

COMPLEXING OF METALLIC IONS WITH ORGANIC ACIDS AND THEIR APPLICATIONS TO ANALYTICAL PROBLEMS

M. R. VERMA

National Physical Laboratory, New Delhi

Abstract

In solutions containing copper and arsenic or antimony, the method of complexing the metallic ions and their estimation have been described.

OXALIC acid has often been described as the king of complexing agents and a very large number of reactions are known in which advantage is taken of the differing complexing tendency of the same with metallic ions in effecting separation from others. In the matter of ability to complexing, I firmly believe, an equal place of honour must also be given to citric, tartaric and other polycarboxylic acids and to acids of the type of sulphosalicylic acid.

The complexing of metallic ions, it is generally agreed, is due to the co-ordinating tendency of the ions concerned, and the relative stability of the complex between the metal ion and given series of acids depends upon a large number of complex factors. In seeking out a set of conditions that may lead to the exploration of the possibility of an analytical method, one has, therefore, to be guided by a tendency to co-ordination and the stability of the complex in a well-defined *pH* range. In a compact article in *Chemical Reviews*, Bailar¹ has sought the elements with a tendency to co-ordination with cyanides, aliphatic amines, amino acids, tartaric acid, etc., and arranged them in an expanded form of periodic table. In dealing with tartaric acid, for example, one does observe that a large proportion of metals have a tendency to undergo complexing with it. Unfortunately such a table has not been drawn for other organic acids, but I am certain that it

shall be worth while. Survey of literature does indicate a very large volume of work on individual metallic ions or group of ions and organic acids. You will agree with me that large-scale separation of rare earths by ion-exchange resins² has been possible on account of slightly graded equilibrium constants of the system amberlite resin-rare earths or rare earth citrate for the individual rare earth ions.

In National Physical Laboratory, we have been engaged for some years now on exploration of reactions of analytical interests in which advantage is taken of the complexing tendency of a metallic ion with alkali salts of organic acids, so that the same is withheld from interference in a certain reaction or it is broken up under controlled condition. We have been able to evolve methods which are comparable in accuracy to some of the time-honoured methods adopting laborious separations. Following a short paper from the Punjab University³ in which a method had been developed for estimating iodate in the presence of copper by complexing the latter with pyrophosphate, Kolthoff⁴ and his colleagues in a series of papers explored the possibility of carrying out the determination alternatively. Finally they evolved a method for complexing of copper ions with potassium citrate and estimating the iodate by adjusting the *pH* value suitably. In the same solution copper may be estimated by lowering the *pH* when the complex breaks down. This reaction has been applied by them to a series of other ions, particularly bromate and permanganate. We have extended this reaction to the system copper and arsenic or antimony⁵ in the presence of one another. An aliquot of a

mixture of solutions of trivalent arsenic and copper(ic) or trivalent antimony and copper(ic) salts is taken, neutralized with

sodium bicarbonate to incipient precipitation of copper and an excess of molar potassium citrate added. It is followed by excess of

