223. *The Alkalimetric Determination of Metals with the Aid of Acid–Base Indicators.*

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This paper deals with the determination of aluminium, cadmium, and cobalt by titration with standard alkali. Completion of precipitation of the metallic hydroxide is determined with the aid of a suitable acid–base indicator. Similarly, free mineral acid may be titrated in the presence of these metals by use of an indicator of proper pH range. This principle has now been applied for the first time to the determination of cobalt. Bayer's procedure for the determination of aluminium has been substantially modified, and a new one proposed for cadmium.

Principle of Method.—During an attempt to develop new adsorption-indicator methods for the determination of phosphates, the possibility arose of estimating metals by alkalimetric titration. With this object, a series of experiments was conducted to find which adsorption indicators would be useful for the alkalimetric determination of those metals which form insoluble phosphates, such as lead and aluminium, and alizarin-red S was investigated. On titration of an aluminium chloride solution with sodium hydroxide in the presence of this compound, a pronounced colour change was observed; however, it was found that this change was not connected with adsorption phenomena, but that the dye merely responded to change in pH, behaving as an acid–base indicator. Hence, it seemed feasible to determine aluminium by first titrating the free mineral acid content of its solutions with the aid of an acid–base indicator of pH range sufficiently low to exclude possible precipitation of aluminium hydroxide, followed by the titration of aluminium by employing an indicator of higher pH range. It was then found that Bayer (*Z. anal. Chem.*, 1885, **24**, 542) had used a similar method for aluminium, but under his conditions, it was tedious and not of great accuracy; also, Carrière, Guiter, and Portal (*Bull. Soc. chim.*, 1946, **13**, 99) had applied the principle to cadmium. However, the wide scope of the method does not appear to have been realized, and it has now been extended to the determination of cobalt with satisfactory results, and further extensions are being examined, particularly to copper, antimony, zinc, mercury, and lead.

Determination of Free Mineral Acid Content of Metal-salt Solutions.—(a) *Relation between activity of metallic ions and their " hydroxide precipitation* pH *value."* Although the addition of bases to metal-salt solutions rarely leads to the precipitation of simple hydroxides, it is nevertheless evident from electrometric studies that the conditions under which precipitation occurs are largely governed by the usual solubility-product relations pertaining to the precipitation of simple hydroxides (Britton, *Ann. Reports*, **1943**, **40**, 43). Consider the precipitation of the hydroxide of a bivalent metal: $a_{M^{++}}a^2_{OH} = L$, where a denotes ion activity and L solubility product. A ten-fold decrease in the value of $a_{M^{++}}$ will result in a ten-fold increase in that of $a^2_{OH^-}$, or about a three-fold increase in a_{OH^-}, corresponding to an increment in the " hydroxide precipitation pH value " of approximately 0·48 unit. This value for a tervalent metal is less susceptible to the activity factor, a ten-fold decrease in the value of $a_{M^{+++}}$ resulting in a rise of only *ca.* 0·33 unit. This dependence of the hydroxide precipitation pH value of a metal upon the activity of its ions has an important bearing upon the determination of the free mineral acid content of metal-salt solutions.

(b) *Selection of indicator.* The particular indicator selected for the determination of the free mineral acid content of such solutions should comply with two primary requisites. First, its colour transformation should occur at a pH value lower than that at which precipitation of the metal commences, which in turn is determined by the nature of the metal and the activity of its ions in the particular solution. The nature of the anions present normally exerts but little effect upon the magnitude of the hydroxide precipitation pH value (Britton, *J.*, 1925, **127**, 2112, 2143) unless complex-ion formation occurs, as with, *e.g.*, mercury and cadmium. Secondly, the indicator selected should have a transformation interval sufficiently high to permit of a well-defined colour change in conjunction with alkali of the particular concentration employed. In practice, any of the recommended indicators (see, *e.g.*, Kolthoff and Rosenblum, " Acid–Base Indicators," Macmillan, N.Y., 1937) showing changes between pH 2 and 12 may be employed in conjunction with N-titrants without introducing very serious errors. With 0·1N-titrants the latitude permissible is reduced to 3—11, and with 0·01N-titrants to 4—10; in certain instances the use of indicator mixtures (*op. cit.*; Kolthoff, *Biochem. Z.*, 1927, **189**, 26) is preferable.

Finally, certain secondary considerations arise, such as the colour of the solution titrated, and the possibility of determining both acid and metal in the same aliquot portion of solution.

