

The mixed acids I have found to give better results for all carbonates, than either alone, although either will answer the purpose in most cases.

The drying chamber is half filled with concentrated sulphuric acid, and to the water chamber is added 10 cc. distilled water freed of the gases it usually contains. Both sections are now brought together and allowed to attain the temperature of the balauce.

The alkalimeter thus charged is carefully tared, and by removing both stoppers the water flows into the body of the apparatus, which causes an immediate generation of carbon dioxide; this moisture-laden gas passes through the capillary tubes into the acid of the drying chamber where it is deprived of its moisture and escapes. When this first evolution of gas ceases, the apparatus is carefully shaken, and this is repeated until no further generation of gas results. No heat is employed for the alkaline carbonates, while for the earthy carbonates a temperature as low as 55° will be found to be sufficient.

The alkalimeter is now freed of its remaining carbon dioxide by causing 0.5 liter of dry air, freed from carbon dioxide, to pass through the apparatus.

The following results were obtained with calcium, barium, and magnesium carbonates:

CARBON DIOXIDE.		
	Found.	Theory.
Calcium carbonate.....	43.98	44.00
Barium carbonate.....	22.38	22.33
Magnesium carbonate.....	52.40	52.38

This method for estimating carbon dioxide will be found useful in the examination of baking-powders, as well as for the alkaline and earthy carbonates.

THE DETERMINATION OF LITHIA IN LEPIDOLITE.

By W. J. SCHIEFFELIN AND W. R. LAMAR.

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THE J. Lawrence Smith method for decomposing the silicate is more convenient than that of dissolving in hydrofluoric acid, as the alkalies are separated from the alumina as chlorides in one step, thus avoiding two precipitates, aluminum hydroxide and barium sulphate, which are sure to hold back lithia. A

modification we have found advisable, is to remove the last traces of calcium by means of ammonium oxalate.¹ The Gooch method² for separating lithia from the other alkalies gives the best results. A small direct vision spectroscope is an important aid in deciding when precipitates are thoroughly washed, etc., by examining a fraction of a drop held in a looped platinum wire.

The decomposition is conducted in the usual way,³ care being taken that the crucible is not heated too highly, as there is danger of loss of the lithium chloride, and also of the mass becoming vitrified and difficult to dissolve.

The trituration must be thorough and the leaching complete or some lithia will be held back. (The residue when treated with hydrochloric acid should leave no undecomposed mineral.)

After the dish containing the alkalies is dry, it is heated on an asbestos disk, or a triangle high above the flame, to drive off the ammonium chloride; this may take three-quarters of an hour; if it is done too rapidly, lithium chloride will go with it.

Ten cc. of hot water and one drop of hydrochloric acid will dissolve the residue in the dish, and the addition of a few drops of ammonia, and 1 or 2 drops of ammonium oxalate precipitate the remaining calcium.⁴

The chlorides of the alkalies are filtered into an Erlenmeyer flask, of thin glass (75 or 85 cc. capacity), which is placed in the air-bath, or on an asbestos disk over a small flame, and evaporated until the salts show signs of crystallizing (the solution will be down to 1 or 2 cc.); then a few drops of water are added, to effect solution, and 1 or 2 drops of concentrated hydrochloric acid to transform any hydroxide or oxychloride into chloride. Fifteen cc. of amyl alcohol (b. p. 129°–132° C.) are now added, and the flask is placed on an asbestos disk, which is slightly slanted so that the lower aqueous layer flows to one side, and the point of a Bunsen flame (1.5 inches high) is applied to the asbestos directly under the raised side of the flask. It is important to adopt this precaution as it allows the amyl alcohol to come to gentle boiling and continue boiling after all watery vapor

¹ Hillebrand: *Bull. U. S. Geol. Survey*, No. 176.

