

QUANTITATIVE ESTIMATION OF GYPSUM BY DIFFERENTIAL THERMAL ANALYSIS

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Abstract. A quantitative method is presented for the estimation of gypsum rich rock by differential thermal analysis, using calcium hydroxide as an internal standard. The effect of variations due to impurities such as quartz, iron oxide, sodium chloride, dolomite, illite and anhydrite are discussed.

Jehan, Qaiser and Khan¹⁻³ have developed methods of estimation of kaolinite in clays, calcite in limestones, and magnesite in magnesite-rich rocks. The sedimentary basis of Pakistan are endowed with about six million tons of gypsum. As gypsum has great potentiality as an industrial and agricultural mineral, a simple and quick method of estimating gypsum content in gypsum-rich rock by DTA is reported in the present paper. The dehydration of gypsum is characterised by two endotherms, one at 150° and the other at 175°. The first endotherm is due to the liberation of 1.5 molecules of water and the other due to 0.5 molecules of water. As the two peaks interfere each other, it was decided that both peaks should be considered as a unit. In the present method calcium hydroxide is used as an internal standard. The effects of quartz, iron oxide, sodium chloride, calcite, dolomite, illite and anhydrite have also been studied.

Experimental

Equipment and Procedure. Samples of about 0.3mg of material (sample and alumina) were placed in the three holes, one containing sample and two containing alumina, of a stainless steel block and subjected to a uniform rise in temperature (10°/min) in a vertical furnace with nichrome wire as the heating element.⁴ The furnace temperature was controlled manually by a variable transformer, and chrome-alumel thermocouple (25 gauge) were used for recording temperatures. The differential temperature was recorded on an automatic Cambridge recorder, having a scale between +1 and -1 mv. The recorder, driven by an electrical clock, marked every twenty seconds on a chart 95 mm wide with a maximum duration of 125 minutes.

Preparation of Mixtures. Analytical reagent grade alumina was ignited to 1000°. This material was cooled and powdered to 150 μ e.s.d. (equivalent spherical diameter). Calcium hydroxide from May & Baker (Dagenham, England) was dried at 140° for 2 hr. The dried material was cooled and kept in an air-tight bottle. Hazara gypsum containing 98.32% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used for the construction of the working curve.

A series of mixtures of Hazara gypsum, calcium hydroxide and alumina were prepared, mixed thoroughly and analyzed thermally. The various DTA curves are given in Fig. 1 and the results are summarized in Table 1. The ratio of the area (measured with a planimeter) of the endothermic peaks of gypsum to that of calcium hydroxide is

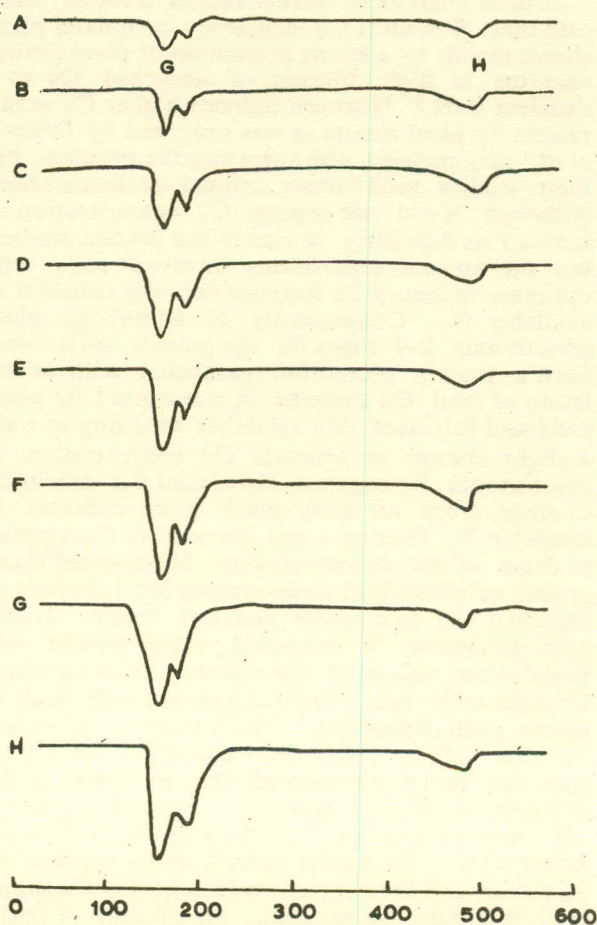
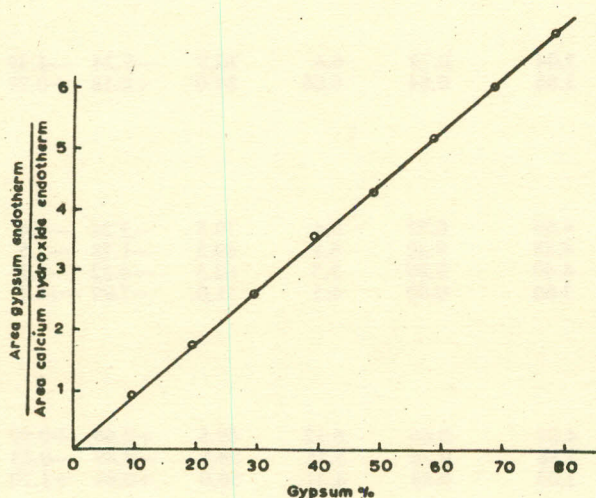