(c) *Electrometric determination of hydroxide precipitation* pH *values.* Britton (*Ann. Reports*, *loc. cit.*) has summarised all available electrometrically determined hydroxide precipitation pH values; those of present interest were reported as follows for 0·02M-solutions: $Hg(NO_3)_2$, 2; $HgCl_2$, 7·3; Al, 4·1; Cu, 5·3; Pb, 6·0; $CdSO_4$, 6·7; $CdCl_2$, 7·6; Co, 6·8; Zn, 6·8—7·1. The author's results are in good agreement with these data.

Precipitation of Metallic Hydroxides.—(a) *Composition of metallic " hydroxides."* The composition of the precipitate produced by gradual addition of alkali to a metal-salt solution depends upon a variety of factors, the more important in the present connection being (i) temperature; (ii) concentration of the titrant and solution, as well as mode of addition of the former and agitation of the latter; (iii) nature of the anions present; (iv) the particular pH value at which the titration has been terminated.

It has been well established that gradual addition of alkali to metal-salt solutions generally results at first in precipitation of basic salts, silver being one of the very few exceptions (Britton, *Ann. Reports*, *loc. cit.*). The stability of these basic salts is of fundamental importance in the application of the principle of alkalimetric titration to any particular metal. The author's results with the aid of acid–base indicators clearly indicate that the order of stability of the more usual basic salts is sulphate > chloride > nitrate. In all instances investigated, the basic nitrates could be quantitatively transformed into the corresponding hydroxides by a rise in pH and temperature; under similar conditions the corresponding basic chlorides were often incompletely decomposed, and certain basic sulphates proved sufficiently stable to serve as a basis for the quantitative alkalimetric determination of the metal in question; for instance, a procedure could be developed for the determination of copper, depending upon the remarkable stability of the basic sulphate $3CuO,CuSO_4,aq$.

(b) *Quantitative precipitation of metallic hydroxides.* Consider the precipitation of the " hydroxide " of a *z*-valent metal:

$$a_M a^z_{OH^-} = L$$

$$\text{i.e.,} \qquad a_{OH^-} = (L/a_M)^{1/z}$$

$$\text{or} \qquad a_{H^+} = K_w(a_M/L)^{1/z} = Ka_M{}^{1/z}$$

From this it follows that an increase of one unit in pH should reduce a_M to 10^{-z} of its original value. With a tervalent metal, such as aluminium, this will correspond to precipitation of 99·9% of the metal. Even with a bivalent metal, a rise in pH value of 2 units should suffice to ensure practically quantitative precipitation.

However, since alkalimetric titration of metals generally results at first in precipitation of basic salts, and not of simple hydroxides, a rise in pH value of even 2 units is insufficient to precipitate the metal quantitatively as hydroxide. The results obtained indicate that in general an increase in pH value of 2·5—3 units, in conjunction with an adequate rise in temperature, is required in order to effect this conversion quantitatively. Only with metals such as copper, where the final stable compound produced is itself a basic salt, is a smaller rise in pH value sufficiently effective for analytical purposes.

(c) *Requisites for a successful alkalimetric procedure.* Any satisfactory alkalimetric procedure should conform to certain requirements, the more important of which are : (i) The results should be independent, over a sufficient range, of the concentration, which not only determines the magnitude of the solubility error introduced, but also exerts a profound influence on the composition of the precipitate produced; (ii) once quantitative formation of the ultimate product has been accomplished, the results should be independent of moderate variations in temperature; (iii) similarly, this final product must also be sufficiently immune to further increase in pH, in order to permit of the satisfactory application of an acid–base indicator; (iv) the degradation of any unstable basic salt into the ultimate stable product should take place with sufficient rapidity, and this should be accomplished within the pH and temperature range attainable during ordinary acid–base titrations.

Determination of Aluminium.—(a) Bayer (*loc. cit.*) employed sufficient N-sodium hydroxide solution to redissolve the initially precipitated aluminium hydroxide. One aliquot portion of the resulting solution was then titrated with N-sulphuric acid and litmus (pH 5·0—8·0), and another with the same acid and tropæolin-OO (1·3—3·2), the difference being calculated as alumina. This procedure is obviously unsound. At the litmus end-point, appreciable dissolution of aluminium hydroxide as sulphate will already be taking place, resulting in an ill-defined colour change. Further, the pH range of tropæolin-OO is so low that this indicator is not sufficiently responsive to titrants of N-concentration. Cross and Bevan (*J. Soc. Chem. Ind.*, 1889, **8**, 252) replaced litmus by phenolphthalein (pH 8·0—9·8), and tropæolin-OO by methyl-orange (3·1—4·4), but (see p. 1001) the latter indicator is unsatisfactory. Similarly, the use of alizarin-red S instead of methyl-orange (Sabalitschka and Reichel, *Arch. Pharm.*, 1925, **263**, 193) is not to be recommended, since solution of aluminium hydroxide is still incomplete at the pH represented by the end-point of this indicator (pH 4·0—6·0). The use of fluoride and oxalate in order to form complex ions has also been recommended (see p. 1001).