TABLE 1 — ARSENIC AND COPPER

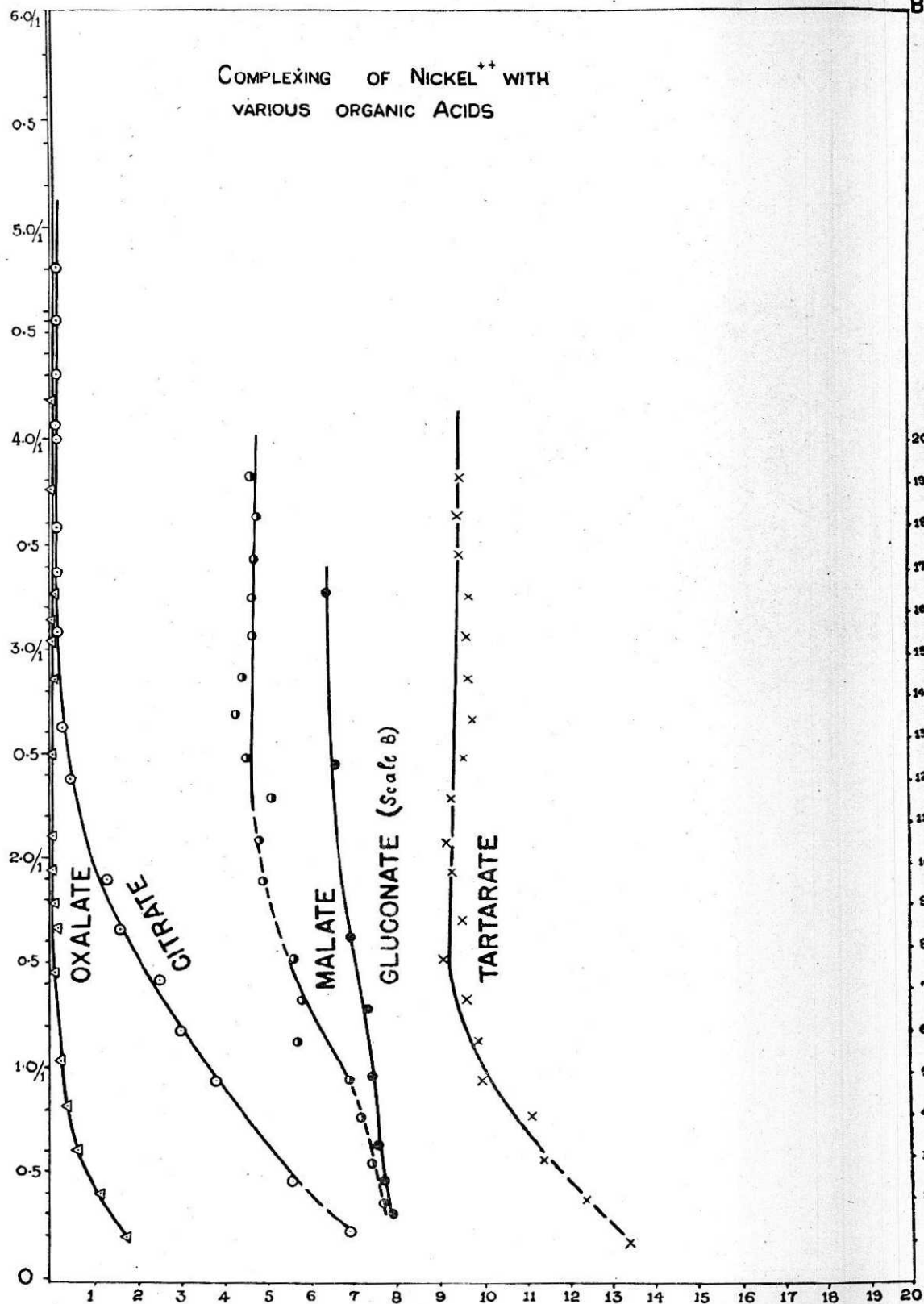
VOL. OF AS SOLN. (ml.)	VOL. OF Cu SOLN. (ml.)	REAGENT ADDED	VOL. OF IODINE (ml.)	REAGENT ADDED	VOL. OF THIO-SULPHATE (ml.)
—	25.0	Ammoniacal till blue colour; neutralized with acetic acid, added potassium iodide	—	—	23.8 23.8 23.9
—	25.0	25 ml. of potassium citrate, ammoniacal till blue colour, acetic acid, 10 ml., sulphuric acid, 25 ml., and potassium iodide	—	—	24.0 24.1
25.0	—	Sodium bicarbonate (excess)	24.8 24.8 24.7	—	—
25.0	—	Sodium bicarbonate (excess) and 25 cc. of potassium citrate solution	24.8	—	—
25.0	25.0	30 cc. of potassium citrate and excess of sodium bicarbonate	24.8 24.8 24.8	After neutralization of sodium bicarbonate with dilute acetic acid, added potassium iodide followed by sulphuric acid, 25 ml., and acetic acid, 15 ml.	24.2 24.0 24.1

TABLE 2 — ANTIMONY AND COPPER

VOL. OF ANTIMONY SOLN. (ml.)	VOL. OF COPPER SOLN. (ml.)	REAGENT ADDED	VOL. OF IODINE (ml.)	REAGENT ADDED	VOL. OF THIO-SULPHATE (ml.)
—	25	Ammonia, acetic acid	—	—	22.30 22.25
—	25	Ammonia, acetic acid, potassium citrate, sulphuric acid, 15 ml., and acetic acid, 15 ml.	—	—	22.35 22.40 22.38
25	50	Ammonia, acetic acid, sodium bicarbonate, and potassium citrate, 50 ml.	20.3	Acetic acid till neutralized, sulphuric acid, 30 ml., and acetic acid, 30 ml.	44.60
25	25	Ammonia, acetic acid, potassium citrate, 50 ml., and sodium bicarbonate	20.4	Acetic acid till neutralized, sulphuric acid, 30 ml., and acetic acid, 30 ml.	22.50

