

hours or overnight. Filter the precipitate through a sintered-glass crucible (porosity G4) and wash thoroughly with 1 *M* ammonia solution (about 100 mL). Rinse the beaker (in which the precipitation was made) with 25 mL of hot 1 *M* hydrochloric acid and allow the liquid to percolate through the filter crucible, thus dissolving the precipitate. Wash the beaker and crucible with a further 10 mL of 1 *M* hydrochloric acid and then with about 75 mL of water. To the filtrate and washings in the filter flask add 35.0 mL of 0.05 *M* EDTA, neutralise the solution with 1 *M* sodium hydroxide, add 4 mL of buffer solution and a few drops of solochrome black indicator. Back-titrate with standard 0.05 *M* magnesium chloride until the colour changes from blue to wine red.

10.73 DETERMINATION OF SULPHATES

The sulphate is precipitated as barium sulphate from acid solution, the precipitate is filtered off and dissolved in a measured excess of standard EDTA solution in the presence of aqueous ammonia. The excess of EDTA is then titrated with standard magnesium chloride solution using solochrome black as indicator.

Procedure. Prepare a standard magnesium chloride solution (0.05 *M*) and a buffer solution (pH 10); see Section 10.72. Standard EDTA (0.05 *M*) will also be required.

Pipette 25.0 mL of the sulphate solution (0.02–0.03 *M*) into a 250 mL beaker, dilute to 50 mL, and adjust the pH to 1 with 2 *M* hydrochloric acid; heat nearly to boiling. Add 15 mL of a nearly boiling barium chloride solution (*ca* 0.05 *M*) fairly rapidly and with vigorous stirring; heat on a steam bath for 1 hour. Filter with suction through a filter-paper disc (Whatman filter paper No. 42) supported upon a porcelain filter disc or a Gooch crucible, wash the precipitate thoroughly with cold water, and drain. Transfer the filter-paper disc and precipitate quantitatively to the original beaker, add 35.0 mL standard 0.05 *M* EDTA solution and 5 mL concentrated ammonia solution and boil gently for 15–20 minutes; add a further 2 mL concentrated ammonia solution after 10–15 minutes to facilitate the dissolution of the precipitate. Cool the resulting clear solution, add 10 mL of the buffer solution (pH = 10), a few drops of solochrome black indicator, and titrate the excess of EDTA with the standard magnesium chloride solution to a clear red colour.

Sulphate can also be determined by an exactly similar procedure by precipitation as lead sulphate from a solution containing 50 per cent (by volume) of propan-2-ol (to reduce the solubility of the lead sulphate), separation of the precipitate, dissolution in excess of standard EDTA solution, and back-titration of the excess EDTA with a standard zinc solution using solochrome black as indicator.

PRECIPITATION TITRATIONS

10.74 PRECIPITATION REACTIONS

The most important precipitation processes in titrimetric analysis utilise silver nitrate as the reagent (argentometric processes). Discussion of the theory will, therefore, be confined to argentometric processes; the same principles can, of

course, be applied to other precipitation reactions. Consider the changes in ionic concentration which occur during the titration of 100 mL of 0.1 M sodium chloride with 0.1 M silver nitrate. The solubility product of silver chloride at the laboratory temperature is 1.2×10^{-10} . The initial concentration of chloride ions, $[\text{Cl}^-]$, is 0.1 mol L^{-1} , or $\text{pCl}^- = 1$ (see Section 2.17). When 50 mL of 0.1 M silver nitrate have been added, 50 mL of 0.1 M sodium chloride remain in a total volume of 150 mL: thus $[\text{Cl}^-] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$, or $\text{pCl}^- = 1.48$. With 90 mL of silver nitrate solution $[\text{Cl}^-] = 10 \times 0.1/190 = 5.3 \times 10^{-3}$, or $\text{pCl}^- = 2.28$.

Now

$$a_{\text{Ag}^+} \times a_{\text{Cl}^-} \approx [\text{Ag}^+] \times [\text{Cl}^-] = 1.2 \times 10^{-10} = K_{\text{sol. AgCl}}$$

or

$$\text{pAg}^+ + \text{pCl}^- = 9.92 = \text{pAgCl}$$

In the last calculation, $\text{pCl}^- = 1.48$, hence $\text{pAg}^+ = 9.92 - 1.48 = 8.44$. In this manner, the various concentrations of chloride and silver ions can be computed up to the equivalence point. At the equivalence point:

$$\text{Ag}^+ = \text{Cl}^- = \sqrt{K_{\text{sol. AgCl}}}$$

$$\text{pAg}^+ = \text{pCl}^- = \frac{1}{2} \text{pAgCl} = 9.92/2 = 4.96$$

and a saturated solution of silver chloride with no excess of silver or chloride ions is present.

With 100.1 mL of silver nitrate solution, $[\text{Ag}^+] = 0.1 \times 0.1/200.1 = 5 \times 10^{-5}$, or $\text{pAg}^+ = 4.30$; $\text{pCl}^- = \text{pAgCl} - \text{pAg}^+ = 9.92 - 4.30 = 5.62$.*

The values calculated in this way up to the addition of 110 mL of 0.1 M silver nitrate are collected in Table 10.7. Similar values for the titration of 100 mL of 0.1 M potassium iodide with 0.1 M silver nitrate are included in the same table ($K_{\text{sol. AgI}} = 1.7 \times 10^{-16}$).

It will be seen by inspecting the silver-ion exponents in the neighbourhood of the equivalence point (say, between 99.8 and 100.2 mL) that there is a marked change in the silver-ion concentration, and the change is more pronounced for silver iodide than for silver chloride, since the solubility product of the latter is about 10^6 larger than for the former. This is shown more clearly in the titration curve in Fig. 10.12, which represents the change of pAg^+ in the range between 10 per cent before and 10 per cent after the stoichiometric point in the titration of 0.1 M chloride and 0.1 M iodide respectively with 0.1 M silver nitrate. An almost identical curve is obtained by potentiometric titration using a silver electrode (see Section 15.20); the pAg^+ values may be calculated from the e.m.f. figures as in the calculation of pH.

*This is not strictly true, since the dissolved silver chloride will contribute silver and chloride ions to the solution; the actual concentration is *ca* $1 \times 10^{-5} \text{ g ions L}^{-1}$. If the excess of silver ions added is greater than 10 times this value, i.e. $> 10\sqrt{K_{\text{sol. AgCl}}}$, the error introduced by neglecting the ionic concentration produced by the dissolved salt may be taken as negligible for the purpose of the ensuing discussion.