The author prefers to determine the free mineral acid content of aluminium solutions by direct titration with the aid of screened dimethyl-yellow (see p. 1002). This procedure is rapid and accurate.

The determination of acid and aluminium in conjunction has been a subject of much controversy. Schmatolla (*Ber.*, 1905, **38**, 1, 985) conducted his titrations at a high temperature in order to avoid formation of basic salts, and used alkali carbonate as titrant. Scott (*J. Ind. Eng. Chem.*, 1915, **7**, 1059) recommended the titration of relatively concentrated solutions at a high temperature, using carbonate-free alkali as titrant. Sutton ("A Systematic Handbook of Volumetric Analysis," 1935) advocated the titration of relatively dilute solutions at room temperature.

It has now been found that titrations conducted at room temperature to the phenolphthalein end-point invariably yield low results, presumably on account of basic salt formation. If, however, an indicator of higher pH range is employed, or phenolphthalein is used at a high temperature, ill-defined, transient end-points are obtained, probably owing to aluminate formation. The circumventing of these difficulties is described on p. 1002.

(b) *Composition of aluminium "hydroxide" precipitates.* The composition of the precipitate produced by gradual addition of alkali to aluminium solutions has been studied by many investigators, chiefly by means of two methods, *viz.*, conductometric and electrometric, but the results obtained are not concordant, though on the whole they indicate the existence of definite basic salts at ordinary temperatures. For instance, Robinson and Britton (*J.*, 1931, 2817) concluded from their conductometric studies that "maximum insolubility" of the precipitate produced from aluminium sulphate solutions corresponded to the consumption of 5·76 equivs. of alkali, a value in good agreement with the electrometrically determined one of 5·70 equivs. (Britton, *J.*, 1925, **127**, 2120). On the other hand, Kanning and Kratli (*Ind. Eng. Chem. Anal.*, 1933, **5**, 381), employing the antimony electrode in aluminium chloride solutions, reported a value of exactly 6 equivs. According to these authors, the presence of 1% of sodium sulphate led to an under-titration error of 1·5%. These results support the contention that the basic sulphates are generally more stable than the corresponding chlorides; they are essentially in harmony with those obtained by the author with the aid of acid–base indicators.

Determination of Cadmium.—Composition of precipitate. Attempts to determine the composition of the precipitate produced at room temperature by gradual addition of alkali to cadmium solutions have been carried out by application of three different methods, *viz.*, electrometric (Britton, *J.*, 1925, **127**, 2152; *Ann. Reports, loc. cit.*) and conductometric (Harned, *J. Amer. Chem. Soc.*, 1917, **39**, 252) analysis, and a method due to Pickering (*J.*, 1907, **91**, 1981), which has been developed by Carrière *et al.* (*loc. cit.*). The results obtained by the first two methods pointed to the existence at room temperature of a definite basic sulphate, $3Cd(OH)_2,CdSO_4$,aq. Pickering's investigations, carried out with the aid of pH indicators, merit closer attention. He attempted to follow the alkalimetric precipitation of cadmium with the aid of phenolphthalein (pH 8·0—9·8) and found that even very gradual addition of alkali resulted in almost instantaneous production of a pink colour. He noted, however, that this was due to the precipitate's turning pink, whereas the supernatant liquid remained colourless. This phenomenon was also observed by the author, and it is hoped that a systematic investigation of the adsorption characteristics of cadmium " hydroxide " precipitates may lead to the development of an adsorption-indicator method for the determination of this metal (cf. cobalt).

It is shown (p. 1002) that quantitative formation of cadmium hydroxide can only be accomplished by conducting the titration at a high temperature. Further, the pH range of phenolphthalein is too low to permit of the quantitative precipitation of cadmium hydroxide at any temperature. Consequently, the precipitate obtained by Pickering was probably an indefinite mixture of basic salts, and his finding that " permanent alkalinity to phenolphthalein " corresponded to the consumption of 1·462 equivs. of alkali is of little analytical importance. Carrière *et al.* (*loc. cit.*) titrated cadmium sulphate solutions with sodium hydroxide to the thymolphthalein end-point, and deduced the formation of the basic sulphate, $3Cd(OH)_2,CdSO_4$,aq.

