

Indirect Complexometric Titration of Barium and Strontium after Stepwise Precipitation as Sulphate from Homogeneous Solution

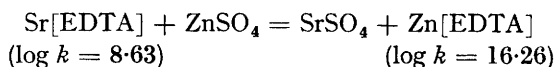
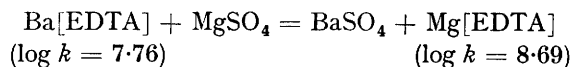
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An indirect method has been developed for the stepwise titration of barium and strontium with EDTA, based on precipitation of the elements as sulphate from a homogeneous solution. Barium, strontium and other multivalent cations are complexed by titration with EDTA at pH 10.0 by using a mixed indicator comprising Eriochrome black T, Titan yellow and Naphthol green B. Barium is then selectively replaced from its EDTA complex and precipitated as the sulphate with an excess of magnesium sulphate solution. The excess of magnesium is determined by titration with EDTA and the equivalent concentration of barium is calculated. Strontium is determined in the same solution in the same way, with an excess of zinc sulphate solution.

The optimum conditions for precipitation and the interferences due to various anions and cations have also been studied. Copper, nickel, cobalt and iron interfere and a second method for the determination of barium alone has been derived wherein the interfering elements are complexed with triethanolamine, potassium cyanide and ascorbic acid. Phosphate and chromate interfere and require to be separated.

VARIOUS methods based on direct and back-titrations of barium and strontium with EDTA (disodium salt) are reported in the literature.¹⁻⁴ In all of the methods, these elements, and other alkaline earth elements, if present, are co-titrated and therefore prior separation of the individual elements is essential for their determination. Belcher, Gibbons and West⁵ reported a method for the determination of barium sulphate that entailed dissolving it in an excess of a strongly ammoniacal (9 M) solution of EDTA and then back-titrating the excess with magnesium ions from magnesium chloride solution. Precipitation of barium as sulphate from a homogeneous solution of its EDTA complex by the replacement reaction with magnesium and nickel in the presence of sulphate ions has been reported for the gravimetric determination of barium.^{6,7} However, precipitation from a homogeneous solution has not yet been utilised in complexometric titration of the element in the presence of other alkaline earth elements. This paper describes a method in which barium, strontium and other alkaline earth elements are complexed by titration with EDTA at pH 10.0 with the use of a mixed indicator. Barium and strontium are then precipitated stepwise as their sulphates at the same pH from a homogeneous solution by displacement reactions with a known (excess) volume of magnesium sulphate and zinc sulphate, respectively, according to the following equations—



The excess amounts of magnesium and zinc ions are then titrated stepwise with EDTA solution. Barium and strontium are calculated from the equivalent amounts of magnesium and zinc consumed during their respective displacement reactions.

EXPERIMENTAL

REAGENTS AND SOLUTIONS—

All reagents were of analytical-reagent grade quality unless otherwise stated.

Calcium chloride solution, 2.0 mg ml⁻¹.

Barium chloride solution, 2.0 mg ml⁻¹.

Strontium chloride solution, 2.0 mg ml⁻¹.

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Magnesium sulphate solution, 0.05 M.

Zinc sulphate solution, 0.05 M.

Standard magnesium solution, 0.05 M—Dissolve 1.2160 g of pure magnesium turnings in 1 + 1 hydrochloric acid, almost neutralise the solution with 1 M sodium hydroxide solution and dilute to 1 litre with water.

Mixed indicator solution—Dissolve Eriochrome black T (0.03 g), Titan yellow (0.04 g) and Naphthol green B (0.01 g) in 25 ml of triethanolamine.

EDTA solution, 0.05 M—Dissolve 18.6125 g of the disodium salt of EDTA in water and dilute the solution to 1 litre. Standardise the EDTA solution thus obtained with the magnesium sulphate solution at a pH of 10.0 by using mixed indicator and calculate the equivalent amounts of barium oxide and strontium oxide per millilitre of EDTA solution.

Buffer solution, pH 10.0—Dissolve 67.5 g of ammonium chloride in 250 ml of water and 570 ml of ammonia solution (sp. gr. 0.88), dilute to 1 litre and mix thoroughly.

PROCEDURE I. STEPWISE DETERMINATION OF BARIUM AND STRONTIUM OXIDES IN THE PRESENCE OF CALCIUM AND MAGNESIUM—

Transfer a portion of the solution containing barium, strontium, calcium and magnesium into a 250-ml conical flask. Add 2 to 3 g of ammonium chloride, followed by dilute ammonia solution (1 + 4) dropwise until the contents of the flask smell of ammonia. Add 10 to 15 ml of buffer solution and titrate the mixture with 0.05 M EDTA solution in the presence of 10 to 12 drops of mixed indicator until a sharp green colour is obtained.

