I venture to believe in the light of the foregoing facts that the method laid down in the paper read by me before the New York Section of the Society of Chemical Industry in May, 1902, is satisfactory.

If errors occur, they are due to bad work and not imperfection in the methods of analytical separation.

I desire to thank Mr. W. Woodcock for his assistance.

LONDON, ENGLAND,
May 5, 1904.

A RAPID METHOD FOR THE DETERMINATION OF LIME IN CEMENT.[1]

BY BERNARD ENRIGHT.

Received June 7, 1904.

A RAPID determination of the lime in cement, a method by which the lime content can be accurately determined, in a brief space of time, without waiting for the lengthy evaporations and dehydration of the silica present, is frequently very desirable in the manufacture of the highest grade of Portland cement. For these reasons the following method has been devised; it has been thoroughly tested and has given very satisfactory agreement with accurate lime determinations made by lengthy methods in common use.

The method of procedure is as follows: Five-tenths of a gram of a cement, as a precautionary measure repulverized in an agate mortar, is weighed out, preferably into a casserole of about 12 ounces capacity. About 100 cc. of hot water are introduced in a stream from a wash-bottle in such a manner as to keep the cement in complete suspension, about 30 cc. of hydrochloric acid (1 : 1) then added, the rapid agitation of the liquid being continued during its introduction. After the addition of a few drops of bromine water the solution is rapidly brought to a boil and boiled a few minutes to effect complete solution of practically everything but a few flakes of silica and to expel the bromine. Dilute ammonia is now cautiously added with constant stirring until a faint excess is present, and the solution again brought to a boil for a minute. It is then filtered, preferably on an 11 cm. filter-paper,

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[1] Read before the Lehigh Valley Section of the American Chemical Society, June 1, 1904.

and washed once. The precipitate is washed back into the original casserole, 10 cc. concentrated hydrochloric acid added, and the solution diluted to 100 cc. It is once more made faintly ammoniacal, boiled a minute, then filtered and washed thoroughly, filtrate and washings being caught in the beaker containing the first filtrate. The precipitate is in a form which allows free and rapid filtration and washing. It contains the iron oxide and alumina, and the greater part, but by no means all of the silica present in the sample; generally about three-quarters or more of the total silica is precipitated here. It also contains, of course, small amounts of phosphates, titanic acid, etc., if present.

The filtrate, which has been caught in a beaker of about 20 ounces capacity, is slightly acidulated with hydrochloric acid, brought to a boil and 25 cc. of a saturated solution of ammonium oxalate added. When the clear solution again boils (it should be sufficiently acid to prevent precipitation of calcium oxalate) hot dilute ammonia is added with constant stirring until an excess equivalent to about 5 cc. of concentrated ammonia is introduced. Vigorous stirring and boiling is continued for five minutes, and the solution then set aside in a hot place for fifteen minutes longer. With the precautions noted carefully followed, complete precipitation of the lime will always take place in the time stated. The lime solution is kept acid until the time of precipitation to prevent the formation of calcium carbonate, which frequently happens while an ammoniacal solution of lime is being heated to the boiling-point. This precaution is very essential, as the method contemplates titration with potassium permanganate and it is necessary to have the lime precipitate entirely in the form of oxalate. Three washings by decantation and eight on the filter with hot water are sufficient to remove ammonium salts, etc.

The precipitate is then washed carefully with boiling water into a 16 ounce Erlenmeyer flask (care being taken to prevent the introduction of any pieces of filter-paper), dissolved by the addition of a small amount of hot dilute sulphuric acid, the paper also being washed once or twice with hot, very dilute acid, and the solution is immediately titrated with a potassium permanganate solution, which had previously been standardized by a standard cement, run in exactly the same manner, and in which the lime had been accurately determined by various methods.

This method of standardizing the permanganate solution is decidedly preferable to all others for the purpose intended, as by its use numerous errors, including that due to the solubility of calcium oxalate in hot water, which may, under certain circumstances, be a very considerable one, are entirely eliminated.