Determination of Cobalt.—(a) *Composition of precipitate.* The blue precipitate produced at room temperature by addition of excess of alkali to cobalt solutions changes on heating into a rose-coloured compound, which in turn is gradually converted into a brown one by prolonged heating and exposure to the atmosphere. The composition of these precipitates has been a subject of considerable controversy (Hantzsch, *Z. anorg. Chem.*, 1912, **73**, 304; Stillwell, *J. Physical Chem.*, 1929, **33**, 1247; Hüttig and Kassler, *Z. anorg. Chem.*, 1930, **16**, 24; Weiser and Milligan, *J. Physical Chem.*, 1932, **36**, 722). The modern view, based upon evidence from *X*-radiograms, indicates that both the blue and the rose precipitate are crystalline, differing merely in form. The blue α-hydroxide is relatively unstable, and its conversion into the rose β-variety is aided by increase in alkalinity and rise in temperature, and retarded by the presence of cobalt ions. Both varieties are represented by $Co(OH)_2$.

The procedure developed for the alkalimetric determination of cobalt depends upon the production of the rose β-hydroxide. Its solubility is sufficiently low to permit of practically quantitative precipitation of the metal, even from very dilute solutions (Curtman and John, *J. Amer. Chem. Soc.*, 1912, **34**, 1684; Almkvist, *Z. anorg. Chem.*, 1918, **103**, 240; Britton, *J.*, 1925, **127**, 2117). Atmospheric oxidation of the moist β-hydroxide gives rise to a brown compound, presumably $Co(OH)_3$. Even though this transition takes place without the consumption of additional alkali, $2(CoO,H_2O) + O + H_2O \longrightarrow Co_2O_3,3H_2O$, it should nevertheless be avoided as far as possible, since the colour change of the indicator is largely masked by the presence of appreciable amounts of the brown hydroxide. It is shown (p. 1003) that, with care, atmospheric oxidation of the rose hydroxide may be reduced to negligible proportions, and a well-defined colour change ensured. Only on excessive boiling does the rose colour of the β-hydroxide change into a dirty brown and even then this transition is relatively slow.

Ammonium salts must be rigidly excluded, both because of their solvent action upon cobalt hydroxide to form complex ammines, and because of their reaction with alkali at the relatively high pH value required for quantitative precipitation of cobalt. Cyanides, tartrates, citrates, and glycerol also exert a solvent action upon cobalt hydroxide (Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1946, Vol. 14, 567), and must therefore be absent during the alkalimetric determination of this metal. On the other hand, the possibility exists that a suitable reagent could be deliberately added in order to maintain cobalt in solution during the alkalimetric determination of some other metal in admixture, but obviously such an addition should not affect the acidity of the solution (cf. Wagner, *Z. anal. Chem.*, 1933, **95**, 311).

The electrometric titration of cobalt solutions at room temperature (Britton, *loc. cit.*;

Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531) provided evidence for the existence of definite basic salts, such as $7Co(OH_2),CoCl_2$,aq., corresponding to the consumption of 1·75 equivs. of alkali, and Pickering (*loc. cit.*) found that " permanent alkalinity to phenolphthalein " corresponded to the consumption of 1·518 equivs. of alkali but his precipitate was probably a mixture of basic salts, as with cadmium (p. 1000).

EXPERIMENTAL.

Free Mineral Acid Content of Metal-salt Solutions.

Aluminium.—On account of the relatively low hydroxide precipitation pH value of aluminium, determination of the free mineral acid content of its solutions necessitates careful control of experimental conditions. The titrations should be conducted slowly, since the hydroxide which is locally precipitated as each drop of basic titrant enters the solution redissolves with difficulty. For optimum results the concentration of the aluminium solution should not exceed approximately 0·03M., and the titration should not be continued further than to about pH 3·3, owing to the ease with which local precipitation of the hydroxide occurs in the more immediate vicinity of its true precipitation pH value. Titrations terminated at pH 3·3 require the use of titrants of at least N-concentration. The only simple indicator for this purpose is *p*-sulphobenzeneazobenzylaniline (pH 1·9—3·3), which affords a moderate degree of accuracy provided the titration is continued to its yellow alkaline extreme. A greatly improved end-point and more accurate results can be obtained with the aid of the dimethyl-yellow–methylene-blue " screened " indicator for pH 3·3 (Kolthoff and Rosenblum, *op. cit.*).

