464. *The Alkalimetric Determination of Metals with the Aid of Acid–Base Indicators. Part II.**

By J. F. Coetzee.

This paper deals with the determination of zinc, mercury, copper, and antimony by means of titration with standard alkali, as well as with the alkalimetric analysis of mixtures of mercury and copper with cadmium or cobalt. Completion of precipitation of the metal is determined with the aid of a suitable acid–base indicator. Similarly, free mineral acid is titrated in presence of zinc, mercury, and copper by application of an indicator of proper pH range. This principle has now been applied for the first time to the determination of antimony and to the quantitative analysis of mixtures of metals. The existing procedures for the determination of zinc, mercury, and copper have been substantially modified.

The underlying principles of the alkalimetric method have been treated in Part I (*loc. cit.*), which also dealt with the determination of aluminium, cadmium, and cobalt.

Determination of Zinc.—The fact that addition of alkali to zinc solutions at room temperature leads to precipitation of basic salts, has been well established (see, *e.g.*, Britton, *J.*, 1925, **127**, 2124). From the analytical point of view additional complication arises from the fact that this precipitate is soluble in excess of alkali. Ruoss (*Z. anal. Chem.*, 1896, **35**, 143) added excess of baryta, boiled, and back-titrated with hydrochloric acid. Simplification of the method by direct titration to the phenolphthalein end-point gave moderately accurate results with zinc bound to chlorine, but led to considerable under-titration in presence of sulphate (Kolthoff, " Massanalyse," Vol. II, 1928, p. 167). Kolthoff found that addition of barium chloride improved the titration, but even then the results were insufficiently accurate. He consequently proposed a back-titration method, which in turn suffered from the drawbacks that the zinc oxide precipitate retained adsorbed alkali very tenaciously, and that the phenolphthalein end-point was ill-defined (see below). Hence the accuracy of the method did not exceed 1%.

Determination of Mercury.—As with zinc, addition of alkali to mercuric solutions at room temperature results in basic salt formation (Britton, *loc. cit.*, p. 2150). Direct titration of mercuric chloride proved ineffective when colour indicators were used. The basic chlorides produced could not be quantitatively decomposed into oxide within the pH range attainable by direct titration. Further, the intense colour of these basic chlorides masked the end-point very seriously. Consequently, Rupp *et al.* (*Pharm. Zentr.*, 1926, **67**, 529) added excess of alkali and some hydrogen peroxide, and heated until the precipitate had been completely reduced to metallic mercury. After cooling, they back-titrated to the methyl-red or dimethyl-yellow end-points. Kolthoff (*op. cit.*) found that phenolphthalein could also be used, and considered the method to be accurate to 0·5%.

Determination of Copper.—(a) *Composition of precipitate.* The composition of the precipitate produced by adding alkali to cupric solutions has been a subject of much controversy (see Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 261). Numerous basic salt structures have been reported, ranging in composition from $CuSO_4,CuO,aq.$ to $CuSO_4,14CuO,aq.$, with varying water contents; $Cu(OH)_2$ as such is only precipitated under carefully controlled conditions (Dawson, *J.*, 1909, **95**, 370). The composition of these precipitates has been investigated by electrometric, conductometric, and phase-rule studies, as well as by the colorimetric determination of pH; although the results are conflicting, certain facts have been definitely established. Electrometric studies (Britton, *loc. cit.*, pp. 2152, 2796) have indicated that the composition of the precipitate produced at room temperature is influenced by the manner in which the precipitant is added. A similar conclusion was reached by Pickering (*Chem. News*, 1883, **47**, 181; *J.*, 1883, **43**, 337; 1907, **91**, 1981) and by Carrière *et al.* (*Bull. Soc. chim.*, 1946, **13**, 396) from their colorimetric pH determinations. The author's results bear this out. Pickering also observed that the amount of base required to cause alkalinity to phenolphthalein at room temperature varied with the nature of the base employed; only baryta led to a permanent end-point, the neutralisation of other bases continuing for 2—3 days (cf. also Carrière *et al.*, *loc. cit.*).