COMPLEXING OF NICKEL⁺⁺ WITH
VARIOUS ORGANIC ACIDS

RATIO OF THE ALKALI SALT OF ACID/NICKLE⁺⁺ SULPHATE →

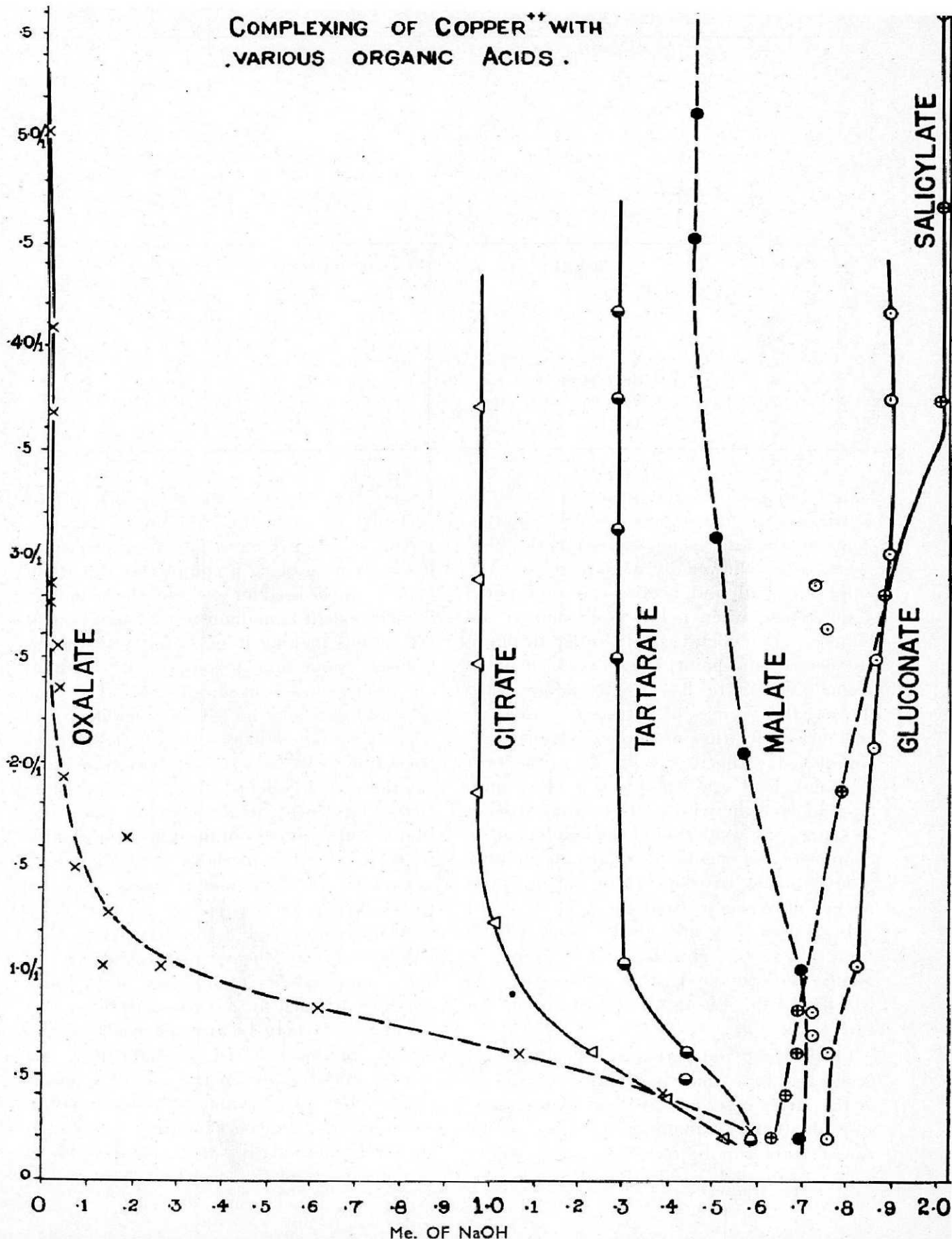


REQUIRED FOR NEUTRALIZATION AFTER 5 Mes OF MOLAR NICKEL SULPHATE ARE TREATED WITH THE ALKALI SALT OF THE ACID

FIG. 1

COMPLEXING OF COPPER⁺⁺ WITH
VARIOUS ORGANIC ACIDS.

