 11, 1319 (1964).
45. Přibil, R. and Veselý, V., *Talanta*, 11, 1545 (1964).
46. Přibil, R. and Horáček, J., *Talanta*, 14, 313 (1967).
47. Přibil, R. and Veselý, V., *Talanta*, 14, 266 (1964).
48. Přibil, R. and Veselý, V., *Talanta*, 12, 475 (1965).
49. Přibil, R. and Veselý, V., *Talanta*, in press.