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THE SELECTION OF MASKING AGENTS FOR USE IN ANALYTICAL CHEMISTRY

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I. INTRODUCTION

Although many analytical methods are available for the determination of elements when they occur alone or in simple combination, such conditions are rarely met in practice. Instead, technological development gives rise to continuing and increasing demands for more rapid and more accurate methods of analysis, especially for the determination of traces of one or more elements in multicomponent mixtures. At the same time, there is the further requirement for simplification, as far as possible, of the analytical procedure. These needs are being met in three main ways: Older methods are being refined, new analytical procedures are being devised, and physical methods of measurement, such as atomic absorption spectrometry, are being used to an ever greater extent. Even in the last group, however, practical chemical treatments such as preliminary separations or concentrations are frequently necessary. For example, the atomic absorptiometric determination of chromium in ashed samples of whole blood requires a separation step if interference from the relatively high concentration of iron in the sample is to be overcome.

The *sensitivity* of a chemical method can often be increased by the use of solvent extraction, electrolytic deposition, or techniques which depend on selective adsorption. There are usually much wider possibilities for improving the *selectivity* of a chemical procedure, even to the extent that, under defined conditions, a reaction might become almost *specific* for a particular component. Masking and demasking procedures frequently provide elegant methods by which to achieve such an objective, especially in complexometry; until recently, however, the choice of masking agents and the control of experimental variables have been largely empirical. It is the aim of the present review to indicate factors governing the qualitative choice of masking agents and to outline quantitative methods by which the effectiveness of masking and demasking procedures can be assessed. Because of their major importance in modern analytical methods, discussion is centered mainly on metal-complex and acid-base equilibria.

A. Masking and Demasking

A *masking reagent* is a substance which prevents the normal course of a chemical change without removal of any component from the

system. This inhibited reaction is then said to be *masked*. Thus, the addition of citric acid to a solution of ferric chloride masks iron(III) against precipitation as the hydroxide when the solution is neutralized. Conversely, the process of *demasking* involves the abolition of the effect of a masking agent that is already present. Qualitative definitions of masking and demasking in these terms were given by Feigl,¹ who made extensive use of masking agents to suppress interference by adventitious ions in qualitative spot tests. A quantitative approach to masking was developed by Ringbom,² who defined masking in terms of a decrease in the value of a conditional stability constant.

Following Ringbom, we shall speak of a desired reaction between a metal ion and a reagent as the *principal*, or *main*, reaction, whereas reactions involving other components of the system are *side* reactions. The latter may be between other metal ions and the reagent or between the desired metal ion and other reagents. Masking diminishes the importance of side reactions without seriously affecting the extent of the principal reaction.

There is wide variation in the extent to which a reaction is required to be masked. Weak complex formation may be sufficient to mask a metal ion against hydrolytic precipitation or to decrease an already low concentration of an interfering species. Conversely, much stronger masking may be required if, for example, an unwanted cation, present in high concentration, forms an intensely colored complex with the reagent in a spectrophotometric method.

A convenient method for expressing the masking ability of an agent under any particular conditions is the *masking ratio*³ or its logarithm, the *masking index*. The masking ratio is defined as the ratio of the total concentration of all forms of a given metal species to the free metal ion concentration in the absence of the principal reagent; the greater this ratio, the more effectively is the metal ion masked.

Notwithstanding the usefulness of masking procedures in analytical chemistry, this topic has been reviewed only infrequently. The more detailed literature is comprised of one monograph³ and a small number of reviews⁴⁻⁸ or chapters,² including several on complexometry.^{6,7}

B. Types of Masking and Demasking Procedures

Masking procedures can be classified into five

main groups, depending on their underlying chemical principle:

1. In the largest group, advantage is taken of differences in the stabilities of complexes of interfering cations and of the desired species with a suitable added complexing agent. Examples can be found in all fields of inorganic analysis. Thus, iron(III), zirconium(IV), and titanium(IV) are masked by fluoride ion when manganese(II) is determined spectrophotometrically by xylenol orange at pH 6.8.⁹ Copper(II) is masked by EDTA when mercury(II) is determined by its catalytic effect on the luminescence produced in the oxidation of luminal by hydrogen peroxide in alkaline medium.¹⁰ In the precipitation of barium as arsenate in ammoniacal solution, iron, aluminum, and titanium are masked by citrate.¹¹ Potassium bis(carboxymethyl)-dithiocarbamate is a masking agent for lead and cadmium in the complexometric titration of zinc with EDTA at pH 5.5.¹² CDTA masks aluminum, zirconium, iron, and uranyl ion when traces of fluoride ion are extracted by triphenylantimony(V) dichloride into carbon tetrachloride.¹³

Alternatively, and particularly in complexometric titrations, the masking agent is added after the total metal ion content has been determined, thereby displacing some of the metal ions from their complexes. The liberated reagent, usually EDTA, is determined by titration against a suitable standard metal ion solution. A method for the analysis of aluminum in zinc alloys is based on reaction with excess EDTA, back-titration with zinc (to determine total zinc + aluminum), addition of fluoride ion to displace aluminum, and titration of the liberated EDTA.¹⁴ Similarly, a selective complexometric method for copper(II) is based on the displacement of copper(II) from its EDTA complex at pH 5 to 6 by a ternary masking mixture comprised of thiourea, ascorbic acid (reducing agent), and thiosemicarbazide or 2, 2'-bipyridine.¹⁵ The liberated EDTA is titrated with standard lead or zinc solutions.

2. Another widely used group of masking agents comprises relatively weak complexing agents which are added to avoid hydrolytic precipitation of the metal ions that are being determined. Examples include acetate, tartrate, and citrate buffers, ammoniacal solutions, and solutions containing halide ions. Typical uses would be tartrate ion to mask aluminum at pH

8.5, ammonia buffer at pH 10 to mask zinc, and fluoride ion to mask uranium(IV) against hydrolysis. The last reaction has been used in the titration of free acid in uranium(IV) solutions.¹⁶ In a method for the potentiometric determination of free nitric acid in the presence of metal nitrates,¹⁷ other masking agents that have been similarly used include ammonium sulfate to mask uranium and potassium oxalate to mask aluminum. A study has been made of the comparative effectiveness of masking by sodium-, calcium-, and barium-EDTA for the purpose of titrating free acid in solutions of hydrolyzable salts such as those of iron(II), iron(III), and aluminum.¹⁸

3. Masking is sometimes possible by changing the oxidation state of an interfering ion. For example, in a complexometric method for zinc and copper in admixture, copper(II) is masked by reduction to copper(I) with sodium thiosulfate while the zinc is titrated; the copper is then demasked by adding hydrogen peroxide and titrated.¹⁹ Thiourea is used as a reducing agent to mask iron(III), copper(II), chromium(VI), and manganese(VII) in an extraction-photometric determination of titanium(IV) with catechol and aniline.²⁰ A complexometric method for mercury(II) depends on the reductive displacement of mercury from its EDTA complex by adding thiourea.²¹ Iron(III) is commonly masked by reduction with ascorbic acid. Thallium(III) is masked by reduction to thallium(I) with ascorbic acid in a complexometric titration of indium(III) at pH 3.5.²² Other recent examples include methods for tin in steel,²³ bismuth in iron,²⁴ and aluminum in plant and soil extracts.²⁵ Oxidation of tellurium(IV) to tellurium(VI) masks it against reaction with sodium diethyldithiocarbamate in a method for estimating copper in selenium.²⁶ Other masking procedures based on oxidation include conversion of chromium(III) to chromium(VI) and manganese(II) or (III) to permanganate.

4. Masking by precipitation without further separation has sometimes been excluded from types of masking procedures although it appears to meet the requirements of the definition. As a technique, it may be slightly suspect because of the danger of coprecipitation of the species sought, the possibility of adsorption of indicators in titrations, and difficulty in detecting endpoints because of turbidity and colored precipitates. The classical example is precipitation of magnesium as

the hydroxide in the EDTA titration of calcium ion above pH 12, but even in this case there may be partial coprecipitation of calcium hydroxide. In general, adsorption of an ion onto a precipitate is likely to occur when the ion forms a sparingly soluble compound with an oppositely charged component of the precipitate, especially if the ion is highly charged. Isomorphic replacement in the crystal lattice may also occur.

5. Most reactions involving metal-complex formation proceed rapidly in solution. In some cases, however, especially where low-spin electronic configurations of the metal ion are involved, reactions may be sufficiently slow that advantage can be taken of rate differences in designing analytical methods. Thus, reaction of chromium(III) with EDTA in the cold at pH 6 is slow enough that cobalt(II), copper(II), and nickel can be titrated in the presence of chromium(III).²⁷ This is an example of "kinetic masking." Unlike cadmium, cobalt(II), copper, lead, and zinc, nickel is only slowly displaced by bismuth from its EDTA complex in cold solutions at pH 2. This provides the basis of a selective complexometric method for nickel.²⁸ In heated solutions, EDTA reacts very slowly with the 4-(2-pyridylazo) resorcinol complex of iron(II) (under reducing conditions) and of cobalt(III) (under oxidizing conditions), whereas other metal-PAR complexes are rapidly dissociated. This provides a highly selective and sensitive spectrophotometric method for these metals.²⁹

A somewhat related type of masking has been used to provide a sensitive method by which to determine microamounts of species that catalyze a reaction. In "catalytic titrations" or "catalimetric titrations," an inhibitor solution is titrated with a solution of a catalyst (or conversely), the endpoint being determined by the catalytic activity on the substrate. The original example, a micromethod for silver ion, was based on titration with iodide ion, the catalyst for oxidation of arsenious acid with cerium(IV).³⁰ Similarly, trace amounts of EDTA can be determined by complexation of manganese(II), the catalyst for the oxidation of malachite green by periodate ion in dilute acid solutions.³¹

These catalytic titrations are to be distinguished from kinetic methods in which, for example, osmium(VIII) is determined by its catalytic effect on the oxidation of *p*-phenetidine by bromate ion

at pH 3.9, using EDTA to mask iron, vanadium, copper, molybdenum, and tungsten.³²

There are also a small number of specialized masking procedures. Thus, in polarography, "electrochemical masking" occurs when one or more polarographic waves are selectively displaced or eliminated by surface-active materials such as gelatin or camphor without any effect on other waves in the system.^{33,34} This type of masking is due to adsorption on the electrode surface. Examples are given in Reference 3. In other cases, complex formation may be used to modify oxidation-reduction potentials and hence to mask chemical reactivity. As an example, equilibria involving ferric and ferrous ions, iodide, and iodine are displaced in favor of ferric and iodide ions in the presence of such complexing agents as EDTA, tartrate, and fluoride ion. Advantage is taken of this fact to mask iron(III) with fluoride ion in an iodometric titration method for copper in sulfide ores.³⁵ The effect of complexing agents on oxidation-reduction potentials has been discussed elsewhere.³⁶

In using masking agents in analytical procedures, more than one type of agent may be present, and more than one type of masking action may be involved. Agents may be used one at a time, as illustrated by a complexometric method for aluminum, zinc, and copper in alloys: fluoride ion is added to one aliquot in order to displace bound aluminum from its EDTA complex so that aluminum can be determined by titration of the liberated EDTA. In another aliquot, triethanolamine masks aluminum while zinc plus copper are titrated. Addition of sodium thiosulfate masks copper(II) by reduction so that the amount of zinc can be determined.³⁷ Alternatively, a mixture of masking agents may be added at the same time. Thus, in the EDTA titration of indium, nickel is masked with 1, 10-phenanthroline, mercury(II) is masked with potassium iodide, and copper(II) is masked with thiourea or 1, 10-phenanthroline.³⁸

Demasking techniques fall into six main groups. These comprise:

1. Displacement of complexed species by more strongly bonding ions. Examples of the use of this technique in complexometric titrations are given above, but the principle is more general. Demasking of nickel(II) from $\text{Ni}(\text{CN})_4^{2-}$ or of copper(II) from its diethyldithiocarbamate by silver ion, followed by determination of the

displaced metal ion, provides a complexometric or spectrophotometric method for the indirect determination of silver. It also serves for the indirect determination of halide, cyanide, thiocyanate and arsenate ions. Small amounts of chloride and bromide ion can be determined by displacement of hydrogen cyanide from mercury (II) cyanide in dilute sulfuric acid.^{3,9} Conversely, small amounts of cyanide ion can be determined by spectrophotometry of the chloranilate released when mercury(II) chloranilate is added to a solution containing cyanide.⁴⁰ Many other examples are known.³

2. Conversion of masking agent to non-reacting species. Cyanide, used to mask zinc and cadmium, can be removed by reaction with formaldehyde or chloral hydrate to form cyanhydrins. Bisulfite can be rendered inactive by reaction with excess aldehyde or methyl ketone to form a bisulfite addition compound. Boric acid converts fluoride ion to tetrafluoroborate ion.

3. Adjustment of pH. The complexing ability of most ligands is strongly pH dependent, so demasking can often be achieved by appropriate pH adjustment. This is particularly important in complexometric titrations. Hydroxyl ion can be considered as a masking agent. Its concentration, and hence its effectiveness, increase as the pH is raised.

4. Destruction of the ligand. Examples include catalytic [iron(III)] decomposition of hydrogen peroxide, oxidation of thiocyanate ion with alkaline hydrogen peroxide, and the use of acid permanganate solutions to destroy EDTA and other polyaminocarboxylic acids.

5. Physical removal of the ligand, as when ammonia is allowed to escape from solution or when anionic ligands such as citrate ion are removed by passage through an ion-exchange column. Boiling with strong mineral acid can be used to eliminate volatile acids such as HF, HCl, HBr, and HI.

6. Change in the oxidation state of the metal ion. Although this technique is familiar as a means of masking a reaction, it is much less well-known for demasking. As an example, copper(I) forms a stable complex with thiosulfate ion in slightly acid solution, which masks it against reaction with 1-(2-pyridylazo)-2-naphthol. In alkaline solution, copper(I) is rapidly oxidized to copper(II), which reacts quantitatively with PAN.

II. QUALITATIVE FACTORS IN THE CHOICE OF MASKING AGENTS

The foregoing examples illustrate the potential scope of masking and demasking reactions but provide no guidance to the selection of reagents suitable to particular applications. In fact, any chemical property may be potentially important, so that an extensive chemical knowledge is valuable in choosing suitable masking agents. In the past, this has led to masking and demasking procedures being largely empirical. With this in mind, the present review seeks to provide guidelines to the selection of appropriate agents, particularly in cases where complex formation is involved.

A. "Hard" and "Soft" Metal Ions and Complexing Agents

The concept of "hardness" and "softness" of metal ions and ligands is a useful one for this purpose. All ligands are bases in that they have a propensity to accept a proton or to donate an electron. A ligand is a "soft" base if its atom which donates electrons to a metal ion is of high polarizability with empty, low lying molecular orbitals. The donor atom is likely to be of low electronegativity and to be easily oxidized. Orbitals of valence electrons can be distorted easily, possibly even to the extent that the electrons themselves are removed. Conversely, in a "hard" base, the donor atom is of lower polarizability, is difficult to oxidize, and has a high electronegativity; its empty molecular orbitals are of high energy and much less readily accessible. "Hardness" is a property of bases that have a high ionic character, whereas "softness" relates more to covalent bond formation.

Similarly, a metal ion is "soft" if it is of low charge, large size, and has several easily excited outer electrons, whereas a "hard" metal ion has a high positive charge, small size, and lacks easily excited outer electrons. In that metal ions are acids, in the Lewis sense of accepting a pair of electrons from a ligand, metal-complex formation is a special class of acid-base reaction for which the useful generalization applies:^{41,42} *that hard acids form stronger bonds with hard bases, whereas soft acids prefer to coordinate to soft bases.* Complexes involving hard acids and soft bases, or soft acids and hard bases, are usually much less stable.