By this rapid method the percentage of lime in a cement can be arrived at in less than one-fifth the time ordinarily consumed in making this determination.

It might not be out of place to briefly note here some experiments, made by the writer several years ago, to determine the extent of the solubility of calcium oxalate under the conditions present in a cement or limestone analysis. Calcium oxalate precipitations, obtained from 0.5 gram and from 1 gram samples of cement by ordinary analysis, were filtered on 11 cm. papers, the size best used for this purpose. They were thoroughly washed (20 to 25 times) with boiling water to insure complete freedom from foreign salts. The washing of the pure oxalate precipitate was then continued with water at about 170° F., washings being combined, acidulated and titrated with a permanganate solution. Each washing on this size paper required approximately 25 cc. Blanks on the same amount of water and acid used, from the same flasks (the water being run through a filter-paper of the same quality and size), were also run, and their slight titration, 0.06 cc., subtracted.

Each combined five washings on the calcium oxalate from the 0.5 gram sample titrated 0.48 cc. to 0.54 cc., equivalent to 0.136 per cent. to 0.154 per cent. CaO, or 0.240 per cent. to 0.275 per cent. $CaCO_3$. The washings were continued indefinitely, each combination of five washings showing about the same titration. On the calcium oxalate precipitate from the 1 gram sample every combined five washings titrated the same, —0.48 cc. to 0.54 cc. The larger weight, however, reduced the percentage error one-half, the equivalents being 0.068 per cent. to 0.077 per cent. CaO, or 0.120 per cent. to 0.138 per cent. $CaCO_3$. This corresponds to 0.00123 to 0.00141 gram of anhydrous calcium oxalate, dissolved by approximately 100 cc. of hot water, the amount dissolved varying with the temperature. Richards, McCaffrey and Bisbee[1] found that 100 cc. of water at 95° C. dissolved 0.00140 gram, at 50° C. 0.0010 gram, and at 25° C. 0.00068 gram of the anhydrous oxalate.

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[1] *Ztschr. anorg. Chem.*, **28**, 83 (1901).

The method described also practically eliminates the error due to solvent action of the solutions on the beakers, etc., used in the determination. A common practice in cement analysis is to catch the filtrate and washings from the calcium oxalate precipitate in a No. 6 beaker and boil or evaporate down to 100 to 150 cc. before precipitation of the magnesia. Whether this solution is kept ammoniacal during the evaporation, or, as more commonly practiced, rendered acid as soon as it is placed over the source of heat, a considerable solvent action takes place on the beaker during the operation. In numerous experiments made in actual determinations and also on blanks on reagents, water, etc., absolutely free from lime and silica, this contamination was found at times to run as high as 0.0030 gram silica, equivalent on a 0.5 gram sample, to 0.60 per cent. silica, and 0.0024 gram, equivalent to 0.48 per cent. lime. While this silica possibly might not come down in the subsequent magnesia precipitate, the lime, if not previously removed, undoubtedly would, and would not be removed by a double precipitation of the ammonium magnesium phosphate. The resulting magnesia would consequently be high, contaminated with lime, obtained, not from cement itself, but from the glassware. If this lime were removed and added to that originally obtained in the regular course of analysis, a high lime determination would result. In the regular methods of analysis used a greater or less solvent action also occurs in the operations preceding the actual precipitation of calcium oxalate. In the rapid method described the solution is in contact with glass only a very short time before the precipitation of the lime, the solvent action is reduced to a minimum, and the possible error from this source is entirely obliterated by the fact that the potassium permanganate used in titration is standardized by a cement run under exactly the same conditions as the regular determinations.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

ACTION OF MUSTARD OILS AND ISOCYANATES ON HYDRAZO ACIDS.

BY J. R. BAILEY.

Received June 11, 1904.

INTRODUCTION.

HYDRAZO compounds, as a rule, do not react readily with mustard oils,[1] although they react more readily with isocyanates.[2] In

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[1] *Ber. d. chem. Ges.*, **25**, 3115.

[2] *Ibid.*, **23**, 490.