Table 10.7 Titration of 100 mL of 0.1M NaCl and 100 mL of 0.1M KI respectively with 0.1M AgNO₃ ($K_{\text{sol. AgCl}} = 1.2 \times 10^{-10}$; $K_{\text{sol. AgI}} = 1.7 \times 10^{-16}$)

Vol. of 0.1M AgNO ₃ (mL)	Titration of chloride		Titration of iodide	
	pCl ⁻	pAg ⁺	pI ⁻	pAg ⁺
0	1.0	—	1.0	—
50	1.5	8.4	1.5	14.3
90	2.3	7.6	2.3	13.5
95	2.6	7.3	2.6	13.2
98	3.0	6.9	3.0	12.8
99	3.3	6.6	3.3	12.5
99.5	3.7	6.2	3.7	12.1
99.8	4.0	5.9	4.0	11.8
99.9	4.3	5.6	4.3	11.5
100.0	5.0	5.0	7.9	7.9
100.1	5.6	4.3	11.5	4.3
100.2	5.9	4.0	11.8	4.0
100.5	6.3	3.6	12.2	3.6
101	6.6	3.3	12.5	3.3
102	6.9	3.0	12.8	3.0
105	7.3	2.6	13.2	2.6
110	7.6	2.3	13.5	2.4

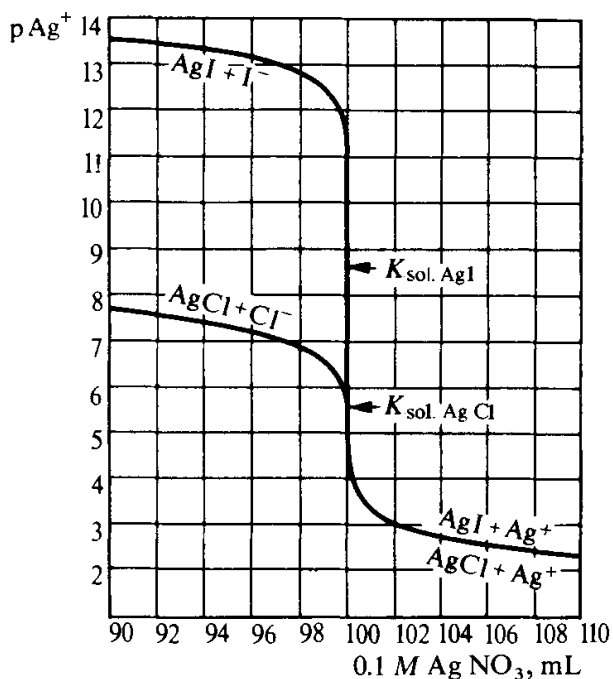


Fig. 10.12 Titration curves of 100 mL of 0.1M NaCl and of 100 mL of 0.1M KI respectively with 0.1M AgNO₃ (calculated).

10.75 DETERMINATION OF END POINTS IN PRECIPITATION REACTIONS

Many methods are utilised in determining end points in these reactions, but only the most important will be mentioned here.

(a) Formation of a coloured precipitate. This may be illustrated by the Mohr procedure for the determination of chloride and bromide. In the titration of a

neutral solution of, say, chloride ions with silver nitrate solution, a small quantity of potassium chromate solution is added to serve as indicator. At the end point the chromate ions combine with silver ions to form the sparingly soluble, red, silver chromate.

The theory of the process is as follows. This is a case of fractional precipitation (Section 2.8), the two sparingly soluble salts being silver chloride ($K_{\text{sol}} 1.2 \times 10^{-10}$) and silver chromate ($K_{\text{sol}} 1.7 \times 10^{-12}$). It is best studied by considering an actual example encountered in practice, viz. the titration of, say, 0.1 M sodium chloride with 0.1 M silver nitrate in the presence of a few millilitres of dilute potassium chromate solution. Silver chloride is the less soluble salt and the initial chloride concentration is high; hence silver chloride will be precipitated. At the first point where red silver chromate is just precipitated both salts will be in equilibrium with the solution. Hence:

$$[\text{Ag}^+] \times [\text{Cl}^-] = K_{\text{sol. AgCl}} = 1.2 \times 10^{-10}$$

$$[\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}] = K_{\text{sol. Ag}_2\text{CrO}_4} = 1.7 \times 10^{-12}$$

$$[\text{Ag}^+] = \frac{K_{\text{sol. AgCl}}}{[\text{Cl}^-]} = \sqrt{\frac{K_{\text{sol. Ag}_2\text{CrO}_4}}{[\text{CrO}_4^{2-}]}}$$

$$\frac{[\text{Cl}^-]}{\sqrt{[\text{CrO}_4^{2-}]}} = \frac{K_{\text{sol. AgCl}}}{\sqrt{K_{\text{sol. Ag}_2\text{CrO}_4}}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 9.2 \times 10^{-5}$$

At the equivalence point $[\text{Cl}^-] = \sqrt{K_{\text{sol. AgCl}}} = 1.1 \times 10^{-5}$. If silver chromate is to precipitate at this chloride-ion concentration:

$$[\text{CrO}_4^{2-}] = \left(\frac{[\text{Cl}^-]}{9.2 \times 10^{-5}} \right)^2 = \left(\frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}} \right)^2 = 1.4 \times 10^{-2}$$

or the potassium chromate solution should be 0.014 M. It should be noted that a slight excess of silver nitrate solution must be added before the red colour of silver chromate is visible. In practice, a more dilute solution (0.003–0.005 M) of potassium chromate is generally used, since a chromate solution of concentration 0.01–0.02 M imparts a distinct deep orange colour to the solution, which renders the detection of the first appearance of silver chromate somewhat difficult. The error introduced can be readily calculated, for if $[\text{CrO}_4^{2-}] =$ (say) 0.003, silver chromate will be precipitated when:

$$[\text{Ag}^+] = \sqrt{\frac{K_{\text{sol. Ag}_2\text{CrO}_4}}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{1.7 \times 10^{-12}}{3 \times 10^{-3}}} = 2.4 \times 10^{-5}$$

If the theoretical concentration of indicator is used:

$$[\text{Ag}^+] = \sqrt{\frac{1.7 \times 10^{-12}}{1.4 \times 10^{-2}}} = 1.1 \times 10^{-5}$$

The difference is $1.3 \times 10^{-5} \text{ mol L}^{-1}$. If the volume of the solution at the equivalence point is 150 mL, then this corresponds to $1.3 \times 10^{-5} \times 150 \times 10^4 / 1000 = 0.02 \text{ mL}$ of 0.1 M silver nitrate. This is the theoretical titration error, and is therefore negligible. In actual practice another factor must be considered, viz. the small excess of silver nitrate solution which must be added before the eye

can detect the colour change in the solution; this is of the order of one drop or *ca* 0.05 mL of 0.1 *M* silver nitrate.