Applications of this concept are mainly qualita-

TABLE 1
Classification of Metal Ions

| Hard | | | |
|------------------------------|------------------|------------------|------------------|
| Li ⁺ | | | |
| Na ⁺ | Mg ²⁺ | | |
| K ⁺ | Ca ²⁺ | Sc ³⁺ | Ti ⁴⁺ |
| Rb ⁺ | Sr ²⁺ | Y ³⁺ | Zr ⁴⁺ |
| Cs ⁺ | Ba ²⁺ | La ³⁺ | Hf ⁴⁺ |
| NH ₄ ⁺ | Ra ²⁺ | | Th ⁴⁺ |

also rare earth ions: U³⁺, U⁴⁺, UO₂²⁺, Ti³⁺, VO²⁺, Fe³⁺, Co³⁺, Np³⁺, Pu³⁺, Am³⁺, Pa⁴⁺

| Moderately hard | | | |
|--|--|--|--|
| Be ²⁺ , Al ³⁺ , V ³⁺ , Cr ²⁺ , Cr ³⁺ , Mn ²⁺ , Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Ga ³⁺ , In ⁺ , As ³⁺ , MoO ³⁺ , Rh ³⁺ , Np ⁴⁺ , Pu ⁴⁺ | | | |

| Moderately soft | | | |
|--|--|--|--|
| Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , In ³⁺ , Mn ³⁺ , Sb ³⁺ , Ru ²⁺ , Os ²⁺ , Ir ³⁺ , Pt ⁴⁺ , Tl ⁺ , Bi ³⁺ | | | |

| Soft | | | |
|--|--|--|--|
| Cu ⁺ , Cd ²⁺ , Sn ⁴⁺ , Ag ⁺ , Hg ²⁺ , Pb ²⁺ , Tl ³⁺ , Pd ²⁺ , Pt ²⁺ , Au ⁺ | | | |

tive because parameters yielding quantitative correlations have not yet been derived, despite efforts by Ahrlund,⁴³ Klopman,⁴⁴ and Marcus.⁴⁵ Table 1 attempts to classify metal ions in terms of their softness, using classes *a* and *b* of Ahrlund et al.,⁴⁶ with modification to take account of some of the softness parameters calculated by Marcus.⁴⁵

"Hard" cations (Marcus σ_p less than -0.3) include alkali metals, alkaline earth metals, rare earths, and many ter- and tetravalent cations. Binding in complexes would be expected to be essentially electrostatic. "Soft" cations (Marcus σ_p greater than 0.3), on the other hand, are highly deformable, have filled or partly filled *d* shells, usually have a low ionic charge, and form predominantly covalent bonds.

A similar grouping of ligands as hard or soft bases is given in Table 2, the anions being grouped in increasing order by their Marcus σ_X softness parameters in cases where these are known.

On the basis of Tables 1 and 2, fluoride or carboxylate ions would be good masking agents for lanthanides in the presence of silver and lead ions, whereas cyanide ion would mask silver and lead in the complexometric titration of lanthanides. The "softness" of metal ions usually increases with atomic number in any group of the periodic table, so that Pb²⁺ is softer than Sn²⁺ and Hg²⁺ is softer than Cd²⁺ which, in turn, is softer than

TABLE 2
Classification of Complexing Species

| Hard | |
|---|--|
| F ⁻ , RCO ₂ ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , Cl ⁻ , ClO ₄ ⁻ , HO ⁻ (also H ₂ O, RO ⁻ , R ₂ O, ROH, PO ₄ ³⁻) | |
| Intermediate | |
| Br ⁻ , ClO ₃ ⁻ (also RNH ₂ , aniline, pyridine, N ₂ H ₄ , NO ₂ ⁻ , N ₃ ⁻ , SO ₃ ²⁻) | |
| Soft | |
| I ⁻ , CN ⁻ , HS ⁻ , SCN ⁻ , S ²⁻ (also R ₂ S, RSH, S ₂ O ₃ ²⁻ , R ₃ P, (RO) ₃ P) | |

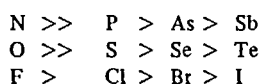
Ligands not in parentheses are arranged in increasing order of softness as calculated by Marcus.⁴⁵

Zn²⁺, Be²⁺, Mg²⁺, and Al³⁺ are softer than heavier Group IIA and IIIA cations. Hardness usually increases with charge, but exceptions occur (Sn²⁺, Sn⁴⁺; In⁺, In³⁺; Tl⁺, Tl³⁺) in cases where two *s* electrons are removed: this is associated with shielding by outer *d* electrons. Cations of the same charge with filled *d*¹⁰ shells become harder as the nuclear charge increases, so that Tl⁺ is harder than Au⁺, Sn²⁺ is harder than Cd²⁺, and Bi³⁺ is harder than Tl³⁺.

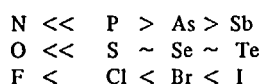
Metal-complex formation in aqueous solution usually involves coordination to the metal through pairs of electrons on oxygen, nitrogen, sulfur, or halogen atoms. The strongest bonds to oxygen are through carboxylate and enolate ions, with much weaker contributions from oxygens in ethers, alcohols, and carbonyl (aldehyde, amide, ester, and ketone) groups. Nitrogen coordinates through amino groups, less strongly through diazo and ring nitrogens. The choice of sulfur-type ligands is limited mainly to thiolate ions and dithiocarboxylate ions or (for weak complexing) thioethers and -S-S- groups.

In choosing masking agents, it is helpful to remember that *ligands containing oxygen as the donor atom are harder than those containing nitrogen, and these, in turn, are much harder than sulfur-containing ligands*. The "hardness" of halide ions decreases from fluoride ion (which is hard) to iodide ion (which is soft). Thus, iron(II) can be determined at pH 2.5 in the presence of the "harder" cation, iron(III), by masking the latter with fluoride ion and reacting the "softer" iron(II) with 1, 10-phenanthroline.⁴⁷

Hard and soft metal ions are further distinguished by the stability sequences in their complexes. For hard metal ions these are:



whereas for soft metal ions the sequences are:



Quantitative aspects of complex stability are discussed below, but it can be noted here that, in general, the stability of a complex of a hard metal ion with a hard ligand increases with the charge on the metal ion; thus, $\text{Zr}^{4+} > \text{Y}^{3+} > \text{Sr}^{2+} > \text{Rb}^+$. For soft metal ions and soft ligands, the converse is usually true. The decrease in the stability of the EDTA complexes in passing from calcium to strontium to barium illustrates how the hardness of a related group of metal ions decreases with increasing ionic radius.

The hardness or softness of a ligand can be modified by attachment of electron-donating or -withdrawing groups in positions where they do not coordinate to the metal ion. This, in turn, can produce quantitative differences in bonding be-

havior. Thus, electron-donating groups such as O^- , NH^- , or alkyl increase the softness of a donor atom, whereas an electron-withdrawing group such as NR_3^+ , NO_2 , CN , F , or CO_2R increases the hardness of a donor atom.

B. The Stability of Metal Complexes

Provided the stereochemical requirements of bonds about a metal ion can be met, enhanced complex stability results from the formation of chelate compounds, in which the ligand is attached to the metal ion by two or more atoms to give five- or six-membered rings. Many metal ions have coordination numbers of four or six and form tetrahedral or octahedral complexes, whereas Hg(I) , Hg(II) , and (if ligands are strongly basic, highly polarizing, or easily polarized) Cu(I) , Ag(I) , and Au(I) prefer linear complex formation. Consequently, a multidentate ligand such as EDTA is a useful general masking agent in analytical procedures for determining the cited metal ions. Similarly, unlike most of the transition metal ions, which form octahedral complexes, Cu(II) , Ag(II) , Au(III) , Ni(II) , Pd(II) , and Pt(II) are most commonly square planar in their complexes, although Cu(II) can also form distorted octahedral complexes in which the fifth and sixth binding sites are relatively weakly held.

With few exceptions (due mainly to stereochemical effects), the stability constants of divalent transition metal ion complexes follow the sequence: $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$. Differences between constants for successive metals are greatest for "soft" ligands and least for "hard" ligands, probably because in aqueous solutions, complex formation is really the replacement of one type of ligand — "hard" water molecules — with another. Within this group, "hard" masking agents would increase the selectivity of "soft" reagents for nickel, copper, and zinc, whereas "soft" masking agents would be used with "hard" reagents for manganese, iron, and cobalt. Commonly, however, advantage is taken of the reduction of copper(II) to copper(I) by thiourea or other reducing agents and of the oxidizability of manganese, iron, and cobalt.

The following sequence is a rough guide to the relative stabilities of complexes of divalent metal ions: $\text{Pt} > \text{Pd} > \text{Hg} > \text{UO}_2 > \text{Be} > \text{Cu} > \text{Ni} > \text{Co} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Ca} > \text{Sr} > \text{Ba}$.

A fuller discussion of the major factors governing the stability of metal complexes includes not

only the size and nature of the metal ion, the types of ligand atoms coordinating to the metal ion, and the stereochemistry of the resulting complex, but also the basicity of the ligand, the number of chelate rings per ligand molecule, their sizes, and resonance effects (see, for example, Reference 36).

III. QUANTITATIVE TREATMENT OF MASKING

For most analytical reactions involving metal-complex and acid-base equilibria, it should be possible (given the relevant equilibrium values) to make calculations to establish the feasibility, precision, and selectivity of a proposed method based on titrimetry, gravimetry, solvent extraction, ion-exchange, or spectrophotometry. This group comprises the bulk of analytical methods in which masking is used.

Some of the more useful sources of data include Sillén and Martell,⁴⁸ Körtum et al.,⁴⁹ Perrin,^{50,51} Marcus et al.,⁵² Kertes et al.,⁵³ Ringbom,² and Linke and Seidell;⁵⁴ in many cases, however, published data relate to different experimental conditions so that calculations are at

best only semiquantitative. In particular, there is only limited information on mixed-ligand and partially hydrolyzed metal complexes, both of which may be important under conditions used in analysis. Also there is commonly doubt as to the effect of temperature and ionic strength. Nevertheless, even approximate calculations are useful as serving to delineate the major features of any given or proposed analytical method and as providing guidance in selecting optimum working conditions. It still remains necessary to confirm by experiment the correctness of the theoretical computations.

Most complexing agents readily add hydrogen ions, so that complex formation of a ligand with a metal ion is a competitive reaction in which the extent of complexation of the metal ion depends on the hydrogen ion concentration in the solution. Thus, EDTA, as the tetraanion, masks barium ion in alkaline solution against precipitation as the sulfate but is ineffective if the solution is made acid.

The effect of pH on complexing ability can be expressed quantitatively in terms of the pH and pK_a values of the ligand. If the complexing form of a ligand is L and it can add x protons to give H_xL , a quantity $\alpha_{L(H)}$ is defined by:⁵⁵

$$\begin{aligned}\alpha_{L(H)} &= ([L] + [HL] + [H_2L] + \dots [H_xL])/[L] \\ &= 1 + 10^{(pK_{a1} - pH)} + \dots + 10^{(pK_{a1} + pK_{a2} + \dots + pK_{ax} - x \cdot pH)} \\ &= 1 + [H^+]/K_{a1} + [H^+]^2/K_{a1}K_{a2} + \dots + [H^+]^x/K_{a1}K_{a2} \dots K_{ax}\end{aligned}\quad (1)$$

where $pK_{a1} > pK_{a2} > pK_{a3} \dots$ are the successive pK_a values of the ligand. The greater the value of $\alpha_{L(H)}$, the less effective is the ligand as a complexing species. Table 3 lists most of the substances used as masking agents and their pK_a values where known, so that from Equation 1, their $\alpha_{L(H)}$ -pH profiles can readily be calculated. Some typical examples are given in Figure 1. In all cases, a ligand exerts its maximum masking activity at pH values near to or above pK_{a1} , whereas at lower pH values, $\alpha_{L(H)}$ increases rapidly, especially when the ligand has more than one pK_a .

This quantity, $\alpha_{L(H)}$, can be combined with the stability constant, β , of a metal complex ML_n to yield an "apparent," "effective," or "conditional" stability constant, $\beta_{\text{conditional}}$, which is more convenient for interpreting analytical chemical reactions. Whereas β is defined as

$$\beta = [ML_n]/[M][L]^n \quad (2)$$

$\beta_{\text{conditional}}$ is expressed in terms of the total concentrations of all ligand species not complexed to the metal ion. The latter is pH dependent and is related to β by

$$\beta_{\text{conditional}} = \beta(\alpha_{L(H)})^n \quad (3)$$

i.e.,

$$\log \beta_{\text{conditional}} = \log \beta - n \log \alpha_{L(H)} \quad (4)$$

A. Ringbom's α -Coefficient Method

Ringbom² developed this approach and showed its utility in quantitative calculations. If the principal reaction is between a metal ion, M, and a ligand, L, the effects of all side reactions can be included in the "side reaction coefficients" $\alpha_{L(X)}$

TABLE 3

Masking Agents, Abbreviations, and pK_a Values^a

| | |
|--|----------------------------|
| Acetic acid | 4.7 |
| Acetylacetone | 8.9 |
| Ammonia | 9.4 |
| Anthranildiacetic acid (ADA) | 7.8, 3.0, 2.2 |
| Ascorbic acid | 11.3, 4.1 |
| 2,2'-Bipyridine (bipy) | 4.4 |
| Bis(2-aminoethyl) sulfide (BAES) | |
| Bis(carboxymethyl) dithiocarbamate (BCMDTC) | |
| Bis(2-hydroxyethyl) dithiocarbamate (BHEDTC) | |
| <i>N, N</i> -bis(hydroxyethyl) glycine (BHG) | 8.1, 2.0 |
| Boric acid | 9.1 |
| Bromide ion | |
| Carboxyethylmercaptosuccinic acid (CEMSA) | |
| Carboxymethylmercaptosuccinic acid (CMMSA) | |
| Chloride ion | |
| Citric acid | 6.1, 4.4, 3.0 ^b |
| Cyclohexanediaminetetraacetic acid (CDTA) | 11.8, 6.2, 3.6, 2.5 |
| Cysteine | 10.5, 8.3, 1.9 |
| 1,2-Diaminopropane | 10.0, 6.9 |
| 1,3-Diaminopropane | 10.7, 9.0 |
| Diethyldithiocarbamate (DDC) | |
| Diethylenetriamine | 10.0, 9.2, 4.4 |
| Diethylenetriaminepentaacetic acid (DTPA) | 10.6, 8.7, 4.4, 2.9, 1.9 |
| Dimercaptopropanol (DMP) | 10.6, 8.6 |
| 2,3-Dimercaptopropionic acid (DMPA) | |
| Dimercaptosuccinic acid (DMSA) | 10.8, 8.9, 3.5, 2.7 |
| Dimethylglyoxime (DMG) | |
| Dithiocarbaminoacetic acid (DTCA) | 6.7, 3.8 |
| Dithiooxalic acid (DTO) | |
| Dithiothreitol (DTT) | |
| Dithizone | |
| Ethanolamine | 9.7 |
| <i>N, N'</i> -Ethylene bis [2-(<i>o</i> -hydroxyphenyl)] glycine (EBHPG) | |
| Ethylenediamine | 10.1, 7.3 |
| Ethylenediaminetetraacetic acid (EDTA) | 10.3, 6.2, 2.8, 2.1 |
| Ethylenediaminetetrapropionic acid (EDTP) | 9.6, 6.8, 3.4, 3.0 |
| Ethyleneglycol bis (2-aminoethylether) tetraacetic acid (EGTA) | 9.5, 8.9, 2.7, 2.1 |
| Formaldehyde | |
| Formic acid | 3.7 |
| Gluconic acid | 3.9 |
| Glutamic acid | 9.2, 4.0, 2.2 |
| Glycine | 9.7, 2.5 |
| Glycol | |
| Hexamethylenediamine- tetraacetic acid (HMDTA) | 10.7, 9.8, 2.7, 2.2 |

TABLE 3 (continued)

Masking Agents, Abbreviations, and pK_a Values^a

| | |
|--|-------------------------------|
| Hydrazine | 8.1 |
| Hydrocyanic acid (as K salt) | 9.2 |
| Hydrofluoric acid (as Na salt) | 3.1 |
| Hydrogen peroxide | 11.7 |
| Hydrogen sulfide | 14, 6.9 |
| 2-Hydroxyethylethylenediamine-triacetic acid (HEDTA) | 9.8, 5.4, 2.7 |
| Hydroxylamine (hydrochloride, HAH) | 6.2 |
| 8-Hydroxyquinoline-5-sulfonic acid (HQSA) | 8.4, 3.8 |
| Iminodiacetic acid | 9.5, 2.7 |
| Iodide ion | |
| Lactic acid | 3.8 |
| Malic acid | 4.7, 3.2 |
| Malonic acid | 5.4, 2.7 |
| β -Mercaptopropionic acid (MPA) | 4.9 |
| Mercaptosuccinic acid (MSA) | 10.4, 4.6, 3.6 |
| Nitrilotriacetic acid (NTA) | 9.8, 2.6, 2.0 |
| Nitrous acid | 3.2 |
| Oxalic acid | 4.0, 1.1 |
| Pentaethylenhexamine (penten) | 10.3, 9.8, 9.2, 8.6 |
| 1,10-Phenanthroline | 5.0 |
| Phenylarsonic acid | 3.5 |
| Phosphoric acid | 11.9, 6.9, 2.0 |
| Propylenediaminetetraacetic acid (PDTA) | 10.8, 6.2, 3.0, 2.6 |
| Pyrophosphoric acid | 8.5, 6.1, 2.5, 1.0 |
| Salicylic acid | 13.1, 2.9 |
| Sulfosalicylic acid (SSA) | 11.6, 2.6 |
| Sulfuric acid | 1.9 |
| Tartaric acid | 4.1, 2.9 |
| Tetraethylenepentamine (tetren) | 9.5, 9.1, 8.1, 4.7, 2.7 |
| Tetrafluoroborate ion | |
| Thenoyltrifluoroacetone | 6.1 |
| Thiocarbohydrazide | |
| Thiocyanic acid (as K salt) | -2 |
| Thioglycolic acid (TGA) | 10.2, 3.4 |
| Thiomalic acid | 10.4, 4.6, 3.6 |
| Thiosemicarbazide (TSC) | |
| Thiosulfuric acid (as Na salt) | 1.4 |
| Thiourea | 2.0 |
| Tiron ^c | 12.7, 7.7 |
| 1,2,3-Triaminopropane | 9.7, 8.0, 3.8 |
| Triaminotriethylamine (tren) | 10.4, 9.7, 8.6 |
| Triethanolamine (TEA) | 7.8 |
| Triethylenetetramine (trien) | 10.0, 9.3, 6.8, 3.4 |
| Triethylenetetraminehexaacetic acid (TTHA) | 10.2, 9.4, 6.2, 4.2, 3.0, 2.4 |
| Tripolyphosphoric acid | 8.7, 5.8, 2.1, 2, 1 |
| Unithiol | |

^aMostly as "practical" constants at 20–25° and $I = 0.1$.^bAlso $pK \sim 16$ for the OH.^cCatechol-3,5-disulfonate.