Many phase-rule studies of the ternary system $CuO–SO_3–H_2O$ have been carried out to determine which of the numerous basic salts reported actually existed. Conflicting results

* Part I, *J.*, 1951, 997.

were obtained (cf., *e.g.*, Bell and Taber, *J. Physical Chem.*, 1908, **12**, 171; Young and Stearn, *J. Amer. Chem. Soc.*, 1916, **38**, 1947; Britton, *loc. cit.*, p. 2796; Fowles, *J.*, 1926, 1845; Britton, *ibid.*, p. 2868; Bell and Murphy, *J. Amer. Chem. Soc.*, 1926, **48**, 1500). Nevertheless the existence of the basic sulphate $4CuO,SO_3$,aq. has been established. Conductometric evidence (Chrétien and Heubel, *Compt. rend.*, 1944, **219**, 363) also indicates this structure. The author's results prove that under specified conditions this is the only stable basic salt of copper.

(b) *Determination of copper as oxide.* Ruoss (*loc. cit.*) titrated cupric solutions in the same manner as zinc solutions (above). The cupric oxide precipitate coagulated rapidly, and he back-titrated the mother-liquor with acid. Kolthoff (*op. cit.*) found the method accurate to *ca.* 1%. Carrière *et al.* (*Bull. Soc. chim.*, 1945, **12**, 75) titrated cupric sulphate directly to the phenolphthalein end-point, and claimed results concordant to 0·5% with those determined iodometrically. These authors apparently titrated at room temperature, and interpreted their results on the assumption that copper hydroxide was produced. Under these conditions the titre depends on the nature of the base employed and even on its mode of addition (see above), with the result that a reproducible end-point cannot be obtained. Further, the error introduced is much bigger than 0·5%.

Alkalimetric Analysis of Mixtures of Metals.—Two general methods are available for this purpose. First, a suitable reagent may often be employed to protect undesirable metals against attack by alkali, without affecting the metal to be determined. Secondly, it is evident from the relative magnitudes of hydroxide precipitation pH values that fractional precipitation of metal " hydroxides " may be effected by careful pH control. Only the second general method will be treated here. The mere separation of metals by pH control is relatively simple (see, *e.g.*, Gilchrist, *J. Res. Nat. Bur. Stand.*, 1943, **30**, 89), since the only requirement for this purpose is formation of insoluble precipitates. From the point of view of quantitative analysis, however, an additional requirement is that the precipitate should be of definite composition.

<div align="center">EXPERIMENTAL.</div>

Free Mineral Acid Content of Metal-salt Solutions.—The electrometrically determined hydroxide precipitation pH values of the metals dealt with here were reported as follows for 0·02M-solutions (Britton, *Ann. Reports*, 1943, **40**, 45): Zn, 6·8—7·1; $Hg(NO_3)_2$, 2; $HgCl_2$, 7·3; Cu, 5·3; $CdSO_4$, 6·7; $CdCl_2$, 7·6; Co, 6·8.

Zinc. Free mineral acid can be determined in solutions diluted to <0·1M. with regard to zinc by titration with N-alkali to the dimethyl-yellow (pH 2·9—4·1), or preferably the bromophenol-blue (pH 3·0—4·6) end-point. If 0·1N-alkali is employed, the titration is best conducted to the methyl-red (pH 4·4—6·3) end-point in a solution diluted to <0·02M. with regard to zinc. As with the other amphoteric metal, aluminium, the titration should be conducted slowly, since any precipitate produced by rapid addition of reagent or inadequate agitation of solution redissolves with difficulty.