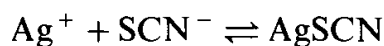
The titration error will increase with increasing dilution of the solution being titrated and is quite appreciable (*ca* 0.4* per cent) in dilute, say 0.01 *M*, solutions when the chromate concentration is of the order 0.003–0.005 *M*. This is most simply allowed for by means of an indicator blank determination, e.g. by measuring the volume of standard silver nitrate solution required to give a perceptible coloration when added to distilled water containing the same quantity of indicator as is employed in the titration. This volume is subtracted from the volume of standard solution used.

It must be mentioned that the titration should be carried out in neutral solution or in very faintly alkaline solution, i.e. within the pH range 6.5–9. In acid solution, the following reaction occurs:

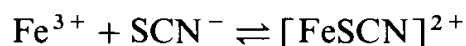


HCrO_4^- is a weak acid; consequently the chromate-ion concentration is reduced and the solubility product of silver chromate may not be exceeded. In markedly alkaline solutions, silver hydroxide ($K_{\text{sol.}} 2.3 \times 10^{-8}$) might be precipitated. A simple method of making an acid solution neutral is to add an excess of pure calcium carbonate or sodium hydrogencarbonate. An alkaline solution may be acidified with acetic acid and then a slight excess of calcium carbonate is added. The solubility product of silver chromate increases with rising temperature; the titration should therefore be performed at room temperature. By using a mixture of potassium chromate and potassium dichromate in proportions such as to give a neutral solution, the danger of accidentally raising the pH of an unbuffered solution beyond the acceptable limits is minimised; the mixed indicator has a buffering effect and adjusts the pH of the solution to 7.0 ± 0.1 . In the presence of ammonium salts, the pH must not exceed 7.2 because of the effect of appreciable concentrations of ammonia upon the solubility of silver salts. Titration of iodide and of thiocyanate is not successful because silver iodide and silver thiocyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

(b) Formation of a soluble coloured compound. This procedure is exemplified by Volhard's method for the titration of silver in the presence of free nitric acid with standard potassium thiocyanate or ammonium thiocyanate solution. The indicator is a solution of iron(III) nitrate or of iron(III) ammonium sulphate. The addition of thiocyanate solution produces first a precipitate of silver thiocyanate ($K_{\text{sol.}} 7.1 \times 10^{-13}$):



When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown coloration, due to the formation of a complex ion:†

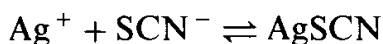
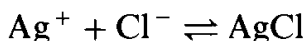


This method may be applied to the determination of chlorides, bromides,

* The errors for 0.1 *M* and 0.01 *M* bromide may be calculated to be 0.04 and 0.4 per cent respectively.

† This is the complex formed when the ratio of thiocyanate ion to iron(III) ion is low; higher complexes, $[\text{Fe}(\text{SCN})_2]^+$, etc., are important only at higher concentrations of thiocyanate ion.

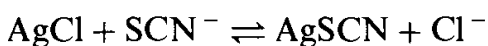
and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:



The two sparingly soluble salts will be in equilibrium with the solution, hence:

$$\frac{[\text{Cl}^-]}{[\text{SCN}^-]} = \frac{K_{\text{sol. AgCl}}}{K_{\text{sol. AgSCN}}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble salt, until the ratio $[\text{Cl}^-]/[\text{SCN}^-]$ in the solution is 169:



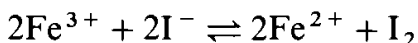
This will take place before reaction occurs with the iron(III) ions in the solution, and there will consequently be a considerable titration error. It is therefore absolutely necessary to prevent the reaction between the thiocyanate and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable:

1. The silver chloride is filtered off before back-titrating. Since at this stage the precipitate will be contaminated with adsorbed silver ions, the suspension should be boiled for a few minutes to coagulate the silver chloride and thus remove most of the adsorbed silver ions from its surface before filtration. The cold filtrate is titrated.
2. After the addition of silver nitrate, potassium nitrate is added as coagulant, the suspension is boiled for about 3 minutes, cooled and then titrated immediately. Desorption of silver ions occurs and, on cooling, re-adsorption is largely prevented by the presence of potassium nitrate.
3. An immiscible liquid is added to 'coat' the silver chloride particles and thereby protect them from interaction with the thiocyanate. The most successful liquid is nitrobenzene (*ca* 1.0 mL for each 50 mg of chloride): the suspension is well shaken to coagulate the precipitate before back-titration.

With bromides, we have the equilibrium:

$$\frac{[\text{Br}^-]}{[\text{SCN}^-]} = \frac{K_{\text{sol. AgBr}}}{K_{\text{sol. AgSCN}}} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5$$

The titration error is small, and no difficulties arise in the determination of the end point. Silver iodide ($K_{\text{sol.}} 1.7 \times 10^{-16}$) is less soluble than the bromide; the titration error is negligible, but the iron(III) indicator should not be added until excess of silver is present, since the dissolved iodide reacts with Fe^{3+} ions:



(c) **Use of adsorption indicators.** K. Fajans introduced a useful type of indicator for precipitation reactions as a result of his studies on the nature of adsorption. The action of these indicators is due to the fact that at the equivalence point the indicator is adsorbed by the precipitate, and during the process of

adsorption a change occurs in the indicator which leads to a substance of different colour; they have therefore been termed **adsorption indicators**. The substances employed are either acid dyes, such as those of the fluorescein series, e.g. fluorescein and eosin which are utilised as the sodium salts, or basic dyes, such as those of the rhodamine series (e.g. rhodamine 6G), which are used as the halogen salts.