DETERMINATION OF BARIUM OXIDE—

Dilute the complexed solution to 100 ml, heat it to 50 to 60 °C on a hot-plate and add an excess (3 to 5 ml) over the theoretical requirement of sulphate ions of 0.05 M magnesium sulphate solution (1 ml of 0.05 M magnesium sulphate solution for every 7.67 mg of barium oxide content) slowly from a pipette, keeping the mixture on the hot-plate for 10 minutes. Cool the mixture, add 5 ml of buffer solution and 10 ml of absolute ethanol and titrate the excess of magnesium in the solution with 0.05 M EDTA solution to the sharp green end-point. Reserve the solution for the determination of strontium oxide.

Then,

$$\text{BaO (mg)} = (A - a) \times f$$

where A ml is the volume of EDTA equivalent to the volume of magnesium sulphate solution added, a ml is the volume of EDTA solution required to titrate the excess of magnesium sulphate and f is the equivalent of barium oxide in milligrams per millilitre of EDTA solution.

DETERMINATION OF STRONTIUM OXIDE—

To the solution reserved after the determination of barium, add 0.05 M zinc sulphate solution (5 ml for every 10 mg of strontium oxide) and 5 g of potassium sulphate. Boil the mixture for 10 minutes in order to precipitate strontium sulphate, then cool it, add 10 ml of buffer and 15 to 20 ml of absolute ethanol. Titrate the excess of zinc with 0.05 M EDTA solution to the sharp green end-point.

Then,

$$\text{SrO (mg)} = (B - b) \times g$$

where B ml is the volume of EDTA equivalent to the volume of zinc sulphate solution added, b ml is the volume of EDTA solution required to titrate the excess of zinc sulphate, and g is the equivalent of strontium oxide in milligrams per millilitre of EDTA solution.

PROCEDURE II. DETERMINATION OF BARIUM OXIDES IN THE PRESENCE OF VARIOUS CATIONS—

To a portion of the solution in a 250-ml conical flask add 5 ml of 0.05 M magnesium sulphate solution. Dilute the mixture to 50 ml, add 2 to 3 g of ammonium chloride and then ammonia solution (1 + 4) dropwise until the contents of the flask smell of ammonia. Acidify the solution to pH 3 to 4 by adding 10 per cent. V/V hydrochloric acid and then add a 1-ml excess of the acid. Add 10 ml of 30 per cent. V/V triethanolamine while shaking the flask, followed by 10 ml of buffer solution, 5 to 10 ml of 10 per cent. m/V potassium cyanide solution and 1 g of ascorbic acid. Heat the solution to 70 to 80 °C to remove the iron colour, cool it and titrate it with 0.05 M EDTA solution to the sharp green end-point in the presence of 10 to 12 drops of mixed indicator solution.

Proceed in the same way as described in procedure I for the determination of barium oxide and calculate the amount of barium oxide from the same equation.

RESULTS AND DISCUSSION

The sulphate ion plays an important rôle in the stepwise precipitation of barium and strontium from homogeneous solution because of its replacement reactions with magnesium and zinc sulphates, respectively. Firsching⁷ studied the co-precipitation of alkaline earths during the homogeneous precipitation of barium sulphate from an equimolar solution of these elements in a 1.5 mM sulphate-ion concentration and reported the co-precipitation of strontium to be less than 4 per cent. In the present study, it was observed that the co-precipitation of strontium increased with the increase of excess of sulphate-ion concentration. An excess of 1.5 to 2.5 mM magnesium sulphate concentration over the theoretical requirement of sulphate ions calculated as magnesium sulphate (1 ml of 0.05 M magnesium sulphate solution for every 7.67 mg of barium oxide content) was found to be satisfactory. Addition of magnesium sulphate in the procedure instead of magnesium chloride and ammonium sulphate⁷ improved the granular nature of the barium sulphate precipitate. For precipitation of strontium sulphate, however, a large excess of sulphate ions (more than 0.25 M) is preferable.

Temperature is also an important factor in the procedure. Quantitative precipitation of barium sulphate at room temperature takes too long, while with boiling solutions, co-precipitation of strontium sulphate (in an equimolar solution) increases. A temperature of 50 to 60 °C is found to be a suitable compromise for barium sulphate precipitation. However, the precipitation of strontium sulphate requires the solution to be boiling.