Mercuric. Use is made of the fact that the presence of halide ions causes a pronounced increase in the hydroxide precipitation pH value of this metal (cf. values above). Solutions <0·1M. with regard to mercury can be titrated with N-alkali in presence of an equivalent amount of chloride by using dimethyl-yellow as indicator. Solutions diluted to <0·02M. can be titrated with 0·1N-alkali to pH 3·8 with the aid of methyl-orange–xylene cyanol-F.F. screened indicator, provided that at least an equivalent amount of chloride be present. An excellent colour change may be obtained with the aid of bromo-cresol-green (pH 3·8—5·4), or preferably the mixed indicator for pH 5·1 (Kolthoff and Rosenblum, " Acid–Base Indicators," 1937, p. 173), provided that at least 3 times the equivalent amount of chloride be present.

Cupric. As in the case of cobalt, interference by the characteristic colour of the cupric ion may be sufficiently reduced by dilution. Determination of the free mineral acid content of cupric solutions brought to light an interesting phenomenon. Relatively low pH range indicators, such as dimethyl-yellow, methyl-orange, and bromophenol-blue, were extremely sluggish. Bromocresol-green gave an end-point of moderate definition, such as is to be expected from, say, methyl-orange when employed under usual conditions. Finally, a mixed indicator for the pH range 4·4—6·0 (B.D.H.) gave a well-defined end-point, although the hydroxide precipitation pH value of the solution employed (0·02M.) was 5·3. This indicated a definite lowering of the pH range of the " 4460 " indicator, a contention substantiated by electrometric measurements carried out with a Beckmann glass-electrode pH meter; *e.g.*, the orange intermediate colour of the " 4460 " indicator, which normally corresponds to pH 5·4, was obtained at the pH values 5·1, 4·9, and 4·7 in copper sulphate solutions of 0·001, 0·005, and 0·025M., respectively. A similar repression of the pH range of bromocresol-green was observed.

Bromocresol-green and the " 4460 " indicator are best employed in solutions diluted to <0·02M. with regard to copper.

Determination of Metals in Salt Solutions.—*Zinc.* As with aluminium, cadmium, and cobalt, zinc is best titrated in solutions of its nitrate. Standard solutions of zinc nitrate were prepared as follows : C.P. zinc (Coleman and Bell) was dissolved in 5N-nitric acid, and excess of acid removed by dropwise addition of sodium hydroxide solution until a permanent precipitate just appeared. A slight excess of acid, just sufficient to ensure a practicable titre, was then added, and the solution was boiled for several minutes, cooled, and made up to the required volume.

Results accurate to *ca.* 0·1% have been obtained by the following procedure : (*a*) The approximate titre is determined by titrating hot to the phenolphthalein end-point. The relatively poor definition of this end-point is probably due to zincate formation, since it corresponds to slight over-titration; further, the full alkaline colour of the indicator cannot be developed. (*b*) Another aliquot portion of the solution is then titrated hot to 0·3—0·4 ml. before the approximately determined end-point, cooled, and the titration completed to the end-point of the mixed indicator for pH 9·0 (Kolthoff and Rosenblum, *op. cit.*). This indicator gives a well-defined end-point which corresponds very closely to the theoretical titre for zinc oxide. The method is applicable over a wide concentration range. The results obtained with this method are summarised below.

Zn, g.-ions per l.	Vol. titrd., ml.	Alkali, N.	Acid, ml.	Acid + Zn, ml.	Zn, ml. Found.	Zn, ml. Calc.	Error, ml.
0·6135	20	0·9782	3·26	28·32	25·06	25·09	−0·03
0·6096	20	0·9782	3·43	28·35	24·92	24·93	−0·01
0·07233	20	0·1196	5·21	29·40	24·19	24·18	+0·01
0·07185	20	0·1196	4·80	28·83	24·03	24·03	0
0·01580	100	0·1196	3·45	29·84	26·39	26·42	−0·03
0·01548	100	0·1196	2·87	28·71	25·84	25·87	−0·03

The presence of chloride results in slight under-titration, though the error is very much less than for cadmium and cobalt. It may be practically eliminated by conducting the major part of the titration boiling hot and approaching the end-point as closely as possible before cooling.