The theory of the action of these indicators is based upon the properties of colloids, Section 11.3. When a chloride solution is titrated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions); this may be termed the primary adsorbed layer. By a process known as secondary adsorption, oppositely charged ions present in solution are held around it (shown diagrammatically in Fig. 10.13a). As soon as the stoichiometric point is reached, silver ions are present in excess and these now become primarily adsorbed; nitrate ions will be held by secondary adsorption (Fig. 10.13b). If fluorescein is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than is the nitrate ion, is immediately adsorbed, and will reveal its presence on the precipitate, not by its own colour, which is that of the solution, but by the formation of a pink complex of silver and a modified fluorescein ion on the surface with the first trace of excess of silver ions. An alternative view is that during the adsorption of the fluorescein ion a rearrangement of the structure of the ion occurs with the formation of a coloured substance. It is important to notice that the colour change takes place at the *surface* of the precipitate. If chloride is now added, the suspension remains pink until chloride ions are present in excess, the adsorbed silver ions are converted into silver chloride, which primarily adsorbs chloride ions. The secondary adsorbed fluorescein ions pass back into solution, to which they impart a greenish-yellow colour.

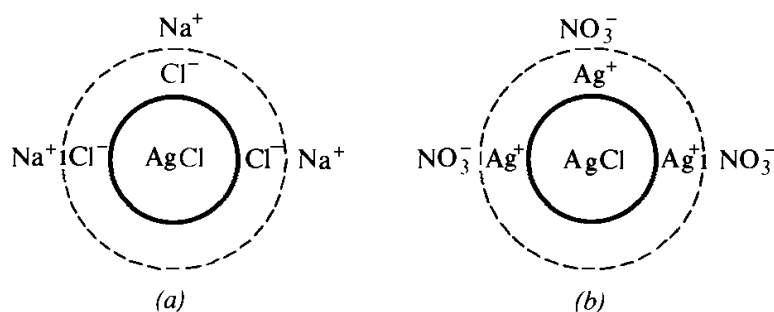


Fig. 10.13 (a) AgCl precipitated in the presence of excess of Cl^- ; (b) AgCl precipitated in the presence of excess of Ag^+ .

The following conditions will govern the choice of a suitable adsorption indicator:

- The precipitate should separate as far as possible in the colloidal condition. Large quantities of neutral salts, particularly of multicharged ions, should be avoided owing to their coagulating effect. The solution should not be too dilute, as the amount of precipitate formed will be small and the colour change far from sharp with certain indicators.
- The indicator ion must be of opposite charge to the ion of the precipitating agent.
- The indicator ion should not be adsorbed before the particular compound

has been completely precipitated, but it should be strongly adsorbed immediately after the equivalence point. The indicator ion should not be too strongly adsorbed by the precipitate; if this occurs, e.g. eosin (tetrabromofluorescein) in the chloride–silver titration, the adsorption of the indicator ion may be a primary process and will take place before the equivalence point.

A disadvantage of adsorption indicators is that silver halides are sensitised to the action of light by a layer of adsorbed dyestuff. For this reason, titrations should be carried out with a minimum exposure to sunlight. When using adsorption indicators, only 2×10^{-4} to 3×10^{-3} mol of dye per mol of silver halide is added; this small concentration is used so that an appreciable fraction of the added indicator is actually adsorbed on the precipitate.

For the titration of chlorides, fluorescein may be used. This indicator is a very weak acid ($K_a = ca\ 1 \times 10^{-8}$); hence even a small amount of other acids reduces the already minute ionisation, thus rendering the detection of the end point (which depends essentially upon the adsorption of the free anion) either impossible or difficult to observe. The optimum pH range is between 7 and 10. Dichlorofluorescein is a stronger acid and may be utilised in slightly acid solutions of pH greater than 4.4; this indicator has the further advantage that it is applicable in more dilute solutions.

Eosin (tetrabromofluorescein) is a stronger acid than dichlorofluorescein and can be used down to a pH of 1–2; the colour change is sharpest in an acetic acid solution (pH < 3). Eosin is so strongly adsorbed on silver halides that it cannot be used for chloride titrations; this is because the eosin ion can compete with chloride ion before the equivalence point and thereby gives a premature indication of the end point. With the more strongly adsorbing ions, Br^- , I^- and SCN^- , the competition is not serious and a very sharp end point is obtained in the titration of these ions, even in dilute solutions. The colour of the precipitate is magenta. Rose Bengal (dichlorotetraiodofluorescein) and dimethyldiiodofluorescein have been recommended for the titration of iodides.

Other dyestuffs have been recommended as adsorption indicators for the titration of halides and other ions. Thus cyanide ion may be titrated with standard silver nitrate solution using diphenylcarbazide as adsorption indicator (see Section 10.44): the precipitate is pale violet at the end point. A selection of adsorption indicators, their properties and uses, is given in Table 10.8.

(d) Turbidity method. The appearance of a turbidity is sometimes utilised to mark the end-point of a reaction, as in Liebig's method for cyanides (see Section 10.44). A method which should be included here is the **turbidity procedure for the determination of silver with chloride**; first introduced by Gay Lussac. A standard solution of sodium chloride is titrated with a solution of silver nitrate or vice versa. Under certain conditions the addition of an indicator is unnecessary, because the presence of a turbidity caused by the addition of a few drops of one of the solutions to the other will show that the end point has not been reached. The titration is continued until the addition of the appropriate solution produces no turbidity. Accurate results are obtained.

The procedure may be illustrated by the following simple experiment, which is a modification of the Gay Lussac–Stas method. The sodium chloride solution is added to the silver solution in the presence of free nitric acid and a small quantity of pure barium nitrate (the latter to assist coagulation of the precipitate).

Table 10.8 Selected adsorption indicators: properties and uses

Indicator	Use
Fluorescein	Cl^- , Br^- , I^- , with Ag^+
Dichlorofluorescein	Cl^- , Br^- , BO_3^{3-} , with Ag^+
Tetrabromofluorescein (eosin)	Br^- , I^- , SCN^- , with Ag^+
Dichloro-tetraiodofluorescein (Rose Bengal)	I^- in presence of Cl^- , with Ag^+
Di-iodo-dimethylfluorescein	I^- , with Ag^+
Tartrazine	Ag^+ , with I^- or SCN^- ; $\text{I}^- + \text{Cl}^-$, with excess Ag^+ , back-titration with I^-
Sodium alizarin sulphonate (alizarin red S)	$[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{MoO}_4]^{2-}$ with Pb^{2+}
Rhodamine 6G	Ag^+ with Br^-
Phenosafranine	Cl^- , Br^- , with Ag^+ Ag^+ , with Br^-

* The colour change is as indicator passes from solution to precipitate, unless otherwise stated.