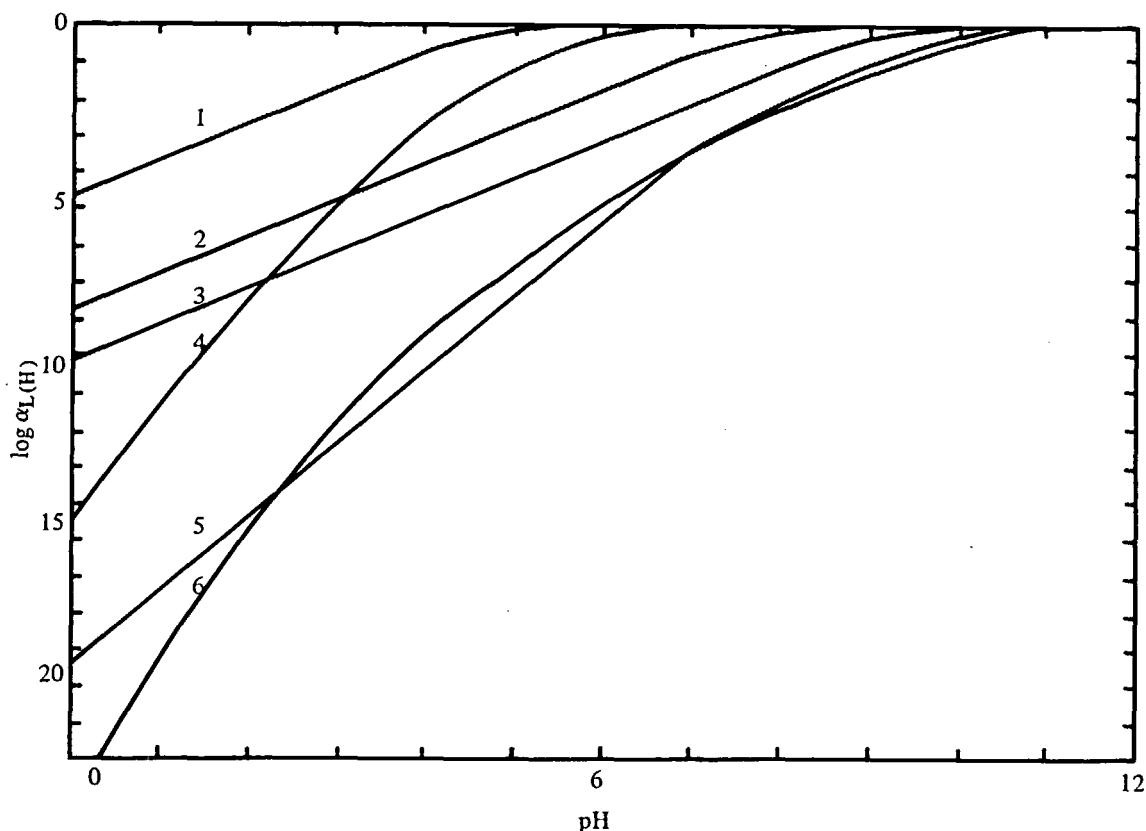


FIGURE 1. The effect of pH on the complexing ability of ligands. 1. Acetic acid. 2. Triethanolamine. 3. Potassium cyanide. 4. Citric acid. 5. Ethylenediamine. 6. EDTA.

and $\alpha_{M(A)}$, where $\alpha_{L(X)}$ is a term allowing for the effect of the species X on the concentration of free L, and $\alpha_{M(A)}$ is, similarly, for the effect of species A on the concentration of free metal ion. These α -coefficients can allow for the effect of pH, other ligands, and other metal ions. Extensive tables of α values for metals and ligands are available.²

Complexation of metal ions by EDTA, as affected by reactions of protons with the ligand and by reaction of hydroxyl ions with the metal ion, provides a useful illustration. Figure 1 includes $\log \alpha_{L(H)}$ for EDTA. The other quantity needed is $\alpha_{M(OH)}$, defined by

$$\alpha_{M(OH)} = ([M] + [MOH] + [M(OH)_2] + \dots) / [M] \quad (5)$$

This can be calculated from pK_a values⁸ for the hydrolysis of metal ions. The approximation is made that in the presence of complexing agents, only mononuclear species need be considered because the free metal ion concentrations in such

solutions are usually very low. Some typical plots of $\log \alpha_{M(OH)}$ against pH are shown in Figure 2. The combined effect of pH on metal ion and ligand is given by

$$\log \beta_{\text{conditional}} = \log \beta - n \log \alpha_{L(H)} - \log \alpha_{M(OH)} \quad (6)$$

which is the equation of a curve passing through a maximum. It is sometimes necessary to consider $\alpha_{ML(H,OH)}$ for the reaction of the principal complex with hydrogen and hydroxide ions, as well as $\alpha_{L(H)}$ (for the reaction of a ligand with hydrogen ion) and $\alpha_{M(OH)}$ (for the reaction of the principal metal ion with hydroxide ion). This is important, for example, with some metal-EDTA complexes. Figures 3 and 4 illustrate conditional constants for some of the more common metal-EDTA complexes, allowing for this effect where necessary.

If the metal ion undergoes appreciable hydrolysis, the maximum value of $\log \beta_{\text{conditional}}$ is much less than for $\log \beta$ and is reached at pH

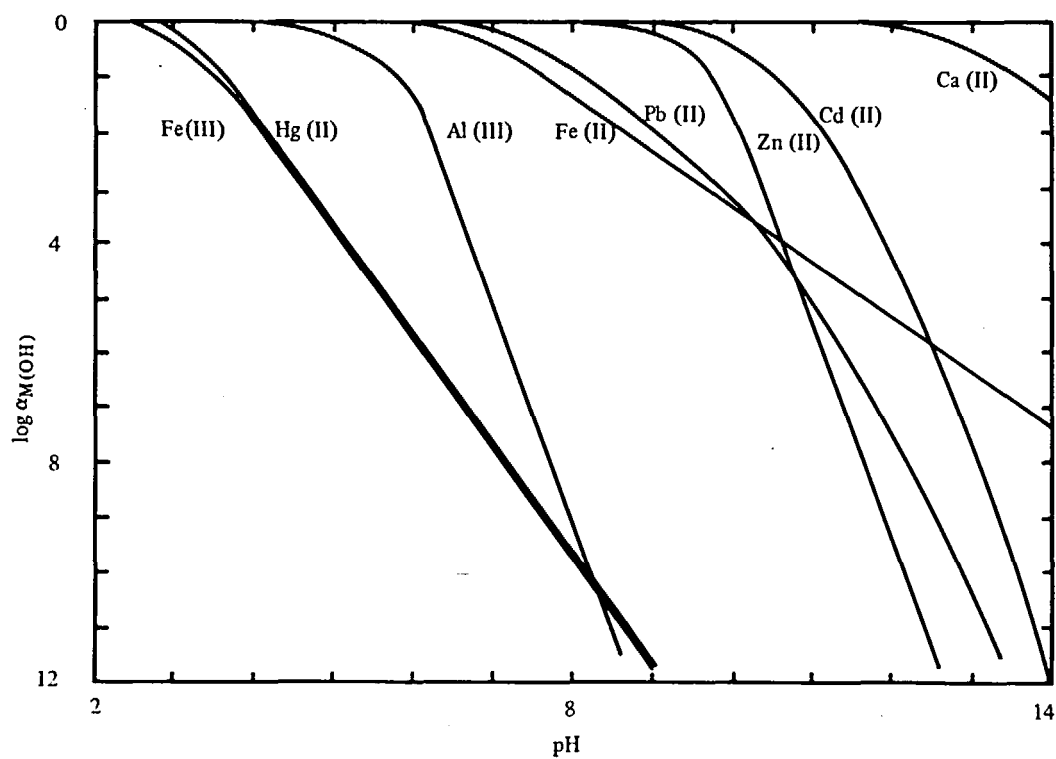


FIGURE 2. The effect of pH on the hydrolysis of metal ions.

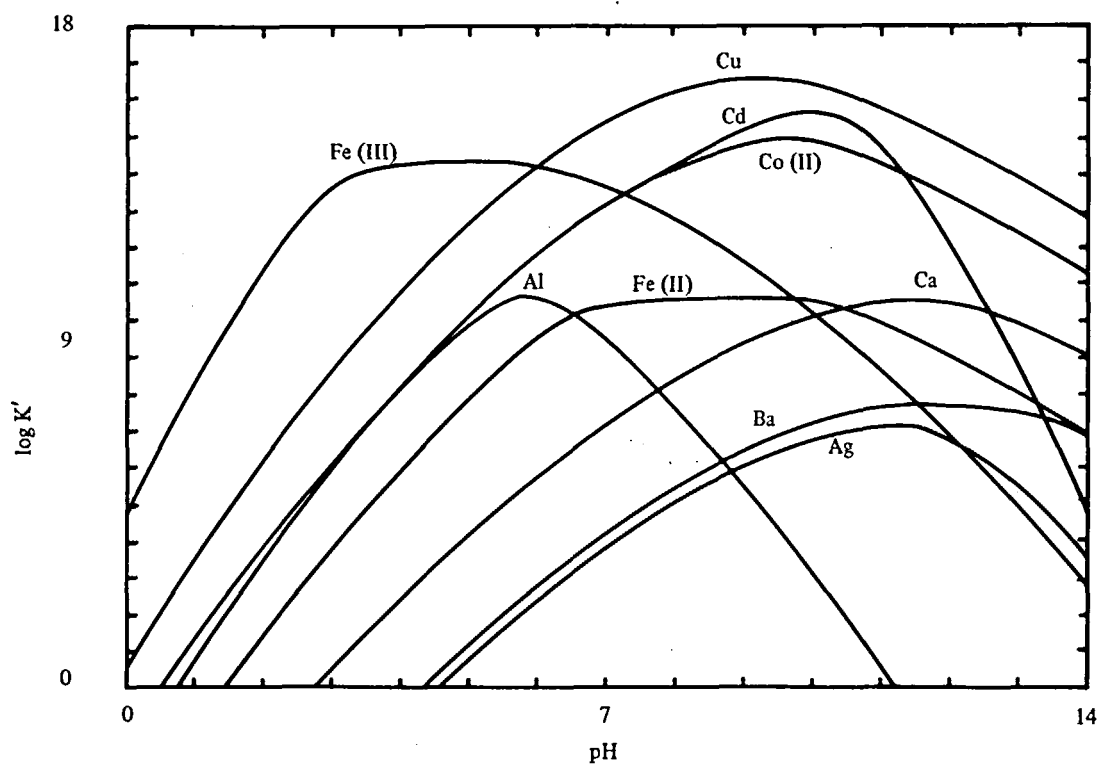


FIGURE 3. Conditional constants for some EDTA-metal complexes as a function of pH. Curves for Ag, Al, Ba, Ca, Cd, Co, Cu, Fe(II), and Fe(III)-EDTA.

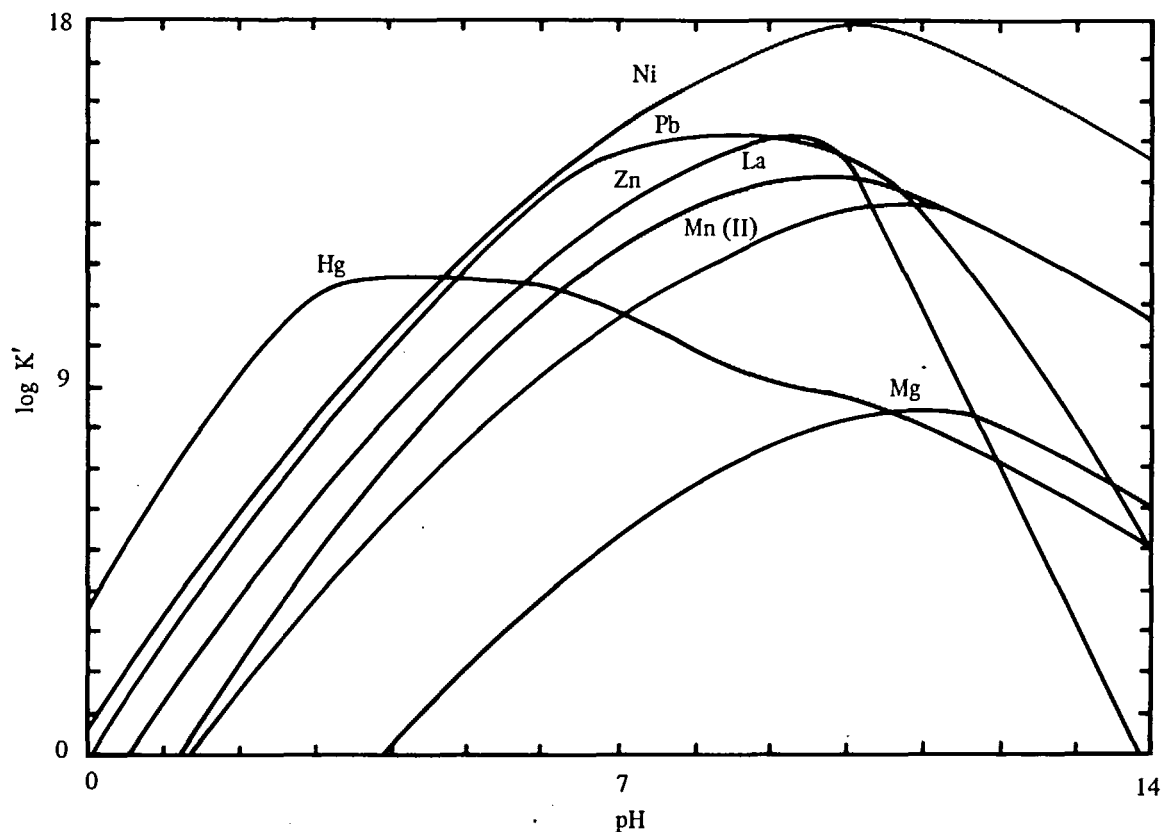


FIGURE 4. Conditional constants for some EDTA-metal complexes as a function of pH. Curves for Hg, La, Mg, Mn(II), Ni, Pb, and Zn-EDTA.

values that may be as low as 4.5 (for Hg^{2+}) or 5.6 (for Al^{3+}). These resulting differences in the pH curves for $\log \beta_{\text{conditional}}$ make it possible in some cases to improve the selectivity in complexometric titrations by using pH control.