RATIO OF THE POTASSIUM SALT OF ACID / COPPER SULPHATE



REQUIRED FOR NEUTRALIZATION AFTER ONE Me. OF MOLAR COPPER SULPHATE IS TREATED WITH THE POTASSIUM SALT OF THE ACID

FIG. 2

TABLE 3—AMINO ACIDS

1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	A
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Yt	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	X
6	Cs	Ba	Re	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		Nt
7		Ra	Ac	Th	U ^x	U												

TABLE 4—*d*-TARTARIC ACID

1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	A
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Yt	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	X
6	Cs	Ba	Re	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		Nt
7		Ra	Ac	Th	U ^x	U												

sodium bicarbonate and antimony or arsenic is titrated against standard iodine solution. The bicarbonate is neutralized with dilute acetic acid followed by a mixture of dilute sulphuric acid and acetic acid and potassium iodide, when iodine equivalent of the copper ion is liberated. In order to obtain the correct end-point, large excess of potassium thiocyanate has to be added early during the course of titration, unlike in the direct titration of copper which is uncomplexed with citric acid. Also the ratio of acetic acid and sulphuric acid is quite critical, for otherwise serious errors arise on account of air oxidation of the iodide and decomposition of pentavalent arsenic or antimony to the trivalent state much in the nature of Weller's reaction.

In Tables 1-4 are given some of the typical results. This method is being extended to alloy and other compositions in which Cu-Sb, Cu-As or Cu-Sn occur together.

Like arsenic and antimony, vanadium also occurs in more than one state of valency; in the latter case, pentavalent, quadrivalent and divalent. Vanadium in its quadrivalent state can be oxidized to the pentavalent state iodometrically. We have ex-

tended the above-described reaction to the system V-Cu⁶. In this case, on account of a fortunate set of circumstances, citrate ions, in addition to being a complexing agent for copper, can be used for effecting the reduction of pentavalent vanadium to the quadrivalent state, thus making it possible to titrate the reduced vanadium iodometrically without any interference from copper ions. The same solution may now be suitably acidified and copper estimated iodometrically. We have been able to show that vanadium is reduced to the quadrivalent state by potassium citrate treatment at all levels of concentration and the results obtained are comparable to those of other methods of dealing with vanadium. The method is being extended to the system Fe-V as well.

Bruhns⁷ observed early that salts of alkaline earths and heavy metals increase the acid characteristics of hydroxy acids considerably, so much so that some of the weaker organic acids may be titrated using methyl orange or methyl red as indicator. Extended investigation of this complex phenomenon by polarographic, potentiometric, electrometric, transport number, and absorptometric methods has indicated very interesting aspects of this complex phenomenon.

While the possibility of complexing of the metal ion with organic acid radical is not denied, general lowering of the pH value under these conditions has not been fully explained. Bobtelsky⁸ and his colleagues, however, noted that when alkali tartrate or citrate solution is mixed in a uni-molar ratio with nickel or copper solution, the acidity developed is titrable and quantitatively proportional to the organic acid ion present. They have tentatively suggested a labilization of H from $-OH$ group. In this laboratory we have extended these investigations to a very large number of organic acids — simple polycarboxylic acid, hydroxy acid — and have noted same peculiarities. Some of the results obtained with Ni and Cu solutions are indicated in a graphic form⁹. The ordinates represent the molar ratio between alkali salt of organic acid and the metallic ion, and the abscissae the volume of normal alkali required on the basis of unit volume of molar solution of the metal ion. On increasing the ratio, the volume of alkali required tends to become constant after a certain ratio. The quantity of alkali used seems to bear the same relation to the number of hydroxy radicals present in the organic acid molecule. While we may reserve our judgement with regard to this phenomenon till further data have been collected, we cannot help noting the peculiar behaviour of nickel with the oxalate and citrate. In these cases, the volume of alkali required for the complex drops off near to zero after a certain stage. This fact places in our hands an extremely neat method for the estimation of boric acid in a nickel-plating bath. To a properly buffered solution consisting of nickel salts and boric acid¹⁰ is added excess of potassium oxalate followed by mannitol, when boric acid becomes available for direct titration and no correction factors have to be used. Reference to ana-

lytical methods in electroplating practice will indicate that methods advocated for estimation of boric acid invariably require a separation of nickel prior to estimation of boric acid. This method based on the complexing of nickel ions with the oxalate places in the hands of electroplating laboratories a rapid method for the estimation of boric acid.

I have thus outlined to you briefly the application of some of the very simple phenomena of complexing with simple organic acids to analytical problems. These acids are both cheap and easily available. The busy metallurgists, whether dealing with ferrous materials or non-ferrous alloys, have very much to depend upon the analytical data with regard to the products developed by them and it is quite possible that a close collaboration with the analytical chemist can lead to the evolution of simple and quick methods employing the complexing characteristic of metallic ions with organic acids.

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