Weigh out accurately about 0.40 g of silver nitrate into a well-stoppered 200 mL bottle. Add about 100 mL of water, a few drops of concentrated nitric acid, and a small crystal of barium nitrate. Titrate with standard 0.1 M sodium chloride by adding 20 mL at once, stoppering the bottle, and shaking it vigorously until the precipitate of silver chloride has coagulated and settled, leaving a clear solution. The volume of sodium chloride solution taken should leave the silver still in excess. Continue to add the chloride solution, 1 mL at a time, stoppering and shaking after each addition, until no turbidity is produced: note the total volume of sodium chloride solution. Repeat the determination, using a fresh sample of silver nitrate of about the same weight, and run in initially that volume of the 0.1 M sodium chloride, less 1 mL, which the first titration has indicated will be required, and thereafter add the chloride solution dropwise (i.e. in about 0.05 mL portions). It will be found that the end point can be determined within one drop.

The following sections are concerned with the use of standard solutions of reagents such as silver nitrate, sodium chloride, potassium (or ammonium) thiocyanate, and potassium cyanide. Some of the determinations which will be considered strictly involve complex formation rather than precipitation reactions, but it is convenient to group them here as reactions involving the use of standard silver nitrate solutions. Before commencing the experimental work, the theoretical Sections 10.74 and 10.75 should be studied.

10.76 PREPARATION OF 0.1 M SILVER NITRATE

Discussion. Very pure silver can be obtained commercially, and a standard solution can be prepared by dissolving a known weight (say, 10.787 g) in nitric acid in a conical flask having a funnel in the neck to prevent mechanical loss, and making up to a known volume (say, 1 L for a 0.1 M solution). The presence of acid must, however, be avoided in determinations with potassium chromate as indicator or in determinations employing adsorption indicators. It is therefore preferable to employ a neutral solution prepared by dissolving silver nitrate (relative molecular mass, 169.87) in water.

Analytical grade silver nitrate has a purity of at least 99.9 per cent, so that a standard solution can be prepared by direct weighing. If, however, commercial

Colour change at end-point*	Further data of interest
Yellowish-green → pink	Solution must be neutral or weakly basic
Yellowish-green → red	Useful pH range 4.4–7
Pink → reddish-violet	Best in acetic (ethanoic) acid solution; useful down to pH 1–2
Red → purple	Accurate if $(\text{NH}_4)_2\text{CO}_3$ added
Orange–red → blue–red	Useful pH range 4–7
Colourless solution → green solution	Sharp colour change in $\text{I}^- + \text{Cl}^-$ back-titration
Yellow → pink	Neutral solution
Orange–pink → reddish-violet	Best in dilute (up to 0.3M) HNO_3
Red ppt. → blue ppt.	Sharp, reversible colour change on ppt., but only if NO_3^- is present.
Blue ppt. → red ppt.	Tolerance up to 0.2M HNO_3

recrystallised silver nitrate be employed, or if an additional check of the molarity of the silver nitrate solution is required, standardisation may be effected with pure sodium chloride. Sodium chloride has a purity of 99.9–100.0 per cent and may be used as a primary standard. Sodium chloride is very slightly hygroscopic, and for accurate work it is best to dry the finely powdered solid in an electric oven at 250–350 °C for 1–2 hours, and allow it to cool in a desiccator.

Procedure. From silver nitrate. Dry some finely powdered analytical grade silver nitrate at 120 °C for 2 hours and allow it to cool in a covered vessel in a desiccator. Weigh out accurately 8.494 g, dissolve it in water and make up to 500 mL in a graduated flask. This gives a 0.1000 M solution. Alternatively, about 8.5 g of pure, dry silver nitrate may be weighed out accurately, dissolved in 500 mL of water in a graduated flask, and the molar concentration calculated from the weight of silver nitrate employed.

In many cases the analytical grade material may be replaced by ‘pure recrystallised’ silver nitrate, but in that case it is advisable to standardise the solution against sodium chloride. Solutions of silver nitrate should be protected from light and are best stored in amber-coloured glass bottles.

10.77 STANDARDISATION OF SILVER NITRATE SOLUTION

Sodium chloride has a relative molecular mass of 58.44. A 0.1000 M solution is prepared by weighing out 2.922 g of the pure dry salt (see Section 10.74) and dissolving it in 500 mL of water in a graduated flask. Alternatively about 2.9 g of the pure salt is accurately weighed out, dissolved in 500 mL of water in a graduated flask and the molar concentration calculated from the weight of sodium chloride employed.

(a) With potassium chromate as indicator: The Mohr titration. The reader is referred to Section 10.75 for the detailed theory of the titration. Prepare the indicator solution by dissolving 5 g potassium chromate in 100 mL of water. The final volume of the solution in the titration is 50–100 mL, and 1 mL of the indicator solution is used, so that the indicator concentration in the actual titration is 0.005–0.0025 M.

Alternatively, and preferably, dissolve 4.2 g potassium chromate and 0.7 g

potassium dichromate in 100 mL of water; use 1 mL of indicator solution for each 50 mL of the final volume of the test solution.

Pipette 25 mL of the standard 0.1 *M* sodium chloride into a 250 mL conical flask resting upon a white tile, and add 1 mL of the indicator solution (preferably with a 1 mL pipette). Add the silver nitrate solution slowly from a burette, swirling the liquid constantly, until the red colour formed by the addition of each drop begins to disappear more slowly: this is an indication that most of the chloride has been precipitated. Continue the addition dropwise until a faint but distinct change in colour occurs. This *faint* reddish-brown colour should persist after brisk shaking. If the end point is overstepped (production of a deep reddish-brown colour), add more of the chloride solution and titrate again. Determine the indicator blank correction by adding 1 mL of the indicator to a volume of water equal to the final volume in the titration (Note), and then 0.01 *M* silver nitrate solution until the colour of the blank matches that of the solution titrated. The indicator blank correction, which should not amount to more than 0.03–0.10 mL of silver nitrate, is deducted from the volume of silver nitrate used in the titration. Repeat the titration with two further 25 mL portions of the sodium chloride solution. The various titrations should agree within 0.1 mL.

Note. A better blank is obtained by adding about 0.5 g of calcium carbonate before determining the correction. This gives an inert white precipitate similar to that obtained in the titration of chlorides and materially assists in matching the colour tints.