When a possible masking ligand, A, is present in a solution, to form MA, MA_2 . . .

$$\alpha_{\text{M(A)}} = 1 + \beta_{\text{MA}}[\text{A}] + \beta_{\text{MA}_2}[\text{A}]^2 + \dots$$

$$\alpha_{\text{M(A + OH)}} = \alpha_{\text{M(OH)}} + \alpha_{\text{M(A)}} - 1 \quad (7)$$

The extent of the complexing of M by A is pH dependent, and if the total concentration of A is used, it must be divided by $\alpha_{\text{A(H)}}$. Similar relations apply to the presence in the solution of another type of metal ion that competes for the principal ligand. Calculation is facilitated by the fact that the masking ligand is usually present in excess, so that to a good approximation, the concentration of total ligand not complexed to the interfering metal ion is given by $[\text{L}]_{\text{T}} - n[\text{M}]_{\text{T}}$.

Ringbom² gives many worked examples using this approach, including titrations, extractions,

and quantitative precipitations. It was also used in the development of a complexometric method for magnesium in alloys of manganese and aluminum.^{5,6} Some further applications to EDTA titrations have recently been published.⁸ They show that in the presence of triaminotriethylamine at pH 11, copper(II) is masked when calcium is titrated with EDTA. At pH 5, aluminum is masked by fluoride ion, whereas nickel can be titrated. Other examples include titration of lead in the presence of zinc (masked by cyanide ion) and an illustration that citrate ion is of limited value as a masking agent for iron(III) in the titration of zinc.

Hence, the masking of inorganic cations usually involves the adequate lowering of the conditional stability constant for the complex of the interfering metal ion with the principal reagent without, at the same time, greatly decreasing the conditional stability constant of the complex of the metal ion that is to be determined.

B. Computer-based Methods

For many purposes it is convenient to have

curves showing conditional stability constants of metal complexes as pH is varied. Although the α -coefficient method can be used for the necessary calculations, the labor rapidly becomes tedious, especially in systems where masking agents have to be included so that numerous pK_a values, metal ion hydrolysis constants, and stability constants are involved. Thus, in the study of the masking effect of citrate ion on iron(III) in the EDTA titration of zinc, 21 constants were used in calculations at each of 140 pH values.⁸

With the current availability of minicomputers, it is a logical step to convert the α -coefficient method to a form suitable for computer operation. Most of the figures in the present review have been obtained in this way, using a graphic plotter operating under computer control.

Where the concentration of the masking agent is comparable with the metal ion concentration, as in substoichiometric masking, an iterative method is necessary for calculating equilibrium concentrations. Three computer programs that are suitable are COMICS,⁵⁷ HALTAFALL,⁵⁸ and EQUIL⁵⁹ (see also Bos and Meershoek⁶⁰). In its present form, COMICS can compute equilibrium concentrations in systems with up to 5 kinds of metal ions, 20 different ligands, and 500 species, whereas the advantage of HALTAFALL lies in its applicability to systems containing more than 1 phase, such as 2 liquids, a liquid and a gas, or a liquid and a solid phase. Examples of the use of HALTAFALL to compute equilibria in systems, including solvent extraction and precipitation, are given in the monograph by Dyrssen et al.⁶¹

The logic on which COMICS is based has also proved to be readily adaptable to two-phase systems. Thus, simpler (MINICOMICS) programs have been applied to the homogeneous precipitation of barium sulfate while strontium is masked by EDTA, and the effects of EDTA and triamino-triethylamine on the selective extraction of zinc by dithizone have been examined.⁶² A program based on COMICS enables the study of the effect of variations in stability constant values on computed concentrations.⁶³

The above examples, and others in the present review, demonstrate the utility of even small computers for rapidly and accurately carrying out computations that are necessary in theoretical studies of masking reactions. With slight modifications, many such programs can readily be adapted

to apply to related systems. A limitation to this approach is the lack of sufficient stability constant, solubility, and extraction data. Where constants are known even approximately, it is very useful to be able to explore the possible conditions for the masking and demasking of chemical reactions.

C. Some Examples of Computer Studies of Masking

A method has been proposed⁶⁴ for the titration of zinc at pH 8 to 9 with triethylenetetramine, using a silver indicator electrode in the presence of iron(III), the latter being masked with sulfosalicylic acid. The quantitative basis of this masking reaction is shown in Figure 5.

The possibility of using *o*-phenanthroline as a masking agent for nickel and cadmium EDTA titration of manganese(II) is examined in Figure 6. In the presence of 0.01 *M* *o*-phenanthroline, $\log \beta_{\text{conditional}}$ for Ni-EDTA is 9 logarithm units below $\log \beta_{\text{conditional}}$ for Mn-EDTA over the pH range of 9 to 14, indicating its suitability as a masking agent for nickel. However, it is less satisfactory for cadmium because here the difference is only 2.1 logarithm units between pH 10 and 12. A similar study (Figure 7) shows *o*-phenanthroline to be a suitable masking agent for zinc and manganese(II) when lead is titrated with EDTA between pH 4 and 10.

Computations presented in Figure 8 confirm the effectiveness of 0.1 *M* cyanide ion as a masking agent for cadmium and zinc in the EDTA titration of magnesium above pH 9.

Figure 9 examines the usefulness of tartrate ion and ammonia as masking agents against the hydrolytic precipitation of zinc as its hydroxide. It indicates the superiority of ammonia. In the presence of 1 *M* ammonia, the solubility of zinc species does not fall below $2 \cdot 10^{-3}$ *M*, whereas 1 *M* tartrate has no masking action above pH 10.

The effect of CDTA, EDTA, and NTA as masking agents against precipitation of calcium oxalate in 1 *M* oxalate solution is shown in Figure 10. Below pH 3.5, none of these masking agents has appreciable activity, but they become increasingly effective as the pH is raised. The weaker masking action of NTA may be advantageous in a method based on homogeneous precipitation of calcium oxalate by decreasing the pH of the solution.

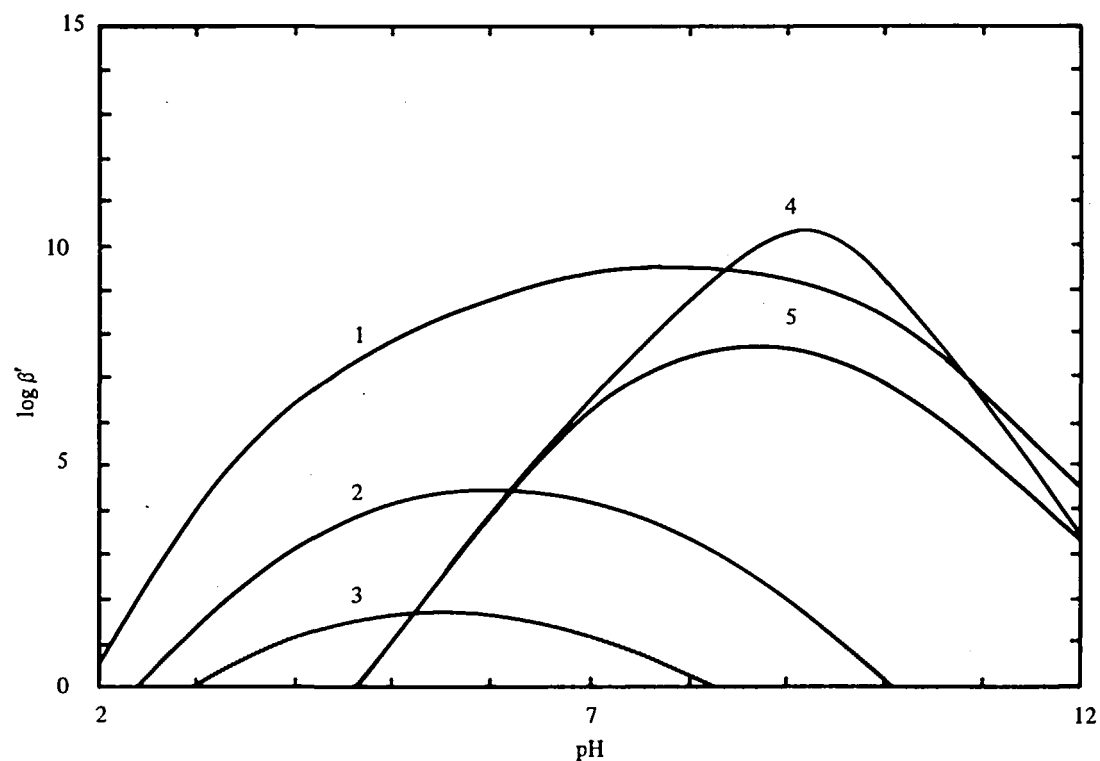


FIGURE 5. The masking of iron(III) by sulfosalicylic acid in the titration of zinc with triethylenetetramine. Plots of $\log \beta'_{\text{conditional}}$ for zinc and iron trien in the presence and absence of SSA. 1. Fe^{3+} alone. 2. $\text{Fe}^{3+} + 0.01 \text{ M SSA}$. 3. $\text{Fe}^{3+} + 0.1 \text{ M SSA}$. 4. Zn^{2+} alone. 5. $\text{Zn}^{2+} + 0.1 \text{ M SSA}$.

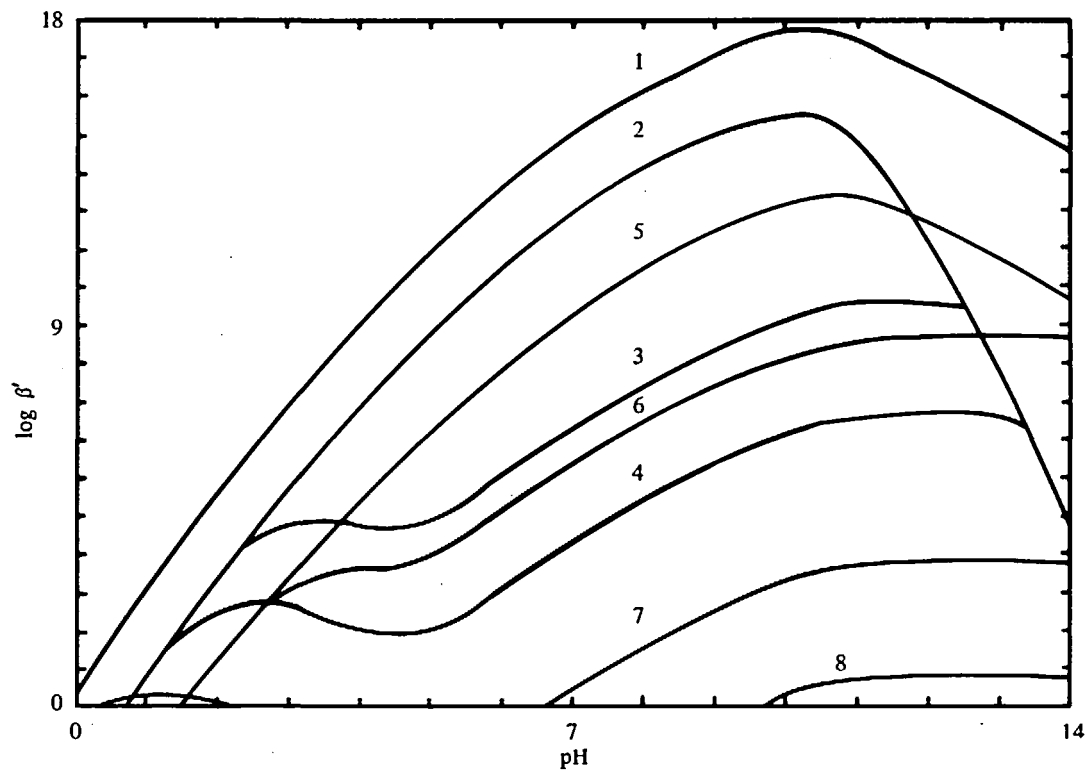


FIGURE 6. The possible use of 1,10-phenanthroline as a masking agent for nickel and cadmium in the EDTA titration of Mn(II) . 1. Ni^{2+} alone. 2. Cd^{2+} alone. 3. $\text{Cd}^{2+} + 0.001 \text{ M phen}$. 4. $\text{Cd}^{2+} + 0.01 \text{ M phen}$. 5. Mn^{2+} alone. 6. $\text{Mn}^{2+} + 0.01 \text{ M phen}$. 7. $\text{Ni}^{2+} + 0.001 \text{ M phen}$. 8. $\text{Ni}^{2+} + 0.01 \text{ M phen}$.

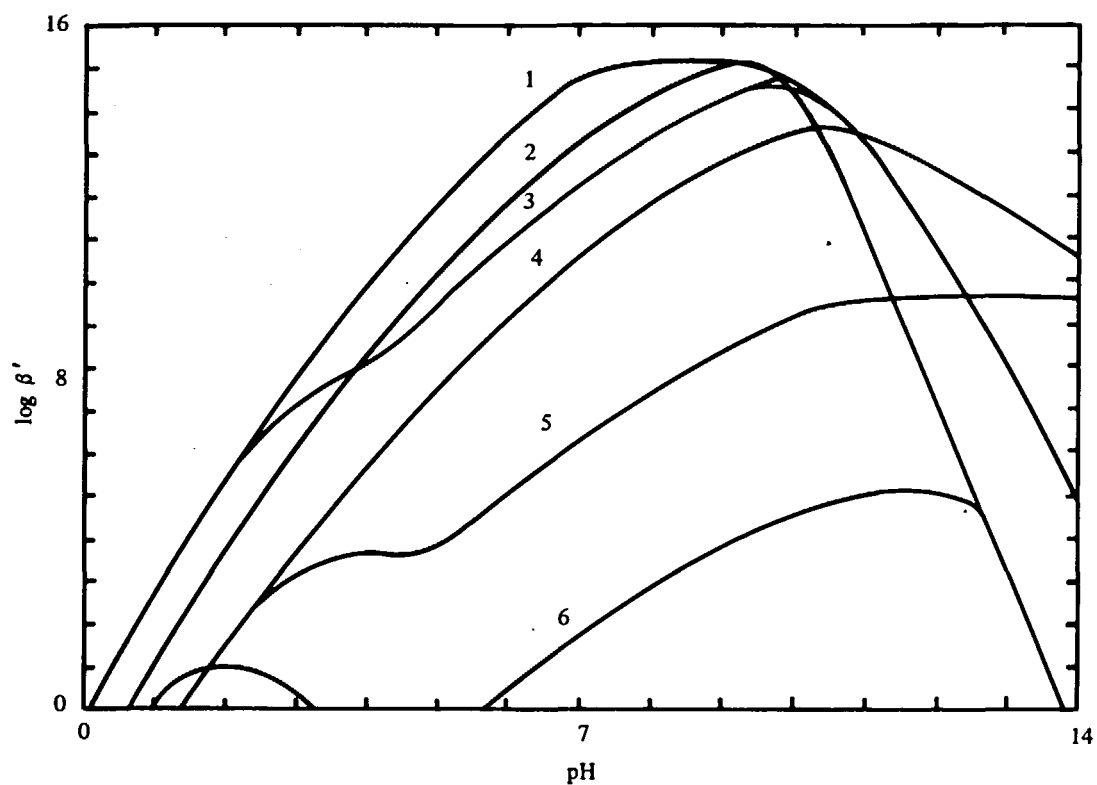


FIGURE 7. 1,10-Phenanthroline as a masking agent for zinc and manganese(II) in the EDTA titration of lead. 1. Pb^{2+} alone. 2. Zn^{2+} alone. 3. $\text{Pb}^{2+} + 0.01 M$ phen. 4. Mn^{2+} alone. 5. $\text{Mn}^{2+} + 0.01 M$ phen. 6. $\text{Zn}^{2+} + 0.01 M$ phen.