The ratio of strontium to barium is also very important in the precipitation of barium sulphate. The determination is possible in solutions containing a molar ratio of up to 1.0, or slightly greater (1.481) when the concentration of strontium oxide is not higher than 20.0 mg per 100 ml of solution (Table I). With increase in strontium-ion concentration, the co-precipitation of strontium sulphate also increased.

TABLE I
STEPWISE DETERMINATION OF BARIUM AND STRONTIUM IN THE PRESENCE OF
CALCIUM (20 mg) AND MAGNESIUM (20 mg)

SrO taken/mg	BaO taken/mg	Molar ratio, SrO : BaO	BaO found*/mg	SrO found*/mg	Difference (BaO)/mg	Difference (SrO)/mg
5	10	0.740	10.02	5.19	+0.02	+0.19
10	10	1.48	10.02	10.07	+0.02	+0.07
20	10	2.96	Drifting of end-point	Drifting of end-point	—	—
5	20	0.37	20.20	5.14	+0.20	+0.14
10	20	0.74	20.12	10.07	+0.12	+0.07
20	20	1.48	20.20	20.10	+0.20	+0.10
30	20	2.22	Drifting of end-point	Drifting of end-point	—	—
10	40	0.37	40.02	10.18	+0.02	+0.18
20	40	0.74	40.10	20.25	+0.02	+0.25
20	60	0.49	59.68	20.35	-0.32	+0.35
20	80	0.37	79.73	20.25	-0.27	+0.25

* Mean of three titrations.

The metallochromic indicator Eriochrome black T is often used in the direct titration of barium and strontium with EDTA solution in the presence of calcium and magnesium at pH 10.0. However, the end-point, from red to blue, is not very sharp and is sometimes confusing. In an attempt to improve the end-point by producing a change from red to green, additions of yellow dyes such as methyl orange,⁸ methyl yellow,^{8,9} Tropaeoline OO^{9,10} and methyl red¹¹⁻¹³ have been reported. In the present work, we used Titan yellow in conjunction with Eriochrome black T and Naphthol green B and this mixed indicator gave a very sharp change from red to green in the titration of barium with EDTA solution. The end-point during the titration of excess of zinc with EDTA solution (procedure I) in the absence of absolute ethanol, however, reverted from green to pink within a few seconds, probably as a result of the greater solubility of strontium sulphate. The addition of 10 to

15 ml of absolute ethanol so as to reduce the solubility of strontium sulphate was necessary in order to eliminate this effect.

The stepwise determination of barium and strontium is possible in the presence of calcium, magnesium and lead. However, iron and manganese, even at a concentration of 1 p.p.m., affected the end-point by causing the colour of the indicator to fade. Copper, nickel and cobalt interfered by inactivating the indicator. In the presence of any of these interfering elements, the procedure for the stepwise determination of barium and strontium fails. Procedure II, in which the interferences due to iron (5.45 mg), aluminium (11.0 mg), titanium (2.0 mg), nickel (31.8 mg), cobalt (20.0 mg), manganese (9.0 mg) and copper (32.0 mg) were eliminated (see Table II) by complexing with triethanolamine and potassium cyanide, and the iron and manganese complexes were subsequently reduced with ascorbic acid, was found to facilitate the determination of barium in the presence of these ions. Higher concentrations of aluminium caused co-precipitation of magnesium during the heating stage of the procedure.

TABLE II
DETERMINATION OF BARIUM IN THE PRESENCE OF VARIOUS CATIONS
BaO taken = 20.0 mg

Ion	Added/mg	BaO found*/mg	Difference/mg
Sr	8.46	19.97	-0.03
Fe	2.62	19.89	-0.11
Fe	5.24	20.04	+0.04
Al	5.50	20.12	+0.12
Al	22.00	21.10	+1.10
Ti	0.30	20.04	+0.04
Ti	1.50	20.20	+0.20
Mn	3.00	19.89	-0.11
Mn	8.95	20.04	+0.04
Ni	12.59	20.20	+0.20
Ni	31.80	20.20	+0.20
Cu	16.00	20.20	+0.20
Cu	32.00	20.04	+0.04
Co	20.00	20.04	+0.04

*Mean of three titrations.

Manganese, titanium and zirconium, when present in higher concentrations than those mentioned above, were also precipitated during heating. In such instances, the removal of iron, aluminium, titanium and zirconium by precipitating them as hydroxides with ammonia solution was found to be satisfactory. Phosphate and chromate ions, even in small amounts, precipitated the alkaline earth elements and thus interfered in both procedures. Chromate could be removed as hydroxide together with R_2O_3 -type elements after reduction with ethanol. Phosphate, when present, is required to be removed as zirconium phosphate.

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