(b) With an adsorption indicator: Discussion. The detailed theory of the process is given in Section 10.75. Both fluorescein and dichlorofluorescein are suitable for the titration of chlorides. In both cases the end point is reached when the white precipitate in the greenish-yellow solution suddenly assumes a pronounced reddish tint. The change is reversible upon the addition of chloride. With fluorescein the solution must be neutral or only faintly acidic with acetic acid; acid solutions should be treated with a slight excess of sodium acetate. The chloride solution should be diluted to about 0.01–0.05 *M*, for if it is more concentrated the precipitate coagulates too soon and interferes. Fluorescein cannot be used in solutions more dilute than 0.005 *M*. With more dilute solutions resort must be made to dichlorofluorescein, which possesses other advantages over fluorescein. Dichlorofluorescein gives good results in very dilute solutions (e.g. for drinking water) and is applicable in the presence of acetic (ethanoic) acid and in weakly acid solutions. For this reason the chlorides of copper, nickel, manganese, zinc, aluminium, and magnesium, which cannot be titrated according to Mohr's method, can be determined by a direct titration when dichlorofluorescein is used as indicator.

For the reverse titration (chloride into silver nitrate), tartrazine (four drops of a 0.2 per cent solution per 100 mL) is a good indicator. At the end point, the almost colourless liquid assumes a blue colour.

The indicator solutions are prepared as follows:

Fluorescein. Dissolve 0.2 g fluorescein in 100 mL of 70 per cent ethanol, or dissolve 0.2 g sodium fluoresceinate in 100 mL of water.

Dichlorofluorescein. Dissolve 0.1 g dichlorofluorescein in 100 mL of 60–70 per cent ethanol, or dissolve 0.1 g sodium dichlorofluoresceinate in 100 mL of water.

Procedure. Pipette 25 mL of the standard 0.1 *M* sodium chloride into a 250 mL conical flask. Add 10 drops of either fluorescein or dichlorofluorescein indicator, and titrate with the silver nitrate solution in a diffuse light, while rotating the flask constantly. As the end point is approached, the silver chloride coagulates appreciably, and the local development of a pink colour upon the addition of a drop of the silver nitrate solution becomes more and more pronounced. Continue the addition of the silver nitrate solution until the precipitate suddenly assumes a pronounced pink or red colour. Repeat the titration with two other 25 mL portions of the chloride solution. Individual titrations should agree within 0.1 mL.

Calculate the molar concentration of the silver nitrate solution.

10.78 DETERMINATION OF CHLORIDES AND BROMIDES

Either the Mohr titration or the adsorption indicator method may be used for the determination of chlorides in neutral solution by titration with standard 0.1 *M* silver nitrate. If the solution is acid, neutralisation may be effected with chloride-free calcium carbonate, sodium tetraborate, or sodium hydrogencarbonate. Mineral acid may also be removed by neutralising most of the acid with ammonia solution and then adding an excess of ammonium acetate. Titration of the neutral solution, prepared with calcium carbonate, by the adsorption indicator method is rendered easier by the addition of 5 mL of 2 per cent dextrin solution; this offsets the coagulating effect of the calcium ion. If the solution is basic, it may be neutralised with chloride-free nitric acid, using phenolphthalein as indicator.

Similar remarks apply to the **determination of bromides**; the Mohr titration can be used, and the most suitable adsorption indicator is **eosin** which can be used in dilute solutions and even in the presence of 0.1 *M* nitric acid, but in general, acetic (ethanoic) acid solutions are preferred. Fluorescein may be used but is subject to the same limitations as experienced with chlorides [Section 10.77(b)]. With eosin indicator, the silver bromide flocculates approximately 1 per cent before the equivalence point and the local development of a red colour becomes more and more pronounced with the addition of silver nitrate solution: at the end point the precipitate assumes a magenta colour.

The indicator is prepared by dissolving 0.1 g eosin in 100 mL of 70 per cent ethanol, or by dissolving 0.1 g of the sodium salt in 100 mL of water.

For the **reverse titration** (bromide into silver nitrate), rhodamine 6G (10 drops of a 0.05 per cent aqueous solution) is an excellent indicator. The solution is best adjusted to 0.05 *M* with respect to silver ion. The precipitate acquires a violet colour at the end point.

Thiocyanates may also be determined using adsorption indicators in exactly similar manner to chlorides and bromides, but an iron(III) salt indicator is usually preferred (Section 10.82).

10.79 DETERMINATION OF IODIDES

Discussion. The Mohr method cannot be applied to the titration of iodides (or of thiocyanates), because of adsorption phenomena and the difficulty of distinguishing the colour change of the potassium chromate. Eosin is a suitable

adsorption indicator, but di-iododimethylfluorescein is better. Eosin is employed as described under bromides (Section 10.78).

The di-iododimethylfluorescein indicator is prepared by dissolving 1.0 g in 100 mL of 70 per cent ethanol. The colour change is from an orange-red to a blue-red on the precipitate.

10.80 DETERMINATION OF MIXTURES OF HALIDES WITH ADSORPTION INDICATORS

(a) **Chloride and iodide in a mixture.** These two ions differ considerably in the ease with which they are adsorbed on the corresponding silver halide. This makes it possible to select adsorption indicators which will permit the determination of chloride and iodide in the presence of one another. Thus the iodide may be determined by titration with standard 0.1 *M* silver nitrate using di-iododimethylfluorescein and the iodide + chloride by a similar titration using fluorescein. Chloride is obtained by difference. If a large excess of chloride is present, the result for iodide may be as much as 1 per cent high. If, however, rose Bengal (dichlorotetraiodofluorescein) is used as indicator (colour change, carmine red to blue-red) in the presence of ammonium carbonate, the iodide titration is exact.

(b) **Bromide and iodide in a mixture.** The total halide (bromide + iodide) is determined by titration with standard 0.1 *M* silver nitrate using eosin or fluorescein as indicator. The iodide is determined by titration with 0.01–0.2 *M* silver nitrate, using di-iododimethylfluorescein as indicator. Bromide is obtained by difference.

Numerous adsorption indicators have been suggested for various purposes, but a full treatment is outside the scope of this work.