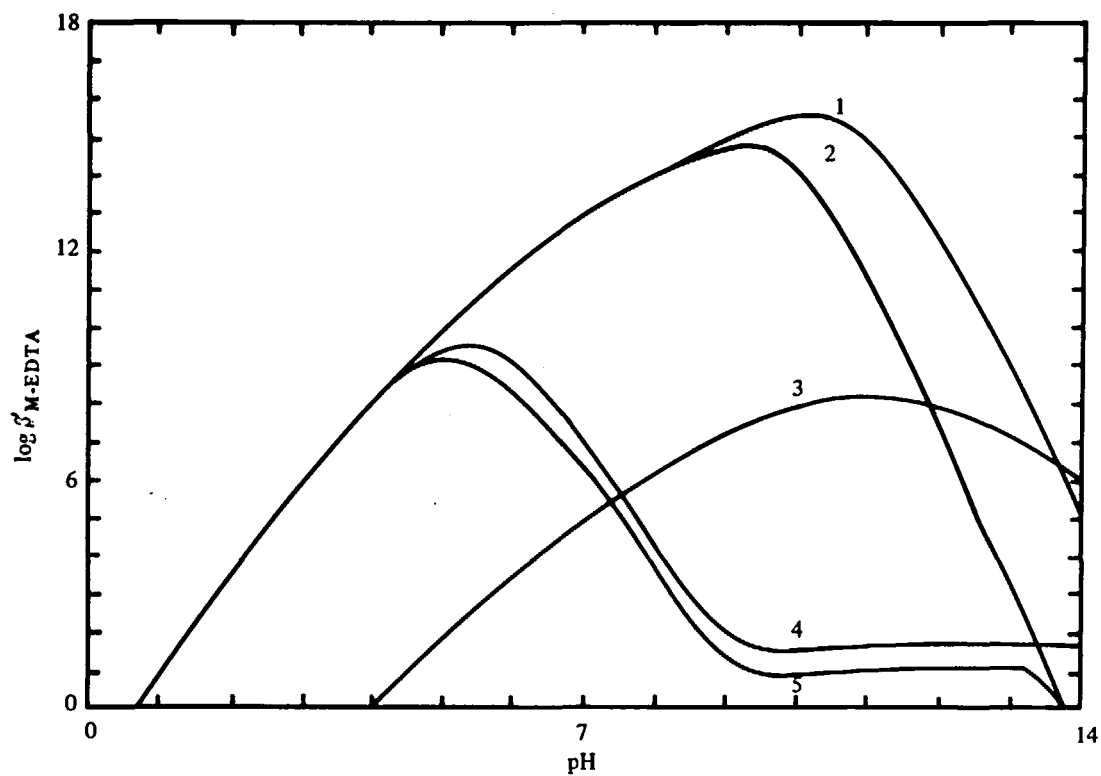


FIGURE 8. Masking of cadmium and zinc with cyanide ion in the EDTA titration of magnesium. 1. Cd^{2+} alone. 2. Zn^{2+} alone. 3. Mg^{2+} alone. 4. $\text{Cd}^{2+} + 0.1 M$ KCN. 5. $\text{Zn}^{2+} + 0.1 M$ KCN.

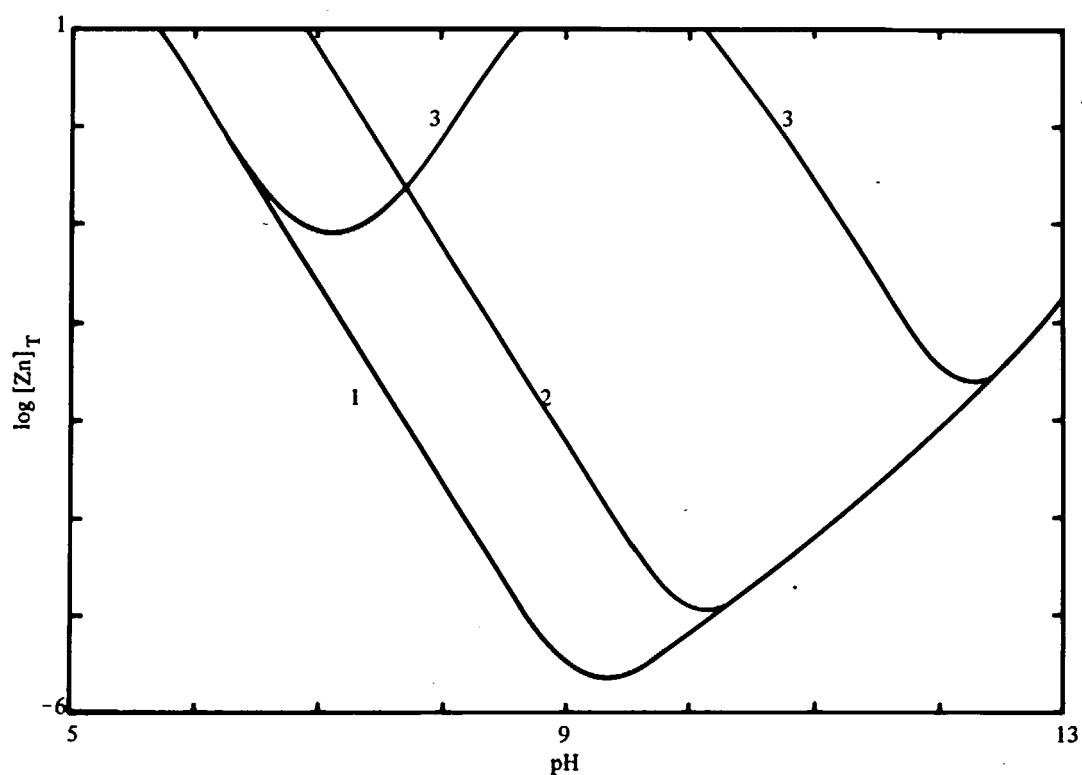


FIGURE 9. Masking by tartrate ion and ammonia against precipitation of zinc as the hydroxide. $\log [Zn]_T$ is the total possible concentration of soluble zinc species (including complexes) at any given pH. 1. Zn^{2+} alone. 2. $Zn^{2+} + 1 M$ tartrate. 3. $Zn^{2+} + 1 M NH_3$.

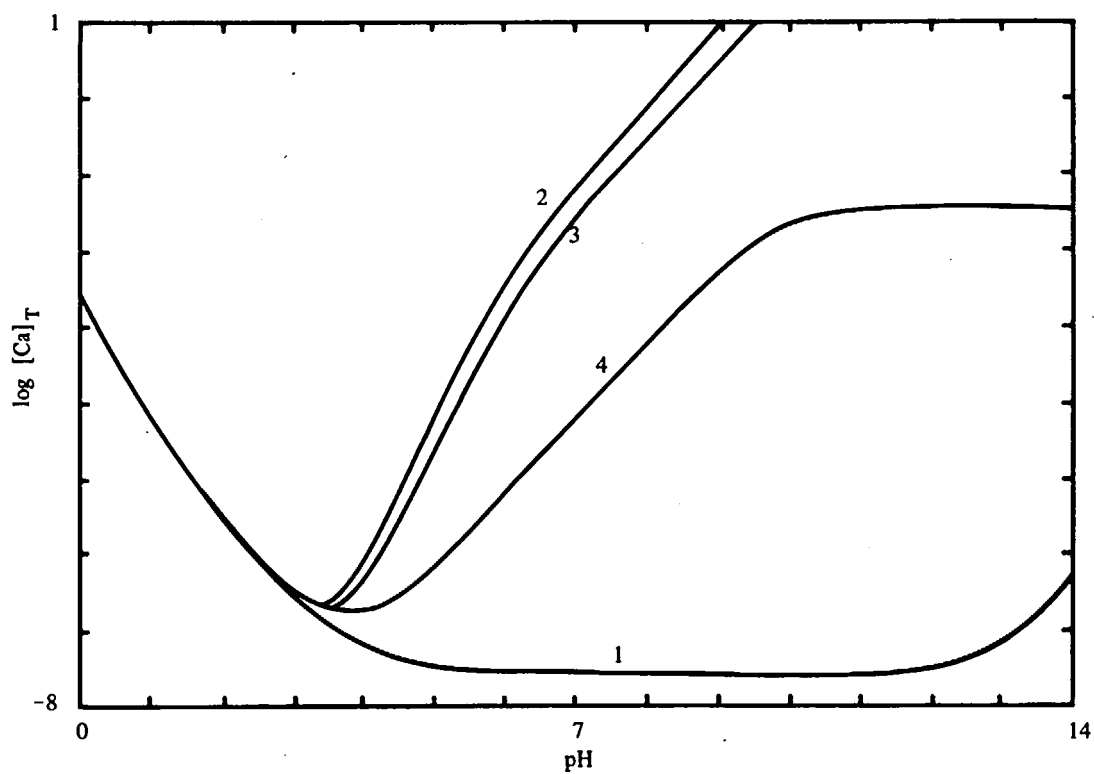


FIGURE 10. Masking of calcium oxalate precipitation in a solution 1 M in oxalate ion. 1. Ca^{2+} alone. 2. $Ca^{2+} + 0.1 M$ CDTA. 3. $Ca^{2+} + 0.1 M$ EDTA. 4. $Ca^{2+} + 1 M$ NTA.

IV. TYPICAL MASKING AGENTS

In general terms, desirable properties of masking agents include chemical stability, lack of toxicity, ready solubility of the agent and any complexes it forms and, usually, absence of color. Masking agents should also react rapidly and effectively with the species to be masked, forming a stable complex (if complex formation is involved), while at the same time reacting only weakly with the principal species.

The choice of such agents is also modified by the particular type of use that is envisaged. The toxicity of cyanide ion is well-known, and below pH 9, its use as a masking agent becomes hazardous because of the evolution of hydrogen cyanide. In spectrophotometric methods and colorimetric titrations, the use of thiocyanate ion or thioglycolic acid to mask iron(III) is unsatisfactory because of the intense color of the iron complexes. Formation of colored complexes is most likely to be a problem where organic reagents are used with transition metal ions. In this example, the intense red color can be avoided by prior masking of the iron(III) with triethanolamine in strongly alkaline solution to form a colorless complex which is not dissociated by thioglycolic acid. Where more than one masking agent is present, it is important that they are mutually stable. Oxidizing agents such as hydrogen peroxide cannot be used in the presence of reducing agents such as bisulfite or ascorbic acid. The intense color and powerful oxidizing action of permanganate ion may make the masking of manganese(II) by oxidation to permanganate unsuitable. Cyanide ion and formaldehyde (to mask ammonium ion) are incompatible. In some instances, alternative masking agents should be sought. For example, wherever possible the use of cyanide ion should be avoided. The bad odor of 2,3-dimercaptopropanol also militates against its choice as a masking agent.

The most commonly used masking agents and the cations they mask are listed in Table 4. The conditions under which they are effective depend largely on their pK_a values, the hydrolysis constants of the metal ions, and the natures of the ligand donor atoms.

Thus, ammonia (pK_a 9.2) is a suitable masking agent above pH 9 for many "soft" metal ions, and these can be demasked by acidifying the solution.

The pK_a values of carboxylic acids are around 5, and the donor properties of oxygen atoms favor

"hard" metal ions, which are usually of high valence. Such metal ions are likely to be strongly hydrolyzed in alkaline solution, so optimum masking is found in weakly acid or neutral solutions.

The "soft" ligand, cyanide ions, binds very strongly to "soft" metal ion, even reducing copper(II) to copper(I). Hydrocyanic acid is very weak (pK_a 9.2), and this limits the masking by cyanide ion to alkaline (ammoniacal) solutions. Surplus cyanide ion can be reacted with formaldehyde to form the cyanhydrin. Added in excess to a buffered solution, formaldehyde, or better, chloral hydrate⁶⁵ demasks zinc and cadmium, but not silver, cobalt, mercury, or nickel, from their cyano complexes. Manganese can be masked with cyanide ion by making a solution containing triethanolamine strongly alkaline so that it is rapidly oxidized by air to the green manganese(III) complex, followed by addition of excess cyanide ion and adjustment to pH 10 to give the weakly colored $Mn(CN)_6^{3-}$. Although the iron(III) triethanolamine complex is colorless, its presence is sometimes undesirable because it can oxidize Erio black T and several other indicators; this difficulty can be avoided by warming with cyanide ion to form $Fe(CN)_6^{3-}$. Oxidation of cobalt(II) cyanide complex with hydrogen peroxide gives the cobalt(III) cyanide complex, which is stable to silver nitrate.

Acetone cyanhydrin has been suggested for use in place of potassium cyanide as a masking agent in complexometric titrations.^{65a} Another alternative, effective over a similar pH range, is 2,3-dimercaptopropanol.

EDTA is a "hard" ligand which reacts with many metal ions; but, as shown in Figures 3 and 4, the conditional stability constants of most metal-EDTA complexes pass through pH maxima which depend on the ease of hydrolysis of the metal ions. The use of EDTA in buffered solutions makes it possible to mask a wide range of metal ions, the selectivity depending on the pH of the solution. Conversely, lowering the pH selectively demasks metal ions and permits the controlled precipitation of alkaline earth sulfates and oxalates or of barium and thallium chromates. Univalent cations, such as those of silver, gold, mercury, and thallium, are relatively weakly complexed by EDTA, so that EDTA is a suitable general purpose masking agent when, for example, Ti(I) is determined spectrophotometrically with sodium diethyldithiocarbamate at pH 10.6 to 11.1⁶⁶ or when Ag(I) is

TABLE 4

Some Common Masking Agents

| Masking agent | Ions masked |
|-----------------------------------|---|
| Ammonia | Ag(I), Cd(II), Co(II), Cu(II), Ni(II), Pd(II), Pt(II), Zn(II) |
| Carboxylic acid anions Citrate | Al(III), Fe(III), Ga(III), Mo(VI), Pb(II), Sc(III), Sn(II), Th(IV), Ti(IV), Zn(II), Zr(IV) |
| Tartrate | Al(III), Bi(III), Fe(III), Nb(V), Sb(III), Sn(IV), Ta(V), Ti(IV), U(VI), W(VI), Zr(IV) |
| Cyanide ion | Ag(I), Cd(II), Co(II), Cu(II), Fe(II), Hg(II), Mn(III), Ni(II), Pd(II), Pt(II), Tl(III), Zn(II) |
| 2,3-Dimercaptopropanol | As(III), Bi(III), Cd(II), Cu(II), Hg(II), Ph(II), Sn(IV), Zn(II) |
| EDTA | Most metal ions |
| Fluoride ion | Al(III), Ba(II), Be(II), Ca(II), Ce(IV), Fe(III), In(III), Mg(II), Nb(V), rare earths, Sb(III), Sc(III), Sn(IV), Sr(II), Ta(V), Th(IV), Ti(IV), Y(III), Zr(IV) |
| Hydrogen peroxide | Co(II), Cr(III), Ti(IV), V(V), W(VI), Zr(IV) |
| Hydroxyl ion | Al(III), Mg(II), Zn(II) |
| Iodide ion | Ag(I), Hg(II), Pb(II), Sb(III), Sn(IV) |
| 1,10-Phenanthroline | Cd(II), Co(II), Cu(II), Mn(II), Zn(II) |
| Reducing agents | |
| Ascorbic acid | Cu(II), Fe(III), Hg(II), Ti(IV), Tl(III), V(V) |
| Hydroxylamine | Cu(II), Fe(III), Mn(III), Mo(VI), V(V), W(VI) |
| Thiosulfate ion | Cu(II), Pb(II), Bi(III) |
| Thiourea | Cu(II), Hg(II), Fe(III), Pt(IV) |
| Thioglycolic acid | Ag(I), Bi(III), Cd(II), Cu(II), Hg(II), In(III), Pb(II), Zn(II) |
| Triethanolamine | Al(III), Cr(III), Fe(III), Sn(IV), Ti(IV) |

titrated potentiometrically with sodium thiosulfate.⁶⁷ Beryllium forms only weak complexes with EDTA. This is the basis for the use of EDTA to mask a wide range of metal ions in methods for beryllium. These include the spectrophotometric determination of beryllium with thoron at pH 10 to 11,⁶⁸ a gravimetric method for beryllium at pH 7 to 7.5,⁶⁹ a polarographic method for beryllium,⁷⁰ and (masking aluminum) a fluorometric method for beryllium.⁷¹ A recent study of the

masking action of propylenediaminetetraacetic acid shows it to be very similar to EDTA.⁷²

The masking action of fluoride ion is almost independent of pH (the pK of hydrofluoric acid is 3.1) and is limited to "hard" cations, including aluminum and the alkaline earth cations with which it forms insoluble salts. Iodide ion, on the other hand, reacts with "soft" cations, forming precipitates; it interacts so strongly with copper(II) as to reduce it to copper(I).

Similar examinations of the properties of other reagents suggest the types of conditions in which they are likely to be suitable as masking agents. Bearing in mind that the extent to which a metal ion requires to be masked depends on many factors, Table 5 lists substances that have been used as masking agents, arranged in groups under the metal ion masked.