Titrations carried out with 0·1N-alkali can only be conducted satisfactorily if the aluminium is first converted into a complex fluoride (Craig, *J. Soc. Chem. Ind.*, 1911, **30**, 185; Scott, *loc. cit.*) or oxalate (Sutton, *op. cit.*). An approximation to the true titration value can be obtained by slowly titrating the dilute solution, at concentrations not greater than 0·005M. with regard to aluminium, with the aid of the methyl orange–xylene cyanol FF indicator for pH 3·8 (Hickman and Linstead, *J.*, 1922, **121**, 2502). In this titration, premature precipitation of aluminium hydroxide is not easily avoided, and the colour transformation is not clearly defined. None of the indicators hitherto advocated, *viz.*, tropæolin-OO (Bayer, *loc. cit.*), methyl-orange (Cross and Bevan, *loc. cit.*), and alizarin-red S (Sabalitschka and Reichel, *loc. cit.*, is even moderately satisfactory for this purpose.

Cadmium.—The determination of free mineral acid in the presence of cadmium is very simple. The hydroxide precipitation pH value of this metal is relatively high, and its ions are colourless. Furthermore, since cadmium ions combine with halide ions to form complex anions, resulting in a decrease in $a_{\mathrm{Cd}^{++}}$ (Moeller and Rhymer, *J. Physical Chem.*, 1942, **46**, 477), precipitation of the hydroxide may be retarded until even higher pH values have been attained (Bersch, *Z. physikal. Chem.*, 1891, **8**, 392; Britton, *locc. cit.*). Experiments to be reported later show that addition of a halide salt retains cadmium in solution during the alkalimetric determination of some other metals in admixture.

Even in the absence of halide ions, a wide variety of indicators is available for the determination of free mineral acid in the presence of cadmium. Titration of relatively concentrated cadmium solutions with N-alkali is best conducted with the aid of dimethyl-yellow (pH 2·9—4·0) or bromophenol-blue (pH 3·0—4·6). For more dilute solutions titrations with 0·1N-alkali may be safely continued to the end-points of α-naphthyl-red (pH 3·7—5·0), bromocresol-green (3·8—5·4), and even methyl-red (4·4—6·3). A mixed indicator for the range 4·4—6·0 (B.D.H.) gives excellent results.

Cobalt.—Here, again, owing to the comparatively high hydroxide precipitation pH value of this metal, the procedure is simple. However, the colour of cobalt ions in solution interferes with the colour of the indicator in solutions of high cobalt content, and for optimum results the solution should be diluted to approximately 0·02M. This dilution has the additional effect of displacing the hydroxide precipitation pH to even higher values, thereby permitting the use of indicators of correspondingly higher range. Further, a colour change to blue or violet is more easily visible in the pink cobalt solution than one to red, yellow, or green, and bromocresol-purple (pH 5·2—6·8) is recommended. The free mineral acid content of cobalt solutions can also be determined at higher temperatures with the aid of this indicator, a fact which has an important bearing upon the determination of copper and cobalt in admixture (to be reported later).

Determination of Certain Metals in Salt Solutions.

Aluminium.—An approximately 0·03M-aluminium nitrate solution was titrated at room temperature by 0·1N-carbonate-free sodium hydroxide solution, with the aid of various indicators. The results are summarised below.

Theoretical titre : 43·87 ml.

Titration no.	Indicator.*	Range : pH units.	Titre, ml.	Nature of colour change.
1	B.T.B.	6·0— 7·6	42·2—43·2	Very gradual
2	C.R.	7·0— 8·8	43·2—43·7	Less gradual, but still ill-defined
3	P.P.	8·0— 9·8	43·6—43·8	Defined to 0·2 ml.
4	T.P.	9·3—10·5	44·5— ?	Fleeting

* The following abbreviations are employed for frequently used indicators : methyl-orange, M.O.; bromophenol-blue, B.P.B.; bromocresol-green, B.C.G.; methyl-red, M.R.; bromocresol-purple, B.C.P.; bromothymol-blue, B.T.B.; phenol-red, P.R.; *o*-cresol-red, C.R.; thymol-blue, T.B.; phenolphthalein, P.P.; thymolphthalein, T.P.

It was evident from the very gradual colour change obtained in titration no. 1 that the precipitate was still absorbing alkali over the pH range 6·0—7·6. Titration no. 2 illustrated how an indicator of higher range afforded a sharper colour change. The P.P end-point, titration no. 3, was still better and corresponded fairly closely to the titre theoretically required for the formation of aluminium hydroxide; however, the end-point lacked definition and brilliance, and its rapid fading rendered it unsuitable for any but approximate determinations. This fading of the P.P. end-point was apparently caused by the gradual redissolution of the hydroxide as aluminate, a process more clearly illustrated by the extremely sluggish development of the T.P. end-point in titration no. 4.

