ART. XXXVII.—*A method for the quantitative separation of Barium from Calcium by the action of Amyl Alcohol on the Nitrates*; by P. E. BROWNING.

[Contributions from the Kent Chemical Laboratory of Yale College—XII.]

THE fact that strontium can be separated quantitatively from calcium by boiling the nitrates with amyl alcohol, as I have recently shown,* naturally suggested a similar separation of barium from calcium by the same general treatment. Solutions of specially purified barium and calcium nitrates were prepared and standardized, either by the evaporation or filtration of definite portions after treatment with sulphuric acid. The mean of several closely agreeing results, both by evaporation and filtration, was taken as the standard. The method followed was essentially the same as described in the method for the quantitative separation of strontium from calcium referred to above. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon barium nitrate alone. Accordingly definite amounts of the barium salt were measured into Bohemian beakers of about 100cm³ capacity and weighed. The water was then evaporated over a water bath, and the dry salts dissolved in a few drops of water and boiled with 30cm³ of amyl alcohol, that amount being determined upon as convenient, until the normal boiling point of the alcohol was reached—128° to 130° C. During the boiling the beaker was placed upon a piece of asbestos board about 15cm square to keep the inflammable fumes of the alcohol from the flame. When the temperature

* This Journal, vol. xliii, p. 50.

of the alcohol reached its normal boiling point the beaker was removed and the barium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed. The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of barium nitrate were removed from the beaker by washing with small amounts of anhydrous amyl alcohol contained in a wash bottle, previously described, to the mouth piece of which a small chloride of calcium tube was connected. The crucible containing the barium nitrate was placed in an air bath and heated to 150° C. The process of heating and weighing was repeated until a constant weight was obtained. Series I shows the results of these experiments the barium being calculated as oxide.

SERIES I.

	BaO taken.	BaO found.	Error.
(1)	0.1040 grm.	0.1039 grm.	0.0001 grm. —
(2)	0.1043 “	0.1043 “	0.0000 “
(3)	0.0524 “	0.0522 “	0.0002 “ —
(4)	0.0519 “	0.0518 “	0.0001 “ —

These results show plainly enough the complete insolubility of the barium salt in the amyl alcohol; but to confirm them the filtrates of (3) and (4) were evaporated to dryness, ignited to burn off any organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness and weighed. The weights in both cases showed the absence of any residue.

SERIES II.

	BaO taken. grams.	BaO found. grams.	Error. grams.	CaO taken. grams.	CaO found. grams.	Error. grams.
(5)	0.1410	0.1406	0.0004 —	0.0112	0.0114	0.0002 +
(6)	0.1300	0.1301	0.0001 +	0.0926	0.0926	0.0000
(7)	0.1043	0.1049	0.0006 +	0.0741	0.0736	0.0005 —
(8)	0.0781	0.0781	0.0000	0.0556	0.0554	0.0002 —
(9)	0.0525	0.0526	0.0001 +	0.0373	0.0372	0.0001 —

SERIES III.

	BaO taken. grams.	BaO found. grams.	Error. grams.	CaO taken. grams.	CaO found. grams.	Error. grams.
(10)	0.1304	0.1308	0.0004 +	0.0927	0.0921	0.0006 —
(11)	0.1043	0.1046	0.0003 +	0.0371	0.0370	0.0001 —
(12)	0.1037	0.1036	0.0001 —	0.0743	0.0744	0.0001 +
(13)	0.0783	0.0776	0.0007 —	0.0427	0.0422	0.0005 —
(14)	0.0519	0.0521	0.0002 +	0.0369	0.0361	0.0008 —
(15)	0.0519	0.0512	0.0007 —	0.0570	0.0567	0.0003 —
(16)	0.0261	0.0259	0.0002 —	0.0925	0.0925	0.0000

The next experiments were directed toward a separation of barium and calcium nitrates. Definite amounts of a solution of barium nitrate were measured from burettes into counterpoised beakers and weighed, as already described, the calcium nitrate was then added in solution and the weight taken again. The water was evaporated and the dry salts dissolved again in the least possible amount of water, and boiled as before with 30cm³ of amyl alcohol. The barium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried and weighed as previously described. The calcium was determined in the filtrate, in the form of the sulphate, by evaporation of the alcohol, treatment with an excess of sulphuric acid and ignition. Series II gives the results of this treatment.

In Series III the effect of a double treatment with the alcohol is recorded. In these experiments, after the first boiling, already described, the alcohol was decanted upon an asbestos felt, under the conditions previously mentioned, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, and this solution was treated with a drop of dilute nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30cm³ of alcohol were added, and the boiling repeated. The residue was filtered off upon the felt through which the first portion had been decanted and washed with amyl alcohol, care being taken to remove all particles from the beaker by careful rubbing. The crucible and residue were heated to 150° C. as before and weighed. The results after one treatment are fully as satisfactory as those after the double treatment,—a point which simplifies the method considerably. In the separation of strontium from calcium the double treatment was necessary. The form in which the salts separate suggested a possible explanation. The strontium nitrate separates in plate-like masses, while the barium is much more granular and therefore less liable to include foreign matter.

Series IV contains the results of certain experiments directed toward the separation of barium and strontium together from calcium. Definite portions of the three nitrate solutions were measured into counterpoised beakers and the successive weights taken as previously described. The method of treatment was the same as that described in the double treatment of the barium and calcium salts. The correction for the solubility of the strontium salt was applied (0.001 grm. of strontium oxide to 30cm³ of the alcohol used) in the manner defined in the paper upon the separation of strontium from calcium. The results are tabulated for the nitrates in the cases in which barium and strontium were treated together, but the errors are also aver-

aged on the oxides for the amounts of barium and strontium nitrates taken in order that they may be compared more conveniently with the results of the previous series.

SERIES IV.

	Ba(NO ₃) ₂ and Sr(NO ₃) ₂ taken.	Ba(NO ₃) ₂ and Sr(NO ₃) ₂ found and corrected.	Error in nitrates.	Error averaged and calculated as oxide.	CaO taken.	CaO found.	Error.
	grams.	grams.	grams.	grams.	grams.	grams.	grams.
(17)	0.3941	0.3945	0.0004 +	0.0002 +	0.0283	0.0277	0.0006 —
(18)	0.1436	0.1442	0.0006 +	0.0003 +	0.0568	0.0558	0.0010 —
(19)	0.3163	0.3152	0.0011 —	0.0006 —	0.0284	0.0274	0.0010 —
(20)	0.1978	0.1987	0.0009 +	0.0005 +	0.0285	0.0280	0.0005 —
(21)	0.1948	0.1932	0.0016 —	0.0008 —	0.0833	0.0835	0.0002 +
(22)	0.1971	0.1971	0.0000	0.0000	0.0830	0.0817	0.0013 —
(23)	0.1973	0.1960	0.0013 —	0.0007 —	0.0830	0.0824	0.0006 —
(24)	0.1959	0.1970	0.0011 +	0.0005 +	0.0830	0.0819	0.0011 —
(25)	0.1971	0.1963	0.0008 +	0.0004 +	0.0834	0.0831	0.0003 —

In experiments (21), (25) 15cm³ of the alcohol were used in each boiling instead of the 30cm³ of the previous experiments, and thus the total amount of the corrections for the solubility of the strontium salt was reduced one-half. In experiments (21), (23) and (25) the calcium was determined by precipitation with sulphuric acid, the precipitate being filtered off, ignited at low redness and weighed.

The rapidity of execution and satisfactory character of the results of this method of separating barium from calcium seem to place it among good analytical methods.