In applying Table 5 to choose a masking agent for metal 1 in the determination of metal 2, it is appropriate to consider the substances that are listed under metal 1 but not under metal 2. Thus, in the analysis of copper/zinc alloys, any iron(III) is masked by fluoride ion in the EDTA titration of zinc plus copper at pH 7 to 11 in ammonia buffer, while thiosulfate ion is used to reduce, and

TABLE 5

Masking Agents^a for Cations

| | |
|----|---|
| Ag | NH ₃ , CN ⁻ , I ⁻ , Br ⁻ , Cl ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , thiourea, TGA, DDC, BHEDTC, TSC, citrate, DMP |
| Al | F ⁻ , BF ₄ ⁻ , carboxylates, ^b gluconate, mannitol, salicylate, SSA, tiron, EDTA, TEA, acetylacetone, BAL, OH ⁻ , HQSA |
| As | S ²⁻ , DMP, unithiol, DTT, carboxylates, HAH, OH ⁻ |
| Au | NH ₃ , CN ⁻ , I ⁻ , Br ⁻ , Cl ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , thiourea, TGA, DDC, BHEDTC, TSC, citrate, DMP, reduction with SO ₂ |
| Ba | APCA, ^c BHG, carboxylates, F ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ |
| Be | Carboxylates, APCA, tiron, SSA, acetylacetone, F ⁻ |
| Bi | I ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , DDC, TGA, unithiol, DMP, BHEDTC, MPA, MSA, DMSA, DTCA, cysteine, dithizone, thionalide, thiourea, carboxylates, APCA, tiron, SSA, TEA, BHG, Cl ⁻ , F ⁻ , OH ⁻ , triphosphate, ascorbic acid |
| Ca | APCA, BHG, carboxylates, F ⁻ , BF ₄ ⁻ , polyphosphate |
| Cd | I ⁻ , CN ⁻ , S ₂ O ₃ ²⁻ , SCN ⁻ , DDC, BHEDTC, DMP, unithiol, cysteine, thionalide, cysteamine, DTCA, MPA, DMSA, DMPA, BCMDTC, dithizone, TGA, carboxylates, glycine, BHG, APCA, Pb-EGTA, NH ₃ , tetren, 1,10-phen |
| Ce | F ⁻ , PO ₄ ³⁻ , P ₂ O ₇ ⁴⁻ , carboxylates, BHG, APCA, tiron, reducing agents |
| Co | CN ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , F ⁻ , NO ₂ ⁻ , carboxylates, tiron, glycine, BHG, TEA, APSA, TGA, BAES, DDC, BHEDTC, cysteamine, DMPA, DMSA, MPA, DMP, DTCA, unithiol, NH ₃ , polyamines, ^d 1,10-phen, DMG, H ₂ O ₂ , triphosphate |
| Cr | Carboxylates, tiron, SSA, BHG, APCA, TEA, F ⁻ , P ₂ O ₇ ⁴⁻ , PO ₄ ³⁻ , triphosphate, SO ₄ ²⁻ , NaOH + H ₂ O ₂ , ascorbic acid, oxidation to CrO ₄ ²⁻ |
| Cu | NH ₃ , polyamines, 1,10-phen, carboxylates, tiron, glycine, BHG, picolinic acid, ADA, APCA, S ₂ ⁻ , TGA, BAEA, DDC, DMSA, DMPA, MPA, thionalide, DTCA, BCMDTC, BHEDTC, DMP, TSC, thiocarbonylhydrazide, cysteine, cysteamine, CN ⁻ , thiourea, S ₂ O ₃ ²⁻ , SO ₃ ²⁻ + SCN ⁻ , I ⁻ , ascorbic acid + I ⁻ , N ₂ H ₄ , HAH, Co(CN) ₆ ³⁻ , NO ₂ ⁻ |
| Fe | Carboxylates, APCA, TEA, glycerol, acetylacetone, EBHPG, tiron, SSA, BHG, OH ⁻ , F ⁻ , PO ₄ ³⁻ , P ₂ O ₇ ⁴⁻ , S ²⁻ , trithiocarbonate, S ₂ O ₃ ²⁻ , DMP, DMSA, unithiol, MSA, MPA, BHEDTC, TGA, HQSA, CN ⁻ , reducing agents, ^e 1,10-phen, bipy |
| Ga | Carboxylates, SSA, APCA, OH ⁻ , Cl ⁻ , unithiol |
| Ge | Carboxylates, F ⁻ |
| Hf | Carboxylates, APCA, SSA, TEA, BHG, PO ₄ ³⁻ , P ₂ O ₇ ⁴⁻ , F ⁻ , SO ₄ ²⁻ , H ₂ O ₂ |

TABLE 5 (continued)

Masking Agents^a for Cations

| | |
|---------------------------------|--|
| Hg | CN ⁻ , Cl ⁻ , I ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , carboxylates, BAES, APCA, TEA, BHG, thionalide, cysteamine, potassium ethylxanthate, cysteine, TGA, DMP, unithiol, thiourea, DDC, BHEDTC, CMMSA, MPA, DTCA, DMSA, TSC, polyamines, reducing agents |
| In | Tartrate, EDTA, TEA, F ⁻ , Cl ⁻ , SCN ⁻ , TGA, unithiol, thiourea |
| Ir | CN ⁻ , SCN ⁻ , carboxylates, thiourea |
| La | Carboxylates, APCA, tiron, F ⁻ |
| Mg | Carboxylates, tiron, glycol, TEA, BHG, APSA, OH ⁻ , F ⁻ , BF ₄ ⁻ , PO ₄ ³⁻ , P ₂ O ₇ ⁴⁻ , hexametaphosphate |
| Mn | Carboxylates, tiron, SSA, APCA, TEA, TEA + CN ⁻ , BHG, F ⁻ , P ₂ O ₇ ⁴⁻ , triphosphate, CN ⁻ , DMP, HAH, N ₂ H ₄ , oxidation to MnO ₄ ⁻ |
| Mo | Carboxylates, acetylacetone, tiron, APCA, BHG, F ⁻ , triphosphate, H ₂ O ₂ , SCN ⁻ , mannitol, reducing agents, oxidation to MoO ₄ ²⁻ |
| Nb | Carboxylates, tiron, F ⁻ , OH ⁻ , H ₂ O ₂ |
| Nd | EDTA |
| (NH ₄ ⁺) | HCHO |
| Ni | Carboxylates, APCA, SSA, BHG, glycine, ADA, picolinic acid, F ⁻ , CN ⁻ , SCN ⁻ , BAES, cysteamine, DDC, BCMDTC, BHEDTC, potassium ethylxanthate, TGA, DMSA, DMPA, NH ₃ , polyamines, 1,10-phen, DMG, triphosphate |
| Np | F ⁻ |
| Os | CN ⁻ , SCN ⁻ , thiourea |
| Pa | H ₂ O ₂ |
| Pb | Carboxylates, tiron, APCA, TEA, BHG, OH ⁻ , F ⁻ , Cl ⁻ , I ⁻ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , DTCA, TGA, DMP, potassium ethylxanthate, unithiol, thionalide, DMSA, DMPA, MPA, DDC, BCMDTC, BHEDTC, PO ₄ ³⁻ , triphosphate, tetraphenylarsonium chloride |
| Pd | CN ⁻ , SCN ⁻ , I ⁻ , NO ₂ ⁻ , S ₂ O ₃ ²⁻ , carboxylates, APCA, TEA, BHG, acetylacetone, NH ₃ , thiourea |
| Pt | CN ⁻ , SCN ⁻ , I ⁻ , NO ₂ ⁻ , S ₂ O ₃ ²⁻ , carboxylates, APCA, TEA, BHG, acetylacetone, NH ₃ , thiourea |
| Pu | Reduction to Pu(IV) with sulfamic acid |
| Rare earths | Carboxylates, APCA, F ⁻ |
| Re | Oxidation to perrhenate |
| Rh | Carboxylates, thiourea |
| Ru | CN ⁻ , thiourea |
| Sb | Carboxylates, TEA, F ⁻ , Cl ⁻ , I ⁻ , OH ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , DMP, potassium ethylxanthate, unithiol |
| Sc | F ⁻ , tartrate, APCA |
| Se | F ⁻ , I ⁻ , S ²⁻ , SO ₃ ²⁻ , carboxylates, reducing agents |

TABLE 5 (continued)

Masking Agents^a for Cations

| | |
|----|--|
| Sn | Carboxylates, EDTA, TEA, F ⁻ , Cl ⁻ , I ⁻ , OH ⁻ , PO ₄ ³⁻ , TGA, DMP, unithiol, bromine water (oxidation) |
| Sr | APCA ^c , BHG, carboxylates, F ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ |
| Ta | Carboxylates, EDTA, F ⁻ , OH ⁻ , H ₂ O ₂ |
| Te | Carboxylates, F ⁻ , I ⁻ , S ²⁻ , SO ₃ ²⁻ , reducing agents |
| Th | Carboxylates, SSA, TEA, BHG, APCA, F ⁻ , SO ₄ ²⁻ , 4-sulfobenzenearsonic acid, tiron, acetylacetone |
| Ti | Carboxylates, gluconate, mannitol, SSA, TEA, BHG, APCA, EDTA + H ₂ O ₂ , tiron, ascorbic acid, ferron, OH ⁻ , SO ₄ ²⁻ , F ⁻ , H ₂ O ₂ , PO ₄ ³⁻ , triphosphate |
| Tl | Carboxylates, TEA, BHG, APCA, DTCA, BHEDTC, unithiol, TGA, Cl ⁻ , CN ⁻ , HAH |
| U | Ammonium carbonate, carboxylates, acetylacetone, SSA, EDTA, F ⁻ , H ₂ O ₂ , PO ₄ ³⁻ |
| V | Carboxylates, TEA, tiron, mannitol, EDTA, CN ⁻ , reducing agents, H ₂ O ₂ , oxidation to vanadate |
| W | Carboxylates, tiron, mannitol, APCA, F ⁻ , PO ₄ ³⁻ , SCN ⁻ , H ₂ O ₂ , triphosphate, HAH, oxidation to tungstate |
| Y | APCA, F ⁻ |
| Zn | NH ₃ , polyamines, 1,10-phen, carboxylates, APCA, glycol, glycerol, TEA, glycine, BHG, CN ⁻ , OH ⁻ , SCN ⁻ , Fe(CN) ₆ ⁴⁻ , DMP, unithiol, BAES, TGA, dithizone, triphosphate |
| Zr | Carboxylate, malate, salicylate, SSA, pyrogallol, tiron, TEA, BHG, APCA, F ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , + H ₂ O ₂ , PO ₄ ³⁻ , P ₂ O ₇ ⁴⁻ , OH ⁻ , cysteine |

^aAbbreviations as in Table 3.^bAcetate, citrate, formate, malonate, oxalate, tartrate.^cAminopolycarboxylic acids: CDTA, DTPA, EDTA, EDTP, EGTA, HEDTA, HMDTA, NTA, PDTA, TTHA.^dPolyamines: en, tren, tetren, penten.^eAscorbic acid, HAH, SO₃²⁻, SnCl₂, sulfamic acid, thiourea.

thereby mask, copper(II) in the EDTA titration of zinc.⁷³ Similarly, in the spectrophotometric determination of calcium with methyl xylene blue at pH 11.5 to 12, cyanide ion is a suitable masking agent for cadmium, cobalt, copper, mercury, nickel, and zinc.^{73a} On the other hand, triethanolamine masks iron(III), aluminum, and manganese(II) while allowing copper(II) to be titrated with EDTA. Dimercaptopropanol and bis(2-hydroxyethyl)dithiocarbamate mask di- and trivalent transition metal ions at pH 3 when thorium is titrated with EDTA.⁷⁴

Few generalities are possible in discussing the masking of anions and neutral molecules, using the agents given in Table 6. Although inorganic anions masks many cations, the converse is not often

true. One example is the use of silver sulfate to mask bromide, iodide, and thiocyanate ions by precipitation in a spectrophotometric method for nitrate and nitrite.⁷⁵ Cyanide ion can be determined by the extent to which it binds silver, promoting the dissociation of the colored ternary complex, silver(I)-1,10-phenanthroline-bromopyrogallol red.⁷⁶ Table 6 also includes reactions in which the anion or neutral molecule is partly or wholly destroyed, although these are not strictly masking reactions. Thus, in the determination of hydrogen peroxide by a chemiluminescence method based on the copper catalysed oxidation of luminol, chlorite ion is destroyed (not masked) by ammonia.⁷⁷ On the other hand, in the determination of chlorite ion by the same method, hydrogen peroxide is masked by sodium vanadate.

TABLE 6

Masking Agents for Anions and Neutral Molecules

| | |
|---|---|
| Boric acid | F ⁻ , polyols, ^a hydroxy acids, fructose |
| Br ⁻ | Hg(II), Ag(I) |
| Br ₂ | Phenol, sulfosalicylic acid |
| BrO ₃ ⁻ | Reducing agents (N ₂ H ₄ , SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , AsO ₂ ⁻) |
| Citrate | Ca ²⁺ |
| CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻ | Reducing agents (hydroxylamine HCl, N ₂ H ₄ , SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , AsO ₂ ⁻ , ascorbic acid) |
| Cl ⁻ | Hg(II), Sb(III) |
| Cl ₂ | SO ₃ ²⁻ |
| ClO ⁻ | NH ₃ |
| ClO ₃ ⁻ | S ₂ O ₃ ²⁻ |
| ClO ₄ ⁻ | SO ₃ ²⁻ , NH ₂ OH·HCl |
| CN ⁻ | Hg(II), HCHO, chloral hydrate, transition metal ions |
| EDTA | Cu(II), H ₂ O ₂ + heat (molybdic acid is a catalyst ^{1,4,6}) |
| F ⁻ | H ₃ BO ₃ , Al(III), Be(II), Zr(IV), Th(IV), Ti(IV), Fe(III) |
| Fe(CN) ₆ ³⁻ | Reducing agents (NH ₂ OH·HCl, N ₂ H ₄ , S ₂ O ₃ ²⁻ , AsO ₂ ⁻ , ascorbic acid) |
| Germanic acid | Polyols, glucose |
| H ₂ O ₂ | NaVO ₃ , Fe(III) |
| I ⁻ | Hg(II), Ag(I) |
| I ₂ | S ₂ O ₃ ²⁻ |
| IO ₃ ⁻ | Reducing agents (SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , N ₂ H ₄) |
| IO ₄ ⁻ | Reducing agents (SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , N ₂ H ₄ , AsO ₂ ⁻ , ascorbic acid), MoO ₄ ²⁻ |
| MnO ₄ ⁻ | Reducing agents (NH ₂ OH·HCl, ascorbic acid, NaN ₃ , N ₂ H ₄ , SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , AsO ₂ ⁻ , oxalic acid) |
| MoO ₄ ²⁻ | Citrate, oxalate, F ⁻ , H ₂ O ₂ , SCN ⁻ + Sn(II) |
| NO ₂ ⁻ | Urea, sulfanilic acid, sulfamic acid, Co(II) |
| Oxalate | MoO ₄ ²⁻ , MnO ₄ ⁻ , Ca ²⁺ |
| Phosphate | Tartrate, Fe(III), Al(III) |
| S | CN ⁻ , S ²⁻ , SO ₃ ²⁻ |
| S ²⁻ | KMnO ₄ + H ₂ SO ₄ , S |
| SCN ⁻ | Ag(I) |
| SO ₃ ²⁻ | Hg(II), KMnO ₄ + H ₂ SO ₄ , HCHO |
| S ₂ O ₃ ²⁻ | MoO ₄ ²⁻ + H ₂ O ₂ + H ₂ SO ₄ |
| SO ₄ ²⁻ | Ba(II), Cr(III) + heat, Th(IV) |
| SO ₅ ²⁻ | Reducing agents (NH ₂ OH·HCl, S ₂ O ₃ ²⁻ , ascorbic acid) |
| Se and its anions | S ²⁻ , SO ₃ ²⁻ , diaminobenzidine |
| Tartrate | Cu(II) + H ₂ O ₂ |
| Te | I ⁻ |
| Tungstate | Citrate, tartrate |
| Vanadate | Tartrate |

^aGlycols, glycerol, mannitol, sorbitol.

A. Combinations

From the foregoing discussion, it is apparent that no general mixture of masking agents is likely to be applicable to the determination of given metal ion by different methods. Unless quantitative calculations are carried out, any possible selection of masking agents remains largely empirical. However, some practical guidance can be given by considering examples in which mixtures of masking agents have been used.