Sulphate should be removed by addition of barium nitrate solution in excess. It is important to add the barium at room temperature, for if it is added to the hot solution, considerable under-titration results. Alternatively, the sulphate solution may be added to the barium, with thorough agitation of the latter. The resulting zinc nitrate is then titrated in the presence of the precipitate.

Free mineral acid alone, and acid and zinc together, may be conveniently titrated in the same aliquot solution. The yellow alkaline colour of methyl-red does not appreciably affect the colour change of the " 9·0 " indicator from yellow to violet, provided a relatively small amount of methyl-red is employed.

Mercuric. Standard solutions of mercuric nitrate were prepared by dissolving C.P. mercury (Merck's *pro analysi*) in excess of 4N-nitric acid, boiling until oxidation of mercurous salt was complete, and then proceeding as with zinc.

Mercuric can be determined as oxide with an accuracy of *ca.* 0·1% by direct titration of its nitrate solution, any indicator being used of pH range between those of bromocresol-green (3·8—5·4) and thymol-blue (8·0—9·6). The orange precipitate settles rapidly, leaving the supernatant liquor almost clear. Nevertheless, it is advantageous to use an indicator with a violet or blue alkaline colour, which is better visible in presence of the orange precipitate than a red, yellow, or green one : thymol-blue, bromothymol-blue (pH 6·0—7·6), and bromocresol-purple (pH 5·2—6·8) are suitable.

Titration at room temperature leads to slight under-titration when a high-range indicator is used, such as thymol-blue; this error becomes more serious with increasing dilution. With very dilute solutions the titre is furthermore influenced by the mode of addition of alkali. The use of low-range indicators leads to considerable under-titration with relatively concentrated solutions, but the under-titration error diminishes with increasing dilution. Hence the titration is best conducted at a high temperature, which eliminates the under-titration error and also promotes coagulation of the precipitate. If the concentration of the solution can be adjusted at will and the pH range of the indicator used is immaterial, it is best to titrate hot at a concentration *ca.* 0·05M. to the bromothymol-blue end-point.

A very simple modification of the above method permits of the titration of mercuric chloride solutions. Chloride is precipitated by addition of excess of silver nitrate, and mercuric salt determined in presence of the resulting precipitate by titrating to the bromocresol-purple end-point, which is unaffected by the silver in excess; silver oxide is not precipitated until pH 7·5—8 is reached. In this connection the following observations are of importance : (*a*) if chloride is precipitated before addition of alkali, the results are low and not accurately reproducible. This may be attributed to occlusion of mercury by the silver chloride precipitate and/or the appreciable solubility of silver chloride in mercuric nitrate solutions (see Mellor, *op. cit.*, p. 398); (*b*) if the major part of the titration is conducted hot and the silver added just before the end-point, the basic mercuric chloride often fails to separate; this leads to considerable under-titration, especially with relatively dilute solutions.

Hence the following procedure is recommended : (i) the approximate titration value is determined by precipitating chloride before adding alkali, and then titrating hot to the bromocresol-purple end-point; (ii) the major part of the titration is conducted at room temperature in presence of chloride, and excess of silver is added just before the approximately determined end-point is reached : $x\text{HgO},y\text{HgCl}_2 + 2y\text{AgNO}_3 \longrightarrow x\text{HgO} + 2y\text{AgCl} + y\text{Hg(NO}_3)_2$. The silver chloride precipitate coagulates rapidly, and does not darken upon exposure to light (see, *e.g.*, Mellor, *op. cit.*, p. 409). The solution is then heated just to boiling, and the titration continued to the bromocresol-purple end-point, which is vivid and reproducible to 0·1%.

