

A TURBIDIMETRIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF SULPHUR IN LIMESTONE AND DOLOMITE

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Abstract.

It has been observed that on applying the combustion method to the determination of small amounts of sulphur in limestone and dolomite the bulk of sulphur may remain in the sample when no oxygen stream is used, and that it is difficult to remove the last trace of sulphur even in a stream of oxygen. Following an examination of the many turbidimetric methods reported in the literature, an alternative analytical procedure has been devised for the determination of small amounts of sulphur in limestone and dolomite. The procedure is based upon dissolving the sample in Lunges solution and determining the sulphur turbidimetrically as barium sulphate.

Introduction.

Limestone and dolomite have many technological uses and are of considerable commercial importance. Accurate chemical analyses are therefore of great interest. In addition to the determination of the main components, it is sometimes desirable to determine sulphur and phosphorus since the limiting specifications of the acceptable contents of these elements are often strict.

Limestone is usually burned to lime in special furnaces at a temperature of about 1000° C. It has been observed, however, that instead of

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being removed in the form of SO_2 during this process, the sulphur content may remain more or less quantitatively in the lime.

This observation has also some bearing on the determination of sulphur, since the most common analytical method for the determination of small amounts of this element in silicate rocks, dolomite and limestone, is the combustion method by which the substance is heated in a combustion tube in a stream of oxygen at a temperature of about 1300°C . While this combustion removes sulphur quantitatively from silicate rock samples, a trace of sulphur may still remain in carbonate rocks. The reason is probably the formation of calcium sulphate which is stable at this particular temperature. The situation is illustrated by the following experimental example.

A sample was analysed for sulphur after being heated in a combustion tube at different temperatures. The sample was heated first without an oxygen stream and then in an oxygen stream for 30 minutes (Table I).

Table I. Determination of sulphur content in the samples after heating.

Temperature	Combustion without oxygen stream. Sulphur content	Combustion in oxygen stream. Sulphur content
800°C	0,15 %	
900°C	0,15 %	0,10 %
1000°C	0,15 %	0,07 %
1100°C	0,13 %	0,10 %
1200°C	0,14 %	0,03 %
1300°C	0,13 %	0,02 %

The original content of sulphur in the sample was found to be 0,15 %. The procedure used for the analyses was the same as that described later in the present paper. The results show that there is no essential loss of sulphur in the sample heated without the oxygen stream and further that it seems to be difficult to remove the last trace of sulphur even in a stream of oxygen.

Investigations of Method.

To avoid the difficulty mentioned above a method was worked out based upon decomposing the sample in Lunge's solution and determining

the sulphur turbidimetric as barium sulphate. In the literature many turbidimetric methods for the determination of sulphur in water and organic matter have been suggested, and in the present work use has been made of the different analytical experience mentioned in these publications. To attain a stable barium sulphate suspension, the methods proposed by different authors have been examined. Steinbergs (1953) recommended adding the sulphate solution to a supersaturated barium chloride solution. He concluded too that nuclei were necessary for the formation of uniform sized barium sulphate. Napier and Stone (1958) have investigated the procedure of adding barium chloride to the sulphate solution. These authors stated that the greatest degree of reproducibility would be expected when solid barium chloride is added. Some of the numerous methods described in the literature about turbidimetric and nephelometric determination of sulphate involve the inclusion of various types of additives for the purpose of stabilizing the suspension. Yokosuka and Shirakawa (1958) made use of ethanol and dipropylene glycol. This same additive was also proposed by Krober and Howell (1958), while Omit (1963) recommended the use of a mixture of glycol and ethanol. A turbidimetric method using gelatine has been developed by Gassner and Friedel (1956). Later Dahlgren (1960) improved this method. Berglund and Sørbo (1960) described a method wherein barium chloride gelatine reagent contained preformed barium sulphate particles. The particles function as nuclei for the formation for the sulphate suspension.

In the present work, all the methods mentioned above were examined. A reproducible reading of the extinction was obtained by adding barium chloride crystals under a constant stirring of the sulphate solution. The pH of the solution should, according to Gassner and Friedel (1956), be kept between 1 and 2,5. In this work extinction maxima were attained for pH values between 1,3 and 2,5.

Butters and Chenery (1959) have investigated the effect of foreign ions in the turbidimetric sulphur determination. According to their results the interfering effect of foreign ions occurring in small concentrations is negligible. However, the present samples contain calcium carbonate corresponding to nearly 56 % calcium oxide and a number of investigations had to be made to measure the interfering effect of calcium.

From a stock solution of sodium sulphate corresponding to 0,1 mg sulphur per ml, 10 ml portions were added to a series of 7 volumetric

flasks (250 ml), and this was followed by 10 ml of hydrochloric acid (1:1) and 0, 5, 10, 15, 20, 25 and 30 ml portions of calcium chloride solution, corresponding to 20 mg calcium oxide per ml, the solutions then being diluted with distilled water to the mark. From this stage the solutions were treated as described in the procedure.

Table II. Extinction values at different calcium concentrations.

ml calcium chloride solution	Extinction
0	0,383
5	0,390
10	0,387
15	0,386
20	0,397
25	0,400
30	0,395

As can be seen from Table II, there is a slight increase in the extinction for higher calcium concentrations, but this can be regarded as negligible in this particular case. The time needed before reading the extinction after having precipitated the sulphate was found experimentally to be at least 4 hours and not longer than 20 hours.

The following experiments have been carried out to illustrate this: 3 samples containing sulphur corresponding to 0,05, 0,15 and 0,32 % sulphur were treated by the procedure outlined in this paper for the determination of sulphur in limestone.

The extinctions were measured after $\frac{1}{2}$, 2, 4, 6, 18, 22 and 120 hours.