The masking effects of citric and tartaric acids are substantially independent of pH above pH 6. In an EDTA solution in the pH region 5 to 6.5, citric and tartaric acids help to buffer a solution and at the same time augment the masking capability to include the alkaline earth cations, molybdenum(VI), and tungsten(VI) that are poorly masked by EDTA under these conditions. The presence of citrate or tartrate also decreases the risk of hydrolytic precipitation of metal ions. At pH 5, tartrate masks lead against precipitation as lead fluoride but does not prevent the EDTA titration of lead, whereas fluoride ion masks tin(IV) against titration.⁷⁸

On the other hand, as the curve for Al-EDTA in Figure 3 illustrates, in alkaline or weakly alkaline solutions the conditional stability constants of some complexes can be greatly lowered by the hydrolysis of the metal ion. Examples include EDTA complexes of aluminum, chromium(III), iron(III), tin(IV), and titanium(IV). However, these ions form stable soluble complexes with triethanolamine, which exhibits its maximum masking effect above pH 8, so that when these ions are present, triethanolamine is useful to supplement the masking action of EDTA. In strongly alkaline solution, triethanolamine probably loses a proton to form an anionic ligand that binds these metal ions even more firmly. It also has the merit of forming a colorless complex with iron(III). Oxidation of manganese(II) in alkaline solutions of triethanolamine to form the intensely green manganese(III) complex can be avoided by adding ascorbic acid.

When cyanide or thiocyanate ion is added to solutions containing copper(II), reduction to copper(I) occurs, with evolution of cyanogen or thiocyanogen. Cyanide ion also reacts with iron(III) to give intensely colored ferri- and ferrocyanides. Both of these difficulties are avoided by including ascorbic acid as a reducing agent. (Ferrous ferrocyanide is pale straw-colored.)

Similarly, in the presence of a reducing agent, iodine is not liberated when iodide ion is used as a masking agent in solutions originally containing copper(II) or iron(III).

A method for the determination of niobium(V) at pH 6.0 with pyrogallol red⁷⁹ illustrates the use of a mixture of masking agents. Ascorbic acid reduces cerium(IV) to cerium(III) and vanadium(V) to vanadium(IV). Acetate, tartrate, and 0.01 M EDTA mask molybdenum, antimony, tantalum, titanium, and tungsten. Fluoride ion masks aluminum and thorium, phosphate masks uranium(VI) and thorium, and cyanide ion masks silver. Similarly, when thorium is determined with acid alizarine black SN at pH 4.2,⁸⁰ ascorbic acid plus cyanide ion masks cobalt, copper, iron, and nickel, thioglycolic acid masks bismuth, potassium iodide masks antimony(III) and tin(IV), triethanolamine masks titanium, sulfosalicylic acid masks aluminum, tiron masks tungsten(VI) and molybdenum(VI), and the ascorbic acid also masks cerium(IV) by reduction.

The fact that the concentrations of masking agents usually exceed those of the metal ions makes it possible to assess rapidly their relative effectiveness in any given situation. If a metal ion forms the major complex ML_n , stability constant β , with the ligand L when $[L]_T \gg [M]_T$, the approximation

$$[ML_n] \approx [M]_T \quad (8)$$

applies, and the total concentration of ligand not complexed to metal ion is approximately $[L]_T - n[M]_T$. The negative logarithm of the concentration of free metal ion, pM, is given by

$$pM = \log \beta - \log M_T + n \log (L_T - nM_T) - n \log (1 + 10^{pK_1 - pH} + 10^{pK_1 + pK_2 - 2pH} + \dots) \quad (9)$$

where the pK values are for the ligand. *The most effective masking agent is the one for which pM has the greatest value.*

As an example, consider the masking action of 0.1 M citrate, 0.1 M cyanide ion, 1 M fluoride ion and 0.1 M EDTA on 0.001 M solutions of copper, zinc, and aluminum ions at pH 9. Using the equation, computed values for pCu are 24.4, 27.7, and 20.1 for the cyano complexes $Cu^I(CN)_2^-$, $Cu^I(CN)_3^{2-}$, $Cu^I(CN)_4^{3-}$, 19.5 for Cu(II)-EDTA, and only 8.1 for CuCit, 3.7 for CuF. Thus, cyanide ion is the most effective masking agent for copper. Similar calculations for zinc give pZn as 14.5 for

$\text{Zn}(\text{CN})_4^{2-}$, 17.2 for Zn-EDTA, 6.5 for ZnCit, and 3.7 for ZnF, so that here EDTA is the most effective masking agent. For aluminum, on the other hand, complexation with cyanide is negligible, while pAl is 9.0 for AlCit, 20.7 for AlF_4^- , 22.4 for AlF_5^{2-} , 22.7 for AlF_6^{3-} , and 16.8 for Al-EDTA, indicating that in this case fluoride ion is the best masking agent.

B. Ligand Buffers

If an excess of a metal ion is added to a solution containing a ligand so that the complex ML is formed with stability constant β

$$[\text{M}^{2+}] \approx [\text{M}]_{\text{T}} - [\text{L}]_{\text{T}} \quad (10)$$

$$[\text{ML}] \approx [\text{L}]_{\text{T}} \quad (11)$$

$$[\text{L}] \approx 1 / \{ \beta \cdot ([\text{M}]_{\text{T}} / [\text{L}]_{\text{T}} - 1) \} \quad (12)$$

The concentration of L is independent of the pH and pK_a values of the ligand, but varies inversely with β as long as these approximations apply. They fail when the pH is low enough that proton-ligand binding becomes comparable with metal-ligand interaction.

Such a system is a "ligand buffer."⁸¹ It provides a means for selective masking, depending on the choice of the metal ion. Thus, if two metals differ significantly in the stability constants of their complexes, the less strongly complexing metal ion is virtually not masked if the other metal ion is present in excess. Conversely, more strongly complexing metal ions continue to be masked by the ligand. For such a given metal ion, M, the maximum conditional stability constant is decreased by a factor of approximately $\beta_{\text{ML}} \cdot ([\text{M}]_{\text{T}} - [\text{L}]_{\text{T}})$. A theoretical treatment has been given⁸¹ of the use of a ligand buffer (EDTA containing excess calcium ion) in the precipitation of iron(III) hydroxide. This treatment can be applied in the separation of sparingly soluble salts. Similar calculations are given for the extraction of copper-8-hydroxyquinolate from solutions containing masking agents such as EDTA-calcium and NTA-calcium.⁸¹ An EDTA-strontium ligand buffer was used to overcome interference by calcium, lanthanum, and yttrium in a spectrofluorimetric method for magnesium.⁸²

Another application of ligand buffers is in the selective polarographic determination of a metal ion in the presence of a second metal ion which

has a polarographic wave at a less negative potential. Cadmium has been masked by EGTA-barium in the determination of zinc,⁸³ EGTA being preferred to EDTA because of the greater difference between the stability constants of the cadmium and zinc complexes. Other suggested applications include EDTA-thorium to mask indium in the determination of cadmium, and of bismuth in the determination of lead.⁸³

In the paper electrophoresis of metal ions, EDTA-magnesium ligand buffers have been used in obtaining electrophoretic mobility curves of alkaline earth cations; EDTA-zinc has been used for bivalent heavy metal ions and for the rare earth cations.⁸⁴ These curves are independent of pH. The technique has been applied to the quantitative analysis of rare earth mixtures.⁸⁵ The theoretical basis of the method has been discussed.⁸⁶

V. SOME APPLICATIONS OF MASKING AND DEMASKING IN ANALYTICAL PROCEDURES

The extensive use of masking and demasking techniques in analytical chemistry has recently been discussed in detail.³⁸ The present review is intended to outline general principles and to supplement the material given in these references. Also, although there are many specialized applications of masking (such as in improving the separation of phosphate, silicate, arsenate, and germanate by the ring-oven method⁸⁷), discussion has been limited to the major categories of analytical procedures.

A. Titrimetry

Complexometric titrations with EDTA and other aminopolycarboxylic acids offer the advantage that many different cations can be determined using the same volumetric solution. However, to improve the otherwise very poor selectivity of such methods, prior separations or adequate masking procedures are essential. Masking in complexometry has been reviewed,^{6,7} and an earlier tabulation of EDTA titration methods that use masking is available.⁸⁸

In EDTA titrations, an interfering metal ion is masked when the conditional stability constant of its EDTA complex is decreased relative to that of the ion to be determined. The greater the difference, the more effective is the masking. Because the conditional constants of metal-EDTA

complexes are pH dependent, it is sometimes possible to achieve adequate masking simply by pH control. A value of at least 7 for $\log \beta_{\text{conditional}}$ and a difference of at least 4 to 5 between values of $\log \beta_{\text{conditional}}$ for different metal ion-EDTA complexes are needed if metal ions are to be titrated in the presence of one another. (This conclusion is based on the equation for the concentration of free metal ion at the endpoint of a complexometric titration in the presence of a masking agent, A ,^{5,5}

$$pM_{\text{ep}} = 0.5(\log \beta_{\text{conditional}} + pM_T) + \log \alpha_{M(A)} \quad (13)$$

given that $[M]_T$ is usually 10^{-2} to 10^{-4} M and the titration error is to be less than 1%.) Titration of calcium at pH 12 in the presence of aluminum, and of aluminum at pH 5 in the presence of calcium, is an example.⁸ Usually, however, masking agents are required and, for titrations using visual endpoints, the agents and the complexes they form must be either colorless or nearly so.

As a guide, difficulties due to colored complexes are most likely to be found with transition metal cations, especially with ligands containing donor nitrogens or sulfurs or aromatic systems. Thus, iron(III) forms an intensely red acetylacetonate, whereas the aluminum complex is colorless. In alkaline solution, manganese(III) forms an intensely green complex with triethanolamine.

In some instances, high selectivity is achieved by displacement reactions. Addition of thiosemicarbazide displaces mercury(II) from its EDTA complex, and the amount of mercury(II) can be determined by back-titration of the free EDTA with lead nitrate. A method for the determination of copper(II) in the presence of nickel is based on the selective displacement of copper from its EDTA complex by thioglycolic acid.

Reaction between the desired metal ion and the metallochromic indicator is also complex formation; for optimum indicator sensitivity, the value of $\log \beta_{\text{conditional}}$ for the metal-indicator complex should be approximately equal to pM_{ep} . When another metal ion is present that can form a much more stable complex, the indicator is "blocked" and can no longer show the desired endpoint. Thus, traces of cobalt, copper, iron, and nickel ions block Erio black T in EDTA titrations of manganese and zinc. This difficulty can be

overcome by prior addition of suitable masking agents. (In the example given, thiourea would mask copper(II) and fluoride ion would mask iron(III).) The alternative is to use a less strongly complexing indicator, such as murexide.

EDTA binds silver ion only weakly, so that it can be used to mask many cations in the argentometric titration of cyanide ion.^{8,9}

In complexometric titrations, it sometimes happens that a masking agent acts as a bridging ligand to form a mixed-metal binuclear complex with the cation to be determined and an interfering cation. If this complex is "robust" or kinetically inert, it will not be titrated and error will result. Examples are EDTA titrations of aluminum in the presence of uranyl ion and citrate,⁹⁰ copper in the presence of chromium and citrate,⁹¹ and copper in the presence of aluminum and tartrate.⁹²

B. Precipitations

Agents that are intended to mask metal ions against precipitation should either be strongly hydrophilic, bearing many polar groups to favor strong hydrogen bonding to solvent water molecules, or else form a charged complex with the metal ion to be masked. Particularly for ter- and tetravalent cations, the most familiar examples are the hydroxycarboxylic acids, such as citric, tartaric, and sulfosalicylic acids, used to prevent hydrolytic precipitation of these cations as their hydroxides. If the concentration of free metal ion is low enough, formation of polynuclear species can be ignored. Under this condition, the maximum concentration of free metal ion decreases with pH;

$$\log [M^{n+}]_{\text{max}} = (n \cdot pK_w - pK_{sp}) - n \cdot pH \quad (14)$$

where pK_w is for the ionization of water and pK_{sp} is the solubility product of the hydroxide $M(OH)_n$. As the solubility products of many metal hydroxides are known,³ it is easy to calculate the maximum pH at which a specified concentration of metal ion can be maintained in solution without added masking agent.

The general case in which a substance M_xL_y is precipitated from solution in the presence of a masking agent can be examined conveniently by the α -coefficient method using a conditional solubility product, $[M]_T^x [L]_T^y$, which is related to the true solubility product, $S_{M_xL_y}$, by

$$(\alpha_M)^x (\alpha_L)^y \cdot S_{M_xL_y} = [M]_T^x [L]_T^y \quad (15)$$

The α -coefficients include the effects of masking agents and, as α_L is usually pH dependent, the relation also enables the effect of pH to be interpreted. Factors that govern the total concentration, $[M]_T$, of a metal species remaining in solution are the solubility product of its salt with L, the stability constant of the metal complex with added masking agent, the stoichiometry, the effect of pH on $\alpha_{L(H)}$ and $\alpha_{A(H)}$, where A is the masking agent, and the presence of other metal ions that react with the masking agent.

If the masking agent forms a complex MA_a , stability constant β , with the metal ion, and if the total concentrations of precipitant and masking agent are large relative to the metal ion, it can be deduced that the maximum concentration of metal ion $[M]_T$ that can be present in solution is given by

$$x \log [M]_T = \log S_{MX} L_y - y \log [L]_T + x \log \beta + ax \log [A]_T - ax \log \alpha_{A(H)} + y \log \alpha_{L(H)} \quad (16)$$

Provided the solubility products and stability constants are known, it can readily be predicted whether it is possible to separate two metal ions by selectively precipitating one of them; values of $[M]_T$ for each metal ion can be obtained by solving this equation using appropriate constants and concentrations. Where the concentration of masking agent approaches the total metal ion concentration, the more exact relation given by Ryan⁹³ should be used. For a fuller discussion of the quantitative treatment, with examples, based on the generalization of an equation due to Hulanicki⁹⁴ see Kelly and Sutton.⁹⁵

Masking can be combined with other procedures. Thus, for the determination of traces of bismuth (by polarography) and iron (by photometry) in lead, the lead was masked against precipitation using EDTA when the bismuth and iron were coprecipitated with magnesium hydroxide as carrier from alkaline solution.⁹⁶

Selectivity can often be increased by controlled precipitation from homogeneous solution⁹⁷ in which the concentration of one of the components of the species to be precipitated is kept low but is slowly increased, commonly by a demasking procedure. In a recent example, calcium was precipitated as the oxalate in the presence of lead, copper, zinc, and cadmium by masking with EDTA at pH 8.8 and then boiling with hydrogen peroxide (to oxidize EDTA and demask calcium)

after adding excess oxalate ion.⁹⁸ Manganese(II) was precipitated as its 8-hydroxyquinoline complex in the presence of calcium ion by using urease to split urea with the liberation of ammonia, thereby raising the pH.⁹⁹ Separation of barium from strontium and lead by precipitation as the chromate depended on masking with CDTA or PDTA at pH 10.3 in the presence of dilute ammonia and dichromate ion, followed by heating so that ammonia was lost and the pH fell slowly to from 6.7 to 6.8.¹⁰⁰ In the presence of tartaric acid to mask antimony and tin, lead was precipitated as the sulfate by cation replacement by iron(III). The latter was generated by adding EDTA and ferrous ammonium sulfate to a solution at pH 1 to 3 containing lead; by heating on a water bath until the volume became small, iron(II) was oxidized to iron(III).¹⁰¹ A similar method uses copper and nickel instead of iron.¹⁰² For other examples, see Reference 3.

C. Spectrophotometry

Methods based on the formation of a colored complex by a metal ion are more selective than complexometric titrations, and masking requirements are correspondingly less stringent. When photometric measurements are made directly on the solutions, the main specifications are that the masking agents and the complexes formed by the metal ions being masked must be neither colored nor insoluble. When the colored complex formed in the principal reaction is extracted into a solvent, the complexes of the masked metal ions must either not be extracted or, if they are, they must be colorless.