The final addition of alkali after chloride has been precipitated may also be carried out at room temperature without impairing the accuracy of the results. However, under these conditions the indicator is very rapidly adsorbed by the silver chloride precipitate, and an unduly large amount must be employed. The tendency of silver chloride to adsorb the indicator is greatly reduced by heating.

The results obtained by titrating mercuric nitrate and chloride solutions are tabulated below. All titrations were performed in 100-ml. portions.

Hg, g.-ions per l.	Alkali, N.	Acid, ml.	Acid + Hg, ml.	Hg, ml.		Error, ml.
				Found.	Calc.	
0·1183	0·9780	4·36	28·52	24·16	24·19	−0·03
0·1167	0·9780	4·34	28·17	23·83	23·86	−0·03
0·1365	0·1196	3·62	26·44	22·82	22·82	0
0·01348	0·1196	2·80	25·33	22·53	22·54	−0·01
0·01573 *	0·1196	0	26·38	26·38	26·38	0
0·01464 *	0·1196	0	24·45	24·45	24·47	−0·02

* Mercuric chloride (Merck's *pro analysi*) solutions.

Cupric. If copper sulphate is titrated at ordinary rate with alkali at temperatures below *ca.* 50°, no indicator gives an end-point suitable for analytical purposes. At higher temperatures, however, any indicator between chlorophenol-red (pH 4·6—7·0) and thymolphthalein (pH 9·3—10·5) gives a well-defined, stable end-point, corresponding to the consumption of exactly 1·5 equivs. of alkali. Hence under these conditions the basic sulphate $CuSO_4,3CuO$,aq. is precipitated. The precipitate coagulates rapidly, leaving the supernatant liquor almost clear. Nevertheless, it is advisable to use an indicator with a violet or red alkaline colour, which is better visible in the presence of the greenish-blue precipitate than a yellow, green, or blue one.

The titre is independent of concentration over a wide range. If the concentration can be adjusted at will, and the pH range of the indicator used is immaterial, it is recommended to titrate the solution between the concentration limits 0·1—0·01M. at a temperature above 60°, phenolphthalein or preferably *o*-cresol-red (pH 7·0—8·8) being used as indicator.

Titration of cupric chloride and nitrate at room temperature gives rise to the same phenomena as with the sulphate. At higher temperatures, however, basic nitrate precipitates gradually darken with formation of cupric oxide. Basic chloride precipitates are more stable, though the titre is not quite independent of the concentration. This is in harmony with the general observation that the order of stability of basic salts usually follows the sequence sulphate > chloride > nitrate.

The low solubility and remarkable stability of the basic sulphate $CuSO_4,3CuO$,aq. lead to its preferential precipitation from solutions of the nitrate and chloride, provided sufficient sulphate is also present. Results accurate to <0·1% have been obtained with solutions prepared by dissolving C.P. electrolytic copper (Kagerah) in nitric acid and adding the required amount of sodium or potassium sulphate. Even high concentrations of nitrate and chloride do not affect the titration at all.

The results obtained by this method are summarised below. All titrations were conducted in 100-ml. portions.

Cu, g.-ions per l.	Alkali, N.	Acid, ml.	Acid + Cu, ml.	Cu, ml.		Error, ml.
				Found.	Calc.	
0·1664	0·9782	6·31	31·83	25·52	25·52	0
0·1652	0·9782	5·20	30·51	25·31	25·33	−0·02
0·01920	0·1196	5·15	29·20	24·05	24·07	−0·02
0·01893	0·1196	5·64	29·38	23·74	23·74	0
0·001680	0·01047	2·38	26·41	24·03	24·07	−0·04
0·001667	0·01047	3·00	26·86	23·86	23·89	−0·03

This method has been compared with the iodometric one and proved to possess certain definite advantages, such as the brilliance of the end-point, the reliability and stability of standard solutions of alkali as compared with thiosulphate solutions, and the inexpensive reagents required.