² *U. S. Geol. Survey Bull.* No. 42, p. 73; *Am. Chem. J.*, 9, 33; *Proc. Am. Acad.*, p. 177 (1886); *Chem. News*, 55, 18, 29, 40, 56, 78.

³ Fresenius, § 140.

⁴ Hillebrand: *U. S. Geol. Survey, Bull.* No. 176.

has gone off, without the tendency to bumping which causes inevitable loss.

Boiling the amyl alcohol is continued until half has evaporated. Toward the end the flame may be slightly raised and it is well to hold a thermometer in the vapor; it should read 129° – 130° C., showing that the water has been driven off.

The amount of amyl alcohol remaining for the Gooch correction is judged by adding water to a flask of the same size to the same level and measuring the water.

The amyl alcohol is decanted when cold through a small filter into a weighed platinum dish; the filter is first moistened with anhydrous amyl alcohol and the residue in the flask and the filter are carefully washed with the same until free from lithia. This will require 20 cc.

The amyl alcohol is expelled from the platinum dish in a hot air-bath, under the hood, at a temperature not higher than 125° C. At this temperature it rapidly evaporates but does not boil or spatter.

After complete dryness, 0.5 cc. of concentrated sulphuric acid is added to the dish, which is warmed and rotated until all the residue has been moistened and all the chloride decomposed, and the excess of sulphuric acid is now carefully driven off by heating over a small flame or by rotating over a moderate flame. Haste in doing this will cause loss.

The lithium sulphate in the platinum dish is ignited to burn off all carbon left by the amyl alcohol, which takes but a few moments. The sulphate fuses and is kept one minute in fusion, then the dish is allowed to partially cool and covered with a watch-glass or filter-paper, to return any fragments of the fused sulphate, which sometimes splits off when it contracts.

The dish is then cooled in a desiccator and weighed; after fusing again the weight is usually found to be constant. The deduction for sodium and potassium is made as directed by Gooch.¹ That rubidium and caesium chlorides are virtually insoluble in amyl alcohol is shown by the following:

0.1022 gram rubidium chloride dissolved in water, with a drop of concentrated hydrochloric acid, treated as in the analysis with 15 cc. amyl alcohol and boiled down to 9 cc., left 0.0009 gram

¹ Deduct 0.0011 gram for each 10 cc. amyl alcohol exclusive of washings.

residual sulphates, which showed sodium strongly, also potassium, lithium and rubidium in the spectroscopic.

0.1037 gram caesium chloride in the same way, with the amyl alcohol boiled down to 7 cc., left 0.001 gram residual sulphates, showing sodium, lithium, caesium, and potassium.

If the sulphate in the dish is pure, it dissolves readily in a small amount of hot water and gives a good lithium flame. To prove that the sulphate residue obtained in the analysis was lithium sulphate, the following parallel was made: An equivalent weight of pure lithium carbonate (99 per cent.) was weighed into a second platinum dish, transformed into sulphate, ignited, weighed and the lithia in both dishes determined as phosphate as directed in Fresenius, using exactly the same amounts of sodium phosphate, sodium hydroxide and ammonia wash-water, and collecting the precipitates but twice.

	Lithium sulphate. Gram.	Lithium phosphate obtained. Gram.	Lithium phosphate calculated. Gram.
A. From analysis	0.1020	0.0706	0.0717
B. From carbonate	0.1004	0.0670	0.0705

It will be seen that there are a number of precautions to be observed in order to avoid loss of lithia, either by leaving it behind, driving it off, or mechanically carrying it off. Good results will, however, be obtained, if care is taken to use a low red heat in the fusion; to thoroughly leach and triturate the fused mass; to avoid high heat in driving off the ammonium chloride; to avoid bumping when boiling the water out of the amyl alcohol; to filter the amyl alcohol cold; to evaporate the amyl alcohol in the dish at a temperature below its boiling-point; to drive off the sulphuric acid without any foaming or boiling; and to cover the dish while the lithium sulphate is cooling.

The analysis can be completed in two days.