Ion-pair formation can involve either cationic or anionic species that are to be determined. An example of the latter is the spectrophotometric determination of rhenium by extraction into chloroform from pH 10 borate buffer of the ion-pair formed by tetrabutylammonium ion with perhenate ion. In this system, sodium citrate masks tervalent cations.¹⁰³

The most frequently used masking agents in spectrophotometry are "hard" ligands, such as EDTA, hydroxy acids, and phosphates, which are polyanions or contain many polar groups. Of these, buffered EDTA or metal-EDTA solution is one of the most generally useful, especially in determinations of beryllium, boron, niobium, palladium, antimony, selenium, vanadium, tung-

sten, mercury, silver, and copper. Thus, it is claimed that 60 different cations are masked at pH 10.0 ± 0.2 by large quantities of ammonium citrate and EDTA in the spectrophotometric determination of beryllium with thorin.¹⁰⁴ EDTA is a good masking agent for cations in the spectrophotometric determination of boric acid at pH 8.5 with 4-nitrocatechol.¹⁰⁵ It also masks cadmium when copper is estimated using extraction from alkaline solution as the diethyldithiocarbamate.¹⁰⁶ EDTA masks nickel when cobalt is determined photometrically with violuric acid at pH 8.6.¹⁰⁷ A fluorometric method for ruthenium as the 1,10-phenanthroline complex at pH 7 uses EDTA to mask bismuth, copper, and nickel.¹⁰⁸ Calcium-EDTA was used for the more selective masking of most bivalent cations, iron(III), gallium, indium, and the rare earths in a spectrophotometric method for uranium(VI) based on extraction of the alizarin red S complex into butanol.¹⁰⁹ These examples illustrate the diversity of the applications of EDTA as a masking agent in spectrophotometry.

The main purpose of the hydroxy acids as masking agents is to avoid hydrolytic precipitation of metal ions. As the effect of hydrolysis increases rapidly with pH, the usual conditions for using these acids are in neutral or weakly acid solutions. Thus, in an extraction-spectrophotometric method for cobalt in iron and steel, using 5-dimethylamino-2-nitrosophenol, citrate buffer (pH 5.3) masks nickel and iron.¹¹⁰ Similarly, tartrate (pH 5 to 8) masks manganese, lead, and iron in an extraction-photometric determination of copper in steel using salicylaldehyde.¹¹¹ With polyvalent cations, however, the stability constants of citrate, tartrate, and related complexes are high enough for useful masking to be possible in more acid solutions. As an example, in the spectrophotometric determination of niobium at pH 1 with 4-(2-pyridylazo)resorcinol, tartrate can be used to mask tantalum.¹¹² Zirconium can be masked with oxalic acid in 2.5 to 3 *M* hydrochloric acid when thorium is determined with arsenazo III.¹¹³ Citric acid is more effective than tartaric or oxalic acid for masking tin and titanium in the photometric determination of germanium with phenylfluorone.¹¹⁴ The choice of which carboxylic acid to use is frequently difficult because the masking ability of, say, citrate relative to tartrate varies with pH (because their pK_a values are different) and with the particular metal ion (because

protonated and hydrolyzed metal complexes may also be formed).

As an example of the use of a "soft" ligand in masking, a selective method for cadmium demasks its cyano complex at pH 10 by adding formaldehyde and extracts its complex with 1-(5-chloro-2-pyridylazo)-2-naphthol into chloroform, while cobalt, mercury, manganese, iron, and nickel remain masked as their cyano complexes.¹¹⁵

Selectivity in extraction-photometric methods can sometimes be enhanced by ternary complex formation. Thus, at pH 6.2 to 6.6, iron(II) is extracted into chloroform as the hexanoate of its tris(2,2'-bipyridyl)complex, whereas copper(II) is masked by EDTA.¹¹⁶ EDTA is a general masking agent when germanium is extracted as its 4-nitrocatechol complex into dichloroethane by forming an ion-pair with the tris(bipy)Fe²⁺ ion.¹¹⁷ Many examples are known of ternary complexes in which a metal anionic complex with a bidentate organic ligand forms an ion-pair with a basic dye. Thus, at pH 9 to 9.2, in the presence of oxalate to mask calcium and strontium, and tartrate to mask iron(III) and aluminum, magnesium is extracted as its 1:1:1 complex with thenoyltrifluoroacetone and rhodamine B.¹¹⁸ Similarly, lanthanum can be extracted into benzene as a ternary complex with salicylic acid and rhodamine B; sodium fluoride masks yttrium.¹¹⁹ At pH 3.3 to 3.4, gallium is extracted as a ternary complex with xylenol orange and oxine, while iron(III), copper(II), and vanadium(V) are masked by mercaptoacetic acid and EDTA.

Oxidation or reduction may provide a useful masking procedure. Thiourea reduces copper(II) to copper(I), ascorbic acid reduces thallium(III) and iron(III), and hydroxylamine reduces manganese(III) to manganese(II). As an example, in the photometric determination of molybdenum with 8-hydroxy-7-(2-hydroxy-5-nitro-3-sulfophenylazo)naphthalene-1,6-disulfonic acid at pH 1 to 3, iron is masked with ascorbic acid, copper is masked with thiourea, and zirconium is masked with EDTA.¹²¹

Provided they are mutually compatible, mixtures of masking agents may be used. Thus, in the determination of molybdenum at pH 1 to 1.6 with thiolactic acid, 4 masking agents were used, namely thiourea (to mask copper), tartaric acid (tungsten), phosphoric acid (iron), and EDTA (bismuth).¹²² Masking agents in the spectrophoto-

metric determination of zirconium with stilbazo at pH 2.4 to 5 were sulfosalicylate (for titanium, manganese, and aluminum), mercaptoacetic acid (molybdenum), ascorbic acid (iron), ascorbic acid plus thiocyanate (tungsten), and thiourea (copper).¹²³

Other examples of the use of masking agents in spectrophotometry are given in Reference 3.

D. Solvent Extraction

Solvent extraction, where applicable, is usually a selective method by which to separate a metal ion or its complex from interfering species. The selectivity of the process can usually be further improved by appropriate masking, a typical situation being one in which a chelate-forming extractant is present in an organic phase immiscible with water while the aqueous phase is buffered and also contains a masking agent. The latter may be an aminopolycarboxylic acid, citric or tartaric acids, or a phosphate, the requirement being that stable, water-soluble, nonextractable complexes, preferably anionic, are formed with unwanted cations. Related to this group is the use of a chloroform solution of phenylacetic acid for the extraction (and colorimetric determination) of copper(II) from a hexamine buffer containing ammonium fluoride to mask iron and uranium.¹²⁴

More specialized masking agents are possible so long as they contain numerous hydrophilic groups to ensure retention in the aqueous phase. For example, the change from diethyldithiocarbamate to bis(carboxymethyl)dithiocarbamate alters the properties of the resulting metal complexes so that their solubility in water is improved and they are no longer extracted. This permits copper, lead, cadmium, and nickel to be masked against extraction by dithizone.¹²⁵ A similar situation, treated quantitatively by Budevsky et al.,¹²⁶ was the use of dithiocarbaminoacetic acid to mask lead, cadmium, and cobalt in the selective extraction of zinc dithizonate.

A method based on sequential solvent extraction, followed by atomic absorption spectrophotometry, permitted the determination of 11 metals in small samples of blood;¹²⁷ selectivity was achieved by pH control and the use of citrate buffer to mask metal ions against hydrolytic precipitation.

In a novel extraction of zinc as its oxine complex at pH 9.1 and 90°C into molten naph-

thalene, aluminum was masked with fluoride ion.¹²⁸

Factors that govern the extent to which a species is extracted into a given solvent include the distribution coefficient between the two phases, the pH of the solution, and the pK_a values of the organic extractant and the masking agent. As in other chemical procedures, the effectiveness of a masking agent decreases rapidly at pH values less than its pK_a . There are several convenient treatments, with worked examples, of masking in solvent extraction.^{2,3,129}

E. Ion-Exchange

Unlike solvent extraction, adsorption on to an ion-exchange resin is essentially non selective, so that any separations using this technique usually rely heavily on masking procedures.

Metal ions can be masked in two ways against adsorption onto cation-exchange resins. In some cases, including chromium, manganese, molybdenum, rhenium, vanadium, and tungsten, they can be oxidized to anionic species such as chromate and permanganate or converted to heteropolyanions such as phosphotungstate. More commonly, use can be made of ligands which form anionic complexes with metal ions. Examples are aminopolycarboxylic acids, including EDTA, and di- and tricarboxylic acids. Conversely, such metal complexes are retained on anion-exchange columns. Separations of metal ions can also be achieved using strong solutions of chloride and fluoride ions and, to a more limited extent, other inorganic ligands.³

The pH of the solution is a major factor in controlling metal ion separations by an ion-exchange resin in the presence of a masking agent. The extent of complex formation with different metal ions varies with $\alpha_{L(H)}$, $\alpha_{M(OH)}$, and $\log \beta_{ML}$. Quantitative calculations have been made based on systems where the masking agent was EDTA, CDTA, or other aminopolycarboxylic acids.² The technique is versatile and can also be applied to liquid ion-exchangers, in which case conditions resemble solvent extraction. It can also be used to separate complexes such as $Fe(phen)_3^{2+}$ from other masked metal ions. Masking in the application of resin spot tests has been discussed.¹³⁰

F. Electroanalytical Chemistry

The polarographic wave of one kind of metal

ion may interfere with the measurement of the wave due to another. This interference may be overcome, and the first metal ion can be considered to be masked, if the half-wave potentials of the two metal ions can be sufficiently separated, usually by complex formation. The changes produced in $E_{1/2}$ values by a complexing agent are due to differences in the stability constants of the corresponding oxidized and reduced forms of the metal complexes. Because of the pK_a values of the ligand, the values of $E_{1/2}$ are pH dependent, but the effect is often complicated by the formation, in alkaline solution, of hydrolyzed species. As an alternative to the use of masking agents, it is frequently possible to choose a supporting electrolyte in which the desired waves are adequately separated. (See, for example, Meites.¹³¹)

The masking agents most commonly used in polarography are EDTA, cyanide ion, and tartrate ion. Their applications are largely as expected from the effects of pH on the conditional stability constants of their metal complexes. Waves can sometimes be eliminated by reduction or oxidation. Examples are the reduction of iron(III) by ascorbic acid, hydroxylamine, or hydrazine, and of copper(II) to copper(I) by cyanide ion, giving cuprocyanide. Oxidations include the use of permanganate to convert arsenic(III) and antimony(III) to arsenic(V) and antimony(V).

A method for the polarographic determination of aluminum is based on the displacement of lead by aluminum from a chloroform solution of lead 8-hydroxyquinolate at pH 5.2 to 5.6, followed by measurement of the lead wave. Tartrate is added to mask aluminum against hydrolysis.¹³²

Masking procedures in amperometric titrations and polarography are similar. Thus, EDTA is used as a general masking agent for many cations in the amperometric titration of beryllium in aqueous, pH 5 to 6, acetate buffer.¹³³ Microgram amounts of iron(III) and copper in ores and mineral waters have been titrated with mercurous nitrate, with and without pyrophosphate or fluoride to mask iron.¹³⁴

In the electrochemical determination of fluoride ion in the presence of aluminum and calcium using a fluoride selective electrode, ammonium salicylate served as a buffer and masked aluminum, while EDTA masked calcium.¹³⁵ Ammonium citrate with CDTA has been similarly used to demask fluoride ion for its determination in rocks and water by a fluoride

selective electrode.¹³⁶ EDTA or alkali metal tartrates masked metal ions against precipitation when cyanide ion in solution was determined using a silver halide electrode.¹³⁷

VI. FUTURE DEVELOPMENTS

Three factors lead to the expectation that the near future will see a significant expansion in quantitative theoretical studies of possible analytical chemical procedures, including masking reactions. These are the increasing availability of digital computers, the growth in the awareness of their capabilities, and the continuing output of relevant equilibrium data. Such studies should provide a better understanding of the most suitable masking agents to use in a given application and the optimum concentration of the masking agent if interference is to be minimal. This is important, especially in substoichiometrical masking,¹³⁸ where the amount of masking agent added is less than the amount needed for complete masking of the interfering substance: instead, it is the amount that leads to the least disturbance of the principal reaction.

Until recently, most discussions of metal-complex formation dealt with systems containing only one kind of metal ion and one ligand. It is now realized that mixed complex formation is common and that the stability constant of a mixed complex MAB often differs significantly from that expected from MA_2 and MB_2 . Analytical applications of mixed-ligand complexes have been reviewed.^{139,140} These include a number of examples in which one of the ligands is commonly used as a masking agent. Thus, fluoride ion can be estimated spectrophotometrically by the formation by cerium(III) of an intensely blue ternary complex with alizarin complexan and fluoride ion.¹⁴¹ Mixtures of EDTA (or tartaric acid or oxalic acid), niobium (or tantalum), and *o*-dihydroxybenzenes, including pyrogallol, form characteristic colored complexes.¹⁴² In many cases, formation of mixed-ligand complexes leads to a synergistic effect in the solvent extraction of metal chelates. An electrically neutral species MA_aB_b is likely to be more readily extracted than aquo complexes such as $MA_a(H_2O)_x$. For example, the blue mixed-ligand pyridine-copper(II)-salicylate complex is extracted by chloroform, whereas neither the pyridine nor the salicylate complexes can be. Thus, in many analytical methods, the

addition of masking agents may have effects other than the simple suppression of an interfering ion. A wider understanding of the factors involved in mixed complex formation will contribute significantly to improved masking techniques.

Quantitative methods already exist for discussing equilibria in which mixed complexes are present. Ringbom² showed that the presence of some ammonia was advantageous in the complexometric titration of mercury(II) with EDTA. Similar calculations involving other metal ions and ligands are currently handicapped by insufficient stability constant data. The same principles could be applied in the use of oxygen-type chelating agents to diminish hydrolysis (with attendant formation of insoluble polymeric species) of high valent metal ions such as zirconium(IV) and hafnium(IV) so that colored mixed complexes could be formed by the addition of metallochromic indicators.

Developments of new masking agents are likely in at least three directions. Although much has been done in modifying EDTA and other aminopolycarboxylic acids, the field is by no means exhausted. In particular, the building in of lipophilic groups could possibly offer advantages. So, too, could the application of cage-like molecules with selectivity based on cationic radii and metal ion stereochemistry. The possible use of cryptates in this way has been suggested.¹⁴³ The third approach lies in the synthesis of complexing agents with new types of donor atoms, such as phosphorus or arsenic, or which are the analogues of existing ligands except that more selective groups such as thiols and amino groups would replace hydroxyl or carboxyl groups. A current example is *N*-dithiocarboxy-*N*-methylglycine. It has been suggested for use as a masking agent for indium, cadmium, and bismuth in the complexometric determination of gallium at pH 2 to 3, and for molybdenum in an extraction-photometric determination of tungsten with rhodamine B.¹⁴⁴

Kinetic aspects of masking and demasking will no doubt become better understood and give rise to further examples of "kinetic masking." New knowledge may also lead to improvements in analytical methods. This is illustrated in the use of 1,10-phenanthroline or 2,2'-bipyridine to give fast and complete reduction of copper(II)-EDTA with ascorbic acid and thiourea. Thus, at pH 5 to 6, copper(II)-EDTA is only sluggishly reduced by

thiourea or sodium thiosulfate, probably because the metal ion is surrounded by a large saturated ligand. Small amounts of 1,10-phenanthroline or 2,2'-bipyridine catalyze the reduction because of the formation of a stronger complex in which the copper ion is surrounded by a large unsaturated ligand so that the exchange of electrons is much faster, giving copper(I)-bis(phen)₂⁺ and -bis(bipy)₂⁺. An excess of thiourea readily displaces copper(I) from these complexes, giving the more stable copper(thiourea)₄⁺.¹⁵ Thiosemicarbazide can be used instead of 1,10-phenanthroline. It is possible that a similar explanation applies to the ability of 1,10-phenanthroline to overcome the "blocking" of metallochromic indicators by many transition metal ions.¹⁴⁵

The strong influence of pH on the masking ability of most masking agents limits the pH range over which any one of them can be used. The leveling effect observed when ligand buffers are present makes it possible to design masking agents that have comparable activity in acid or in alkaline solution. An alternative approach to pH independent masking action would be to use cyclic ethers and similar chelates in which the ligand is not readily protonated.

Development of improved masking and demasking techniques would also be facilitated if more authors pointed out in descriptions of analytical methods the masking agents they have used and their intended function.

VII. SUMMARY

The masking of interfering elements frequently provides a simple means of improving the selectivity of analytical methods. Some of the principles involved in choosing masking agents are described, with particular emphasis on the concept of "hard" and "soft" metal ions and complexing species. Quantitative methods are outlined for assessing the effectiveness of a masking agent in proposed analytical applications. These methods are illustrated by figures showing the pH dependence of conditional constants for wanted and unwanted metal complexes in the presence and absence of masking agents. A list of the more common masking agents is given in terms of the species they mask, and examples are described in which masking is used in chemical analysis. Finally, some likely developments in this field are suggested.

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