These results indicate that degradation of the unstable basic nitrates of aluminium into the hydroxide must be nearly complete at the lower limit of the pH range of phenolphthalein; however, production of a permanent end-point is being prevented, probably on account of aluminate formation. Any attempt to develop an alkalimetric method for the determination of aluminium should allow for these two facts.

These difficulties have been overcome by addition to the solution of sufficient nitrobenzene to protect the aluminium hydroxide precipitate from the influence of excess of hydroxyl ions. This principle is analogous to that applied by Caldwell and Moyer (*Ind. Eng. Chem. Anal.*, 1935, **7**, 38) to render silver chloride precipitates immune against attack by thiocyanate ion in the Volhard titration; according to them, the nitrobenzene causes the silver chloride to be drawn to the interface and thus removes it from the aqueous phase. It does not necessarily follow that the " covering up " of aluminium hydroxide precipitates by nitrobenzene depends upon exactly the same principle; nevertheless, both silver chloride and aluminium hydroxide precipitates are characterised by their powerful adsorption capacity, and this may account for their analogous behaviour with nitrobenzene.

The phenolphthalein end-point under these conditions is well-defined, brilliant, and remarkably permanent, and permits of the titration of aluminium solutions with a high degree of accuracy. It is immaterial whether the nitrobenzene is present from the commencement of the titration, or whether it is added just before the end-point. Consequently, its tendency to " cover up " basic aluminium salts must be considerably less pronounced than it is for the normal hydroxide. Excessive amounts of nitrobenzene do no harm, except that unduly high concentrations of indicator must be employed.

A series of titrations conducted on this basis clearly indicated that quantitative formation of of aluminium hydroxide can only be effected from hot solutions. Titration at room temperature invariably yields low results, the under-titration error depending upon the anions present: sulphate > chloride > nitrate. Quantitative conversion of the basic nitrates into the hydroxide is easily effected by conducting the titration above 70°. The corresponding chlorides are considerably more stable, but may nevertheless be quantitatively decomposed by adding the alkali slowly to the boiling solution. The under-titration error caused by the presence of sulphate ions can only be avoided if these are first removed by addition of excess of barium nitrate solution. The resulting barium sulphate need not be removed, since it is immune to attack by hydroxyl ions over the entire pH range covered during ordinary acid–base titrations.

Nitrobenzene, being volatile in steam, should only be used at room temperature. The following procedure is therefore recommended: (*a*) An approximation to the true titration value is obtained by titration at room temperature to the phenolphthalein end-point, by use of 2—3 ml. of nitrobenzene per 0·1 g. of aluminium present and 10—15 drops of 0·1% phenolphthalein solution per 100 ml. of liquid present at the end-point. (*b*) The titration is conducted in boiling solution to the stage corresponding to (*a*), the liquid cooled, the nitrobenzene and phenolphthalein added, and the last few drops of alkali introduced at room temperature. The results obtained by this procedure are summarised in the following table.

Standard solutions of aluminium nitrate were prepared as follows: Aluminium sheet (C.P.; supplied by the South African Bureau of Standards) was dissolved in 10% sodium hydroxide solution, the aluminium precipitated as hydroxide by addition of N-nitric acid, and the hydroxide just dissolved by further addition of acid. A slight excess of acid of appropriate concentration, just sufficient to ensure a practicable titration value, was then added, and the solution boiled for several minutes, cooled, and made up to the desired volume.

Free mineral acid was titrated with the aid of "screened " dimethyl-yellow when N-alkali was used, and of fluoride when 0·1N-titrant was required. Two solutions of carbonate-free sodium hydroxide were standardised against Merck's *pro analysi* potassium hydrogen phthalate and found to be 1·004N. and 0·1202N. All aluminium solutions were titrated in 25-ml. portions.