Table III. Extinctions of three solutions after different standing times.

% sulphur	Standing time before measurement (hours).						
	Extinction of solution						
	$\frac{1}{2}$	2	4	6	18	22	120
0,05	0,032	0,140	0,160	0,162	0,172	0,168	0,168
0,15	0,648	0,653	0,651	0,650	0,647	0,622	0,552
0,32	1,500	1,444	1,440	1,440	1,395	1,381	1,275

These figures show an increase in the extinction for small sulphate concentrations (0,05 %) and a decrease in the extinctions for higher concentrations (0,32 %) up to 4 hours after the precipitations of the sulphate. After that time, the extinctions are almost constant up to 20 hours.

In the literature different wavelengths have been proposed for measuring the extinctions of the barium sulphate turbid solution. J. F. Thomas and J. E. Cotton (1954) recommended the 380 nm wavelength because an absorption maximum had been observed at this particular wavelength. However, in the present work no absorption maximum was observed at this wavelength, probably because of the use of glass cells, although the curve had a continual rise from about 720 to 200 nm. The absorption curves measured after half an hour and 18 hours have a point of intersection near 480 nm. This point varies somewhat with the sulphate concentration in the solution. At 480 nm the blank solution gives no interference. Because of these facts the wavelength of 480 nm was selected.

Table IV. The calibration data.

Amount of sulphur in mg	Extinctions
0,1	0,027
0,3	0,098
0,5	0,176
0,8	0,305
1,0	0,394
1,5	0,642
2,0	0,819
2,5	1,070
3,0	1,289
4,0	1,635

Preparation of the analytical calibration curve.

From a stock solution of sodium sulphate, corresponding to 0,1 mg sulphur per ml, 1, 3, 5, 8, 10, 15, 20, 25, 30, and 40 ml solutions were added from calibrated pipets into 10 of series of 11 volumetric flasks (250 ml). To all the flasks was then added 10 ml of hydrochloric acid

(1:1) and 25 ml of calcium chloride solution, corresponding to 20 mg calcium oxide per ml. The solutions were further treated as described in the procedure. Table IV shows the calibration data.

Procedure.

1 g of the powder sample (containing not more than 30 mg sulphur) is weighed out and transferred into a 250 ml beaker.

The powder is moistened with about 10 drops of distilled water and 20 ml of Lunge's solution (hydrochloric acid and nitric acid in the proportion 1 : 3) is added. Further, 3-4 drops of bromine water (saturated) is added and the beaker is covered with a watch glass and placed on a water bath. When the development of gases has stopped, the watch glass is removed and the solution is evaporated to complete dryness. 5 ml of hydrochloric acid (1 : 1) is added to the residue and the solution is again evaporated to dryness. The residue is then moistened with 8 ml of hydrochloric acid (1 : 1) and 100 ml of water is added. This solution is heated to boiling, cooled and filtered through a dense filter directly into a volumetric flask (250 ml) and water is added to a point just below the graduation mark. The flask is placed in a thermostat bath ($20^{\circ}\text{C} \pm 0,2$) for half an hour and the solution is diluted to the mark with thermostated water. 200 ml of the solution is then pipetted into an Erlen Meyer flask (250 ml) and 0,6 g of barium chloride dihydrate is added. The barium chloride dihydrate must be delivered without any hesitation while the solution is being stirred. The bottle is stoppered and after being stirred for 10 minutes taken off the magnetic stirrer and put aside for at least 5 hours. In the present work, the solution was put aside for about 18 hours. Before measuring, the solution is stirred again for 3 minutes. The extinction is measured immediately with a spectrophotometer at 480 nm against a blank solution. Each solution is measured 5 times using 40 mm glass cells and the arithmetic mean is calculated.

The blank solution is prepared in the following way:

10 ml of hydrochloric acid (1 : 1) and 25 ml of calcium chloride solution corresponding to 20 mg calcium oxide per ml, is pipetted into a volumetric bottle (250 ml). After dilution with distilled water and thermostating in the usual way, 200 ml of the solution is pipetted out and transferred into an Erlen Meyer flask (250 ml) equipped with stopper. The Erlen Meyer flask is placed on a magnetic stirrer and

0,6 g of barium chloride dihydrate is added under continuous stirring. The total content of sulphur in the sample is calculated as follows:

$$\% S = \frac{\text{Read content of sulphur on the analytical calibration curve in mg}}{10}$$

Examples of analytical results are given in Table V. The samples are taken from a selection of limestones that were sent to the Norwegian Geological Survey for the determination of sulphur.

Table V. Analytical results and statistical data from 14 limestones.

Analyses	n	\bar{x}	s
1	4	0,0548	0,0031
2	4	0,0330	0,0018
3	4	0,0500	0,0014
4	4	0,0602	0,0017
5	4	0,3306	0,0018
6	4	0,3125	0,0112
7	4	0,0438	0,0017
8	4	0,0430	0,0014
9	4	0,0635	0,0032
10	4	0,3733	0,0022
11	4	0,0510	0,0008
12	4	0,0123	0,0005
13	4	0,0205	0,0005
14	4	0,0930	0,0008

\bar{x} Arithmetic mean value.

s Standard deviation.

n Number of determinations.

Instruments

Zeiss Spectrophotometer. Type P.Q. II.

Ph-meter. Radiometer.

Haake-Ultra-Thermostat. N.B.S.

Reagents

Hydrochloric acid (36–38 %).

Nitric acid (70 %).

Bromine water (water saturated with bromine).
 Barium chloride dihydrate p.a.
 Sodium sulphate p.a.

Acknowledgements.

The author wishes to thank his co-workers for their technical assistance, and to Dr. D. Roberts for kindly correcting the English manuscript.

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Manuscript received in November 1970.