10.81 DETERMINATION OF MIXTURES OF HALIDES BY AN INDIRECT METHOD

Discussion. The method is applicable to the determination of a mixture of two salts having the same anion (e.g. sodium chloride and potassium chloride) or the same cation (e.g. potassium chloride and potassium bromide). For example, to determine the amount of sodium and potassium chlorides in a mixture of the two salts, a known weight (w_1 g) of the solid mixture is taken, and the total chloride is determined with standard 0.1 *M* silver nitrate, using Mohr's method or an adsorption indicator. Let w_2 g of silver nitrate be required for the complete precipitation of w_1 g of the mixture, which contains x g of NaCl and y g of KCl. Then:

$$x + y = w_1$$

$$\frac{169.87x}{58.44} + \frac{169.87y}{74.55} = w_2$$

Upon solving these two simultaneous equations, the values for x and y are deduced.

Now suppose that the determination of potassium chloride and potassium bromide in a mixture is desired. The total halide is determined by Mohr's method or with an adsorption indicator. Let the weight of the mixture be w_3 g and w_4 g, be the weight of silver nitrate required for complete precipitation,

p g be the weight of the potassium chloride, and q g be the weight of the potassium bromide. Then:

$$p + q = w_3$$

$$\frac{169.87p}{74.55} + \frac{169.87q}{119.00} = w_4$$

The values of p and q can be obtained by solving the simultaneous equations.

It can be shown that the method depends upon the difference between the relative molecular masses of the two components of the mixture and that it is most satisfactory when the two constituents are present in approximately equal proportions.

10.82 PREPARATION AND USE OF 0.1M AMMONIUM OR POTASSIUM THIOCYANATE: TITRATIONS ACCORDING TO VOLHARD'S METHOD

Discussion. Volhard's original method for the determination of silver in dilute nitric acid solution by titration with standard thiocyanate solution in the presence of an iron(III) salt as indicator has proved of great value not only for silver determinations, but also in numerous indirect analyses. The theory of the Volhard process has been given in Section 10.75. In this connection it must be pointed out that the concentration of the nitric acid should be from 0.5 to 1.5 M (strong nitric acid retards the formation of the thiocyanato-iron(III) complex $[\text{FeSCN}]^{2+}$) and at a temperature not exceeding 25 °C (higher temperatures tend to bleach the colour of the indicator). The solutions must be free from nitrous acid, which gives a red colour with thiocyanic acid, and may be mistaken for 'iron(III) thiocyanate'. Pure nitric acid is prepared by diluting the usual pure acid with about one-quarter of its volume of water and boiling until perfectly colourless; this eliminates any lower oxides of nitrogen which may be present.

The method may be applied to those anions (e.g. chloride, bromide, and iodide) which are completely precipitated by silver and are sparingly soluble in dilute nitric acid. Excess of standard silver nitrate solution is added to the solution containing free nitric acid, and the residual silver nitrate solution is titrated with standard thiocyanate solution. This is sometimes termed **the residual process**. Anions whose silver salts are slightly soluble in water, but which are soluble in nitric acid, such as phosphate, arsenate, chromate, sulphide, and oxalate, may be precipitated in neutral solution with an excess of standard silver nitrate solution. The precipitate is filtered off, thoroughly washed, dissolved in dilute nitric acid, and the silver titrated with thiocyanate solution. Alternatively, the residual silver nitrate in the filtrate from the precipitation may be determined with thiocyanate solution after acidification with dilute nitric acid.

Both ammonium and potassium thiocyanates are usually available as deliquescent solids; the analytical-grade products are, however, free from chlorides and other interfering substances. An approximately 0.1 M solution is, therefore, first prepared, and this is standardised by titration against standard 0.1 M silver nitrate.

Procedure. Weigh out about 8.5 g ammonium thiocyanate, or 10.5 g potassium thiocyanate, and dissolve it in 1 L of water in a graduated flask. Shake well.

Standardisation. Use 0.1 *M* silver nitrate, which has been prepared and standardised as described in Section 10.77.

The iron(III) indicator solution consists of a cold, saturated solution of ammonium iron(III) sulphate in water (about 40 per cent) to which a few drops of 6 *M* nitric acid have been added. One millilitre of this solution is employed for each titration.

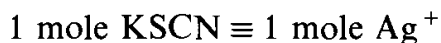
Pipette 25 mL of the standard 0.1 *M* silver nitrate into a 250 mL conical flask, add 5 mL of 6 *M* nitric acid and 1 mL of the iron(III) indicator solution. Run in the potassium or ammonium thiocyanate solution from a burette. At first a white precipitate is produced, rendering the liquid of a milky appearance, and as each drop of thiocyanate falls in, it produces a reddish-brown cloud, which quickly disappears on shaking. As the end point approaches, the precipitate becomes flocculent and settles easily; finally one drop of the thiocyanate solution produces a faint brown colour, which no longer disappears upon shaking. This is the end point. The indicator blank amounts to 0.01 mL of 0.1 *M* silver nitrate. It is essential to shake vigorously during the titration in order to obtain correct results.*

The standard solution thus prepared is stable for a very long period if evaporation is prevented.

Use of tartrazine as indicator. Satisfactory results may be obtained by the use of tartrazine as indicator. Proceed as above, but add 4 drops of tartrazine (0.5 per cent aqueous solution) in lieu of the iron(III) indicator. The precipitate will appear pale yellow during the titration, but the supernatant liquid (best viewed by placing the eye at the level of the liquid and looking through it) is colourless. At the end point, the supernatant liquid assumes a bright lemon-yellow colour. The titration is sharp to one drop of 0.1 *M* thiocyanate solution.

10.83 DETERMINATION OF SILVER IN A SILVER ALLOY

A commercial silver alloy in the form of wire or foil is suitable for this determination. Clean the alloy with emery cloth and weigh it accurately. Place it in a 250 mL conical flask, add 5 mL water and 10 mL concentrated nitric acid; place a funnel in the mouth of the flask to avoid mechanical loss. Warm the flask gently until the alloy has dissolved. Add a little water and boil for 5 minutes in order to expel oxides of nitrogen. Transfer the cold solution quantitatively to a 100 mL graduated flask and make up to the mark with distilled water. Titrate 25 mL portions of the solution with standard 0.1 *M* thiocyanate.

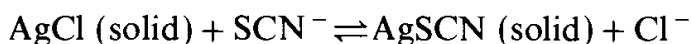


Note. The presence of metals whose salts are colourless does not influence the accuracy of the determination, except that mercury and palladium must be absent since their thiocyanates are insoluble. Salts of metals (e.g. nickel and cobalt) which are coloured must not be present to any considerable extent. Copper does not interfere, provided it does not form more than about 40 per cent of the alloy.

