DETERMINATION OF CALCIUM IN CINDER BLOCK

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The use of Versene (ethylenediaminetetraacetic acid or EDTA) for the determination of calcium ion in aqueous solution was introduced by Schwarzenbach and coworkers in the years 1946 to 1948. Since then numerous papers have been published on the determination of calcium in various mixtures using this reagent. The measurement of the calcium content of limestone has been reported by several experimenters (Cheng *et al.*, 1952, 1953; Gehrke *et al.*, 1954). Analytical procedures for the determination of calcium in soil and plant products (Cheng *et al.*, 1951) and in water (Love, 1953; Diehl *et al.*, 1950) have also been outlined in the literature.

In the study of the physical properties of cinder block, currently being made at the University of Toledo, the calcium oxide and silica present, as complex silicates, has been of considerable interest. The recommended procedure for the analysis of cement products calls for a gravimetric determination of the silica and calcium oxide (Scott, 1939). These methods are very slow and time consuming. In an effort to simplify the analysis, a shorter volumetric method was investigated for the determination of the calcium employing Versene as the titrant.

GRAVIMETRIC PROCEDURE

The gravimetric procedure used in the determination of the acid soluble calcium silicates in cinder block is essentially the same as that outlined by Scott.

1. Representative samples of the block to be analyzed are crushed to pass a no. 20 screen, quartered, and further crushed to pass a no. 70 screen. A 10 g. sample of the finely divided material is heated with 250 ml. of water and 50 ml. of hydrochloric acid (sp. gr. 1.19) and allowed to boil for three minutes with continuous stirring. The mixture is diluted with water to a volume of 400 ml. and digested on a steam bath for 15 min. The mixture is then filtered while hot and washed with hot water.
2. The filtrate is diluted to 500 ml. and two 100 ml. aliquots are withdrawn for the gravimetric analysis of silica and calcium oxide.
3. The silicon dioxide is removed from the sample solutions after a double dehydration process.
4. The aluminum and iron oxides are removed by a double precipitation process.
5. Finally, the calcium is precipitated as the oxalate by the double precipitation method and ignited (at 1200°C) to calcium oxide in platinum crucibles.

VERSENATE METHOD

In the Versenate method, used by the authors for the determination of calcium oxide in cinder block, Step 1 (of the previously described gravimetric procedure) is carried out and the filtrate is diluted to 500 ml. (Step 2). Two 100 ml. aliquots are withdrawn and set aside for the silica determination (Step 3) and three 10 ml. portions of the remaining filtrate are taken for the calcium determinations, using Versene.

Reagents. Versenate Solution—4 g. of the analytical grade di-sodium Versenate, furnished by Versenes Incorporated, are dissolved in recently boiled and cooled distilled water and diluted to 1 liter.

Standard Calcium Solution—1 g. of analytical grade, low magnesium content, calcium carbonate is dissolved in a small amount of dilute hydrochloric acid and diluted to 1 liter. (1 ml. of standard solution = 0.5608 mg. calcium oxide).

Potassium Hydroxide—10 percent aqueous solution of analytical grade potassium hydroxide.

Murexide Indicator—a 0.2 g. portion of Eastman Kodak's Murexide thoroughly ground together with 40 g. of analytical grade potassium sulfate.

Triethanolamine—10 percent aqueous solution of U. S. P. triethanolamine.

Standardization of the Versenate Solution. A 25.0 ml. aliquot of the standard calcium solution is transferred to a 200 ml. porcelain casserole. Ten drops of the triethanolamine solution are added, and the pH of the solution is raised to 12.5 (measured with pHydrion paper) by the careful addition of the 10 percent potassium hydroxide. Approximately 40 mg. of the indicator powder is added by means of a small scoop. The Versenate solution is then run into the casserole from a burette until the color of the indicator changes from pink to a permanent violet.

TABLE 1

Determination of Calcium in Standard Calcium Carbonate Samples Using Versene

Sample Number	Calcium Oxide %: Reported Value	Calcium Oxide %: Versenate Method
1	8.01	7.96
2	16.93	17.01

TABLE 2

Determination of Calcium in Cinder Block

Sample Number	Calcium Oxide %: Gravimetric Method[a]	Calcium Oxide %: Versenate Method[b]	Difference
1	7.59	7.55	−0.04
2	7.57	7.46	−0.11
3	7.71	7.75	+0.04
4	17.35	17.20	−0.15
5	7.52	7.45	−0.07
6	7.24	7.33	+0.09
7	16.93	16.84	−0.09
8	17.65	17.48	−0.17
9	6.64	6.50	−0.14

[a] Average of duplicates.
[b] Average of triplicates.

Procedure for the Analysis of Cinder Block by Versene. Each of the 10 ml. aliquots is transferred to a 200 ml. porcelain casserole, diluted to about 30 ml. and treated in the manner described for the standard calcium solution. For samples containing large amounts of iron it is advisable to add at least 16 to 20 drops of the triethanolamine solution.

RESULTS OF ANALYSIS

Before the standard Versenate solution was used in the analysis of the cinder block, the calcium content of two samples of calcium carbonate, which had been

previously analyzed by standard gravimetric and volumetric methods (Diehl, 1952) was determined by the proposed procedure. The samples were dissolved in dilute hydrochloric acid and treated as outlined in the standardization of the Versenate solution. The results are reported as percent calcium oxide (table 1). To ascertain the accuracy of their technique and the sensitivity of the method, the authors felt that a check should be made on samples of known calcium content.

A comparison of the calcium oxide content of cinder block, as determined by the gravimetric method and by the Versenate method, is shown in table 2.

CONCLUSION

The differences shown in table 2 between the calcium oxide content of cinder block measured by the two aforementioned methods are of little significance. This is especially true when one considers the non-homogeneity of the material being analyzed. Differences as high as 1 percent in calcium oxide content have been noted in samples taken from opposite ends of a given cinder block.

The use of the Versenate method, outlined here-in, is well justified both from the accuracy attained and the time and labor saved. The method does not require the removal of silica and the R_2O_3 group prior to the determination of calcium. Further, there is no need to separate magnesium by the double precipitation of the calcium as the oxalate. In short, the Versenate method enables one to determine the total calcium content of the acid soluble material in cinder block within a few minutes after solution of the sample.

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