Al, g.-ions per l.	Acid, ml.	Acid + Al, ml.	Al, ml.		Error, ml.	Al, g.-ions per l.	Acid, ml.	Acid + Al, ml.	Al, ml.		Error, ml.
			Found.	Calc.					Found.	Calc.	
0·4083	11·23	41·69	30·46	30·51	−0·05	0·04072	10·62	35·94	25·32	25·40	−0·08
0·3536	8·35	34·73	26·38	26·42	−0·04	0·03469	6·34	27·98	21·64	21·64	±0
0·3028	10·40	33·08	22·68	22·62	+0·06	0·03283	7·54	28·00	20·46	20·48	−0·02

Cadmium.—Standard solutions of cadmium nitrate were prepared from C.P. metal (Coleman and Bell). Titration of these solutions at room temperature with the aid of phenolphthalein (8·0—9·8) and thymolphthalein (9·3—10·5) gave low results, and the fact that the titre was not independent of the concentration precluded any possibility of developing a quantitative procedure on this basis. Consequently, an attempt was made to effect quantitative conversion of the basic salts into the hydroxide by heat. Even under these conditions the phenolphthalein end-point corresponded to slight under-titration, but this error could be entirely eliminated by the use of thymolphthalein as indicator. All titrations were conducted at temperatures above 70°, 2 ml. of a 0·05% thymolphthalein solution in

70% alcohol being used per 100 ml. of liquid present at the end-point. The proper " blank " corrections were evaluated and applied. The results obtained by this procedure are given below.

Cd, g.-ions per l.	Vol. titrated, ml.	Alkali used, N.	Acid, ml.	Acid + Cd, ml.	Blank, ml.	Acid + Cd, ml. (corr.).	Cd, ml.		Error, ml.
							Found.	Calc.	
0·5002	20	1·004	3·73	23·68	0	23·68	19·95	19·94	+0·01
0·5007	20	1·004	5·35	25·27	0	25·27	19·92	19·95	−0·03
0·04980	20	0·1202	2·86	19·54	0·08	19·46	16·60	16·58	+0·02
0·05005	20	0·1202	3·45	20·17	0·08	20·09	16·64	16·65	−0·01
0·01003	100	0·1202	2·62	19·53	0·23	19·30	16·68	16·68	0
0·009997	100	0·1202	4·89	21·72	0·23	21·49	16·60	16·63	−0·03

Anion effect. The influence of halide ions has already been referred to (p. 1001). Although the presence of a halide salt may be useful during the determinations of the free mineral acid content of cadmium solutions, as well as during the alkalimetric determination of some other metal in admixture with cadmium, yet it should be absent if cadmium itself is to be titrated. Similarly, sulphate ions must also be absent, but for a different reason. The comparative stability of the basic sulphates of cadmium precludes a well-defined colour change with any available acid–base indicator. The nearest approach to ideal behaviour is afforded by thymolphthalein (9·3—10·5). If the titration is conducted at a normal rate, a transient end-point is obtained, indicating that the precipitate is still absorbing alkali over the indicator pH range. If, however, the titrant is added sufficiently slowly, time being allowed for the repeated reversal of the colour change, the titre corresponding to quantitative formation of cadmium hydroxide can be approached closely. Although this procedure is too tedious for analytical purposes, it indicates that quantitative conversion of the basic sulphates of cadmium into the hydroxide may be accomplished at high temperatures provided a sufficiently high pH value can be attained. According to Carrière *et al.* (*loc. cit.*), the titration curve of cadmium sulphate by sodium hydroxide shows inflections at pH 9·0—10·6 and 11·2—12·8 due, respectively, to formation of $3Cd(OH)_2,CdSO_4,aq.$ and its conversion into hydroxide. They base a method for determination of cadmium on titration of its sulphate to the basic stage by use of thymolphthalein.

With available acid–base indicators, the conversion into hydroxide cannot be effected sufficiently rapidly: titrations conducted with N-alkali may theoretically be continued up to about pH 11, but the pH values attainable with indicators are considerably lower. None of those indicators of higher pH range than thymolphthalein (9·3—10·5) is even moderately satisfactory for volumetric analysis, and several of these, including alizarin-yellow (10·1—12·1) are so rapidly precipitated by metal ions that they are useless for the alkalimetric determination of metals. This method would be of much wider utility if suitable indicators were available for the pH range 10—12. The alkalimetric titration of cadmium should therefore be conducted either to the basic sulphate stage as above or in the absence of sulphate ions; these should be precipitated by addition of chloride-free barium nitrate solution in excess, and cadmium determined directly in the presence of the resulting precipitate (cf. aluminium).