* The freshly precipitated silver thiocyanate adsorbs silver ions, thereby causing a false end point which, however, disappears with vigorous shaking.

10.84 DETERMINATION OF CHLORIDES (VOLHARD'S METHOD)

Discussion. The chloride solution is treated with excess of standard silver nitrate solution, and the residual silver nitrate determined by titration with standard thiocyanate solution. Now silver chloride is more soluble than silver thiocyanate, and would react with the thiocyanate thus:



It is therefore necessary to remove the silver chloride by filtration. The filtration may be avoided by the addition of a little nitrobenzene (about 1 mL for each 0.05 g of chloride); the silver chloride particles are probably surrounded by a film of nitrobenzene. Another method, applicable to chlorides, in which filtration of the silver chloride is unnecessary, is to employ tartrazine as indicator (Section 10.82).

Procedure A (HCl content of concentrated hydrochloric acid). Ordinary concentrated hydrochloric acid is usually 10–11 *M*, and must be diluted first. Measure out accurately 10 mL of the concentrated acid from a burette into a 1 L graduated flask and make up to the mark with distilled water. Shake well. Pipette 25 mL into a 250 mL conical flask, add 5 mL 6 *M* nitric acid and then add 30 mL standard 0.1 *M* silver nitrate (or sufficient to give 2–5 mL excess). Shake to coagulate the precipitate,* filter through a quantitative filter paper (or through a porous porcelain or sintered-glass crucible), and wash thoroughly with very dilute nitric acid (1:100). Add 1 mL of the iron(III) indicator solution to the combined filtrate and washings, and titrate the residual silver nitrate with standard 0.1 *M* thiocyanate.

Calculate the volume of standard 0.1 *M* silver nitrate that has reacted with the hydrochloric acid, and therefrom the percentage of HCl in the sample employed.

Procedure B. Pipette 25 mL of the diluted solution into a 250 mL conical flask containing 5 mL 6 *M* nitric acid. Add a slight excess of standard 0.1 *M* silver nitrate (about 30 mL in all) from a burette. Then add 2–3 mL pure nitrobenzene and 1 mL of the iron(III) indicator, and shake vigorously to coagulate the precipitate. Titrate the residual silver nitrate with standard 0.1 *M* thiocyanate until a permanent faint reddish-brown coloration appears.

From the volume of silver nitrate solution added, subtract the volume of silver nitrate solution that is equivalent to the volume of standard thiocyanate required. Then calculate the percentage of HCl in the sample.

Procedure C. Pipette 25 mL of the diluted solution into a 250 mL conical flask containing 5 mL of 6 *M* nitric acid, add a slight excess of 0.1 *M* silver nitrate (30–35 mL) from a burette, and four drops of tartrazine indicator (0.5 per cent aqueous solution). Shake the suspension for about a minute in order to ensure that the indicator is adsorbed on the precipitate as far as possible. Titrate the residual silver nitrate with standard 0.1 *M* ammonium or potassium thiocyanate with swirling of the suspension until the very pale yellow supernatant liquid (viewed with the eye at the level of the liquid) assumes a rich lemon-yellow colour.

*It is better to boil the suspension for a few minutes to coagulate the silver chloride and thus remove most of the adsorbed silver ions from its surface before filtration.

Bromides can also be determined by the Volhard method, but as silver bromide is less soluble than silver thiocyanate it is not necessary to filter off the silver bromide (compare chloride). The bromide solution is acidified with dilute nitric acid, an excess of standard 0.1 *M* silver nitrate added, the mixture thoroughly shaken, and the residual silver nitrate determined with standard 0.1 *M* ammonium or potassium thiocyanate, using ammonium iron(III) sulphate as indicator.

Iodides can also be determined by this method, and in this case too there is no need to filter off the silver halide, since silver iodide is very much less soluble than silver thiocyanate. In this determination the iodide solution must be very dilute in order to reduce adsorption effects. The dilute iodide solution (*ca* 300 mL), acidified with dilute nitric acid, is treated very slowly and with vigorous stirring or shaking with standard 0.1 *M* silver nitrate until the yellow precipitate coagulates and the supernatant liquid appears colourless. Silver nitrate is then present in excess. One millilitre of iron(III) indicator solution is added, and the residual silver nitrate is titrated with standard 0.1 *M* ammonium or potassium thiocyanate.

10.85 DETERMINATION OF FLUORIDE: PRECIPITATION AS LEAD CHLOROFLUORIDE COUPLED WITH VOLHARD TITRATION

Discussion. This method is based upon the precipitation of lead chlorofluoride, in which the chlorine is determined by Volhard's method, and from this result the fluorine content can be calculated. The advantages of the method are, the precipitate is granular, settles readily, and is easily filtered; the factor for conversion to fluorine is low; the procedure is carried out at pH 3.6–5.6, so that substances which might be co-precipitated, such as phosphates, sulphates, chromates, and carbonates, do not interfere. Aluminium must be entirely absent, since even very small quantities cause low results; a similar effect is produced by boron (>0.05 g), ammonium (>0.5 g), and sodium or potassium (>10 g) in the presence of about 0.1 g of fluoride. Iron must be removed, but zinc is without effect. Silica does not vitiate the method, but causes difficulties in filtration.

Procedure. Pipette 25.0 mL of the solution containing between 0.01 and 0.1 g fluoride into a 400 mL beaker, add two drops of bromophenol blue indicator, 3 mL of 10 per cent sodium chloride, and dilute the mixture to 250 mL. Add dilute nitric acid until the colour just changes to yellow, and then add dilute sodium hydroxide solution until the colour just changes to blue. Treat with 1 mL of concentrated hydrochloric acid, then with 5.0 g of lead nitrate, and heat on a water bath. Stir gently until the lead nitrate has dissolved, and then immediately add 5.0 g of crystallised sodium acetate and stir vigorously. Digest on the water bath for 30 minutes, with occasional stirring, and allow to stand overnight.

Meanwhile, a washing solution of lead chlorofluoride is prepared as follows. Add a solution of 10 g of lead nitrate in 200 mL of water to 100 mL of a solution containing 1.0 g of sodium fluoride and 2 mL of concentrated hydrochloric acid, mix it thoroughly, and allow the precipitate to settle. Decant the supernatant liquid, wash the precipitate by decantation with five portions of water, each of about 200 mL. Finally add 1 L of water to the precipitate, shake the mixture