The reaction between Cu^{++}, SO_4'', and OH' on the one hand, and between Cu^{++} and I' on the other, provides a useful link between alkalimetric and iodometric standards.

Antimony in tartar emetic. As hydrated tartar emetic is efflorescent, standard solutions are best prepared from the anhydrous compound. It is not very soluble in water, and preparation of a 0·2M-solution is just possible at room temperature. Good results can be obtained by titrating the solution boiling hot to the thymolphthalein (pH 9·3—10·5) end-point, which corresponds to the consumption of 1 equiv. of alkali : $2C_4H_4O_6K(SbO) + 2MOH \longrightarrow Sb_2O_3 + C_4H_4O_6K_2 + C_4H_4O_6M_2 + H_2O$. The results obtained by titrating anhydrous tartar emetic (AnalaR) are summarised below. All titrations were performed with 0·1196N-alkali.

Sb, g.-ions per l.	Vol. titrd., ml.	Sb, ml.		Error, ml.	Sb, g.-ions per l.	Vol. titrd., ml.	Sb, ml.		Error, ml.
		Found.	Calc.				Found.	Calc.	
0·2000	10	16·76	16·72	+0·04	0·0800	20	13·39	13·38	+0·01
0·1500	10	12·55	12·54	+0·01	0·0400	50	16·70	16·72	−0·02
0·1000	20	16·73	16·72	+0·01	0·0200	100	16·69	16·72	−0·03

The same procedure applied at room temperature leads to over-titration.

The alkalimetric determination of antimony in tartar emetic provides a useful link between alkalimetric and iodometric standards (cf. copper).

Alkalimetric Analysis of Mixtures of Metals.—Free mineral acid–mercuric–cupric–cobalt mixtures. (i) Free mineral acid is titrated in presence of at least 3 times as much chloride as the mercuric content of

the solution, bromocresol-green (pH 3·8—5·4) or preferably the B.D.H. " 4460 " indicator being used. For optimum results the solution must be diluted to <0·02M. with regard to copper.

(ii) Free mineral acid + mercuric is titrated in absence of chloride at room temperature to the bromocresol-green end-point. For optimum results the solution must be diluted to <0·02M. with regard to copper. However, excessive dilution, especially of solutions of low mercury content, leads to under-titration. If chloride is present, it must be removed by addition of silver (see p. 2100).

(iii) Free mineral acid + mercuric + cupric is titrated slowly to the stage represented by the above, but without addition of indicator; sodium or potassium sulphate is then added in amount equivalent to at least 5 times the copper content of the solution, and the boiling solution titrated slowly to the chloro-phenol-red (pH 4·6—7·0) end-point. For optimum results the solution must be diluted to <0·01M. with regard to cobalt.

(iv) For free mineral acid + mercuric + cupric + cobalt the solution is titrated to the stage represented by the above, but without addition of indicator. The mixed precipitate of mercuric oxide and basic cupric sulphate is filtered off and washed with hot water. Sulphate is precipitated in the cold filtrate by adding excess of chloride-free barium nitrate solution (cf. zinc), and cobalt determined in presence of this precipitate by alkalimetric titration (Part I, *loc. cit.*).

Free mineral acid–mercuric–cupric–cadmium mixtures. The procedure is identical with the one outlined above. The final titration of cadmium should be conducted in absence of sulphate. Titration to the basic sulphate stage (Carrière, Guiter, and Portal, *Bull. Soc. chim.*, 1946, **13,** 99) is much less accurate, since basic cadmium sulphate is unstable to variation in concentration, temperature, and pH. The definition of the end-point deteriorates rapidly with increasing dilution and rise in temperature, and the titre is determined by the mode of addition of alkali. Results are invariably too high owing to partial decomposition of basic sulphate into hydroxide.

UNIVERSITY OF THE ORANGE FREE STATE,
    BLOEMFONTEIN, SOUTH AFRICA.