Cobalt.—Standard solutions of cobalt nitrate were prepared by dissolution in dilute nitric acid of the metal prepared by electrodeposition from ammoniacal solutions of Merck's *pro analysi* cobalt sulphate, a potential difference of 4 v. being used. The alkalimetric titration of these solutions at room temperature was not satisfactory with colour indicators, owing to serious masking of the end-point by the presence of the dark blue precipitate. Quantitative conversion of any basic nitrates and of the dark blue α-hydroxide into the pale rose β-hydroxide was accomplished by conducting the titration hot. The results are summarised below, and certain conclusions may be drawn. For instance, it was evident from titrations nos. 1 and 2 that β-cobalt hydroxide exerted an intense adsorptive power for *o*-cresol-red and thymol-blue. The colour change in the supernatant liquor was indistinct, even when a relatively large amount of indicator was employed. Titration no. 3 was conducted with the aid of phenolphthalein, which showed a fairly distinct colour change despite the presence of the rose hydroxide. Nevertheless, the use of this indicator is not to be recommended since, even at a high temperature, it leads to slight under-titration. Further, in the presence of the rose hydroxide, a colour change to blue, as obtained with the aid of thymolphthalein, is better visible than one to red or violet, and titration no. 4 indicated that this end-point corresponded to quantitative formation of $Co(OH)_2$.

Theoretical titre : 25·35 ml.

Titration no.	Indicator.	pH Range.	Temp. at end-pt.	Titre, ml.	Blank, ml.	Corrected titre, ml.
1	C.R.	7·0—8·8	90°	—	—	—
2	T.B.	8·0—9·6	90	—	—	—
3	P.P.	8·0—9·8	90	25·30	0·04	25·26
4	T.P.	9·3—10·5	90	25·55	0·21	25·34
5	T.P.	9·3—10·5	25	25·35	0	25·35

However, increase in temperature mars the colour changes of most indicators, including thymolphthalein: although its colour change is sufficiently vivid in the presence of white cadmium hydroxide (see above) even at high temperatures, yet the rose cobalt hydroxide tends to mask the end-point. Also, the use of thymolphthalein in hot solution requires the application of " blank " corrections. All these drawbacks may be eliminated by completing the last stage of the titration at room temperature. For instance, titration no. 5 was carried out in hot solution to within 0·2—0·3 ml. of the approximately determined end-point, the solution was cooled, indicator added, and the last few drops of alkali introduced at room temperature. A series of titrations thus conducted has shown that, unless the solution is cooled too soon, the relatively small amount of blue precipitate produced does not interfere appreciably with the definition of the end-point. A latitude of 4—5% of the total titre is permissible when titrating 0·1N-solutions, though it is preferable to approach the end-point more closely once the approximate titration value is known. Incidentally, these results provide additional evidence that the composition of the blue precipitate produced at relatively high pH values also corresponds to $Co(OH)_2$.

Further, it proved to be immaterial whether the major part of the titration was conducted hot or cold, the only requirement being that the solution had to be heated just before the end-point. Nevertheless, it is preferable to conduct the first part of the titration at above 70°, since this results in rapid flocculation of the precipitate, and simplifies detection of slight colour changes in the supernatant liquid.

On the basis of the above considerations, the following procedure is recommended for the alkalimetric titration of cobalt solutions. (*a*) A close approximation to the true titration value is obtained by titrating the solution boiling hot, with thorough agitation near the end-point, 2 ml. of 0·05% thymolphthalein solution in 70% alcohol being used per 100 ml. of liquid present at the end-point. (*b*) Once the approximate titration value is known, the solution is titrated at 70—80° to within 0·2—0·3 ml. of the end-point, then boiled with thorough agitation until the blue precipitate has been converted into the rose one. The solution is then cooled, the indicator introduced, and the titration continued to the first appearance of blue in the supernatant liquid.

The results obtained by this procedure are shown below.

Co, g.-ions per l.	Vol. titrated, ml.	Alkali used, N.	Acid, ml.	Acid + Co, ml.	Co, ml.		Error, ml.
					Found.	Calc.	
0·5001	20	1·003	4·32	24·28	19·96	19·95	+0·01
0·4998	20	1·003	8·14	28·11	19·97	19·94	+0·03
0·05110	20	0·1202	10·05	27·03	16·98	17·00	−0·02
0·05015	20	0·1202	6·24	22·93	16·69	16·69	±0
0·01010	100	0·1202	4·37	21·15	16·78	16·81	−0·03
0·01008	100	0·1202	4·15	20·90	16·75	16·77	−0·02

Anion effect. The recorded results were obtained with solutions containing nitrate as the only anion. Chloride and sulphate must be absent on account of the comparative stability of the corresponding basic salts of cobalt. Sulphate ions can be removed by addition of chloride-free barium nitrate solution in excess, and cobalt determined directly in the presence of the precipitate.

Note.—The alkalimetric determinations described in this paper have been carried out by a large number of degree students, and proved to be accurate, rapid, and expedient.

Investigations are in progress on the extension of the method to several other metals separately and in admixture.

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