Fig. 1. The various DTA curves of mixtures of gypsum, $\text{Ca}(\text{OH})_2$, and Al_2O_3 (A-H) G and H indicate the endothermic peaks of gypsum and calcium hydroxide respectively. (Not to the original scale).

TABLE 1. DTA DATA OF VARIOUS MIXTURES.

| Sample No. | Composition (wt%) | | | Area of gypsum endothermic peak (cm ²) (a) | Area of Ca(OH) ₂ endothermic peak (cm ²) (b) | (a/b) |
|------------|-------------------|---------------------|--------------------------------|---|--|-------|
| | Sample gypsum | Ca(OH) ₂ | Al ₂ O ₃ | | | |
| A | 10 = (9.83) | 10 | 80 | 0.48 | 0.52 | 0.92 |
| B | 20 = (19.66) | 10 | 70 | 1.20 | 0.68 | 1.76 |
| C | 30 = (29.49) | 10 | 60 | 1.96 | 0.76 | 2.58 |
| D | 40 = (39.32) | 10 | 50 | 2.80 | 0.80 | 3.55 |
| E | 50 = (49.16) | 10 | 40 | 3.24 | 0.76 | 4.26 |
| F | 60 = (58.99) | 10 | 30 | 3.92 | 0.76 | 5.16 |
| G | 70 = (68.82) | 10 | 20 | 4.36 | 0.72 | 6.00 |
| H | 80 = (78.65) | 10 | 10 | 5.24 | 0.76 | 6.89 |


 Fig. 2. Area of gypsum endotherm/Area of Ca(OH)₂ endotherm plotted against percentage gypsum. (Not to the original scale).

directly proportional to the concentration of gypsum.

The optimum amount of internal standard was found to be 10% by weight and 10% of inert alumina was normally added to each sample for dilution. Thus each unknown sample is diluted by 20% and the actual amount of gypsum must be obtained by multiplying the amount indicated in the graph (Fig.2) by a factor of 1.25 (and by 1.11 when alumina is not added).

Reproducibility. Measurements of heat effects are influenced not only by the physical properties of the mineral, but also by the amount and degree of compaction in the test cavity. The size of the thermocouple beads also affects the areas of the peaks. Great care is needed to achieve high reproducibility, but in the present method, using calcium hydroxide as an internal standard the effect of some of the variables mentioned above are eliminated. The results of the five repeat analyses of Kohat gypsum are given in Table 2. The deviation ranges between -2.66 to -6.41 and the mean percentage is -5.02.

TABLE 2. REPEAT QUANTITATIVE ESTIMATION OF GYPSUM.

| Sample | Composition (wt %) | | Area of gypsum endothermic peak (cm ²) (a) | Area of Ca(OH) ₂ endothermic peak (cm ²) (b) | (a/b) | Wt % from calibration curve | Gypsum by chemical analysis | Error | Mean error | Error (%) |
|--------|---------------------|--------------------------------|---|--|-------|-----------------------------|-----------------------------|-------|------------|-----------|
| | Ca(OH) ₂ | Al ₂ O ₃ | | | | | | | | |
| 80 | 10 | 10 | 5.24 | 0.84 | 6.24 | 88.75 | 95.16 | -6.41 | -4.78 | -5.02 |
| 80 | 10 | 10 | 5.52 | 0.88 | 6.27 | 89.38 | | -5.78 | | |
| 80 | 10 | 10 | 5.48 | 0.86 | 6.37 | 90.63 | | -4.53 | | |
| 80 | 10 | 10 | 5.40 | 0.84 | 6.43 | 92.50 | | -2.66 | | |
| 80 | 10 | 10 | 5.36 | 0.84 | 6.38 | 90.63 | | -4.53 | | |

Possible Sources of Error. The impurities present influence the measurement of heat effects. Some of these factors are discussed below:

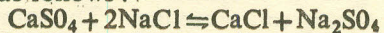
Effects of Various Impurities

Quartz. Quartz frequently occurs pseudomorphous after gypsum and vice versa. A series of mixtures of gypsum (average peak temp. 150° to 175°) quartz average peak (temp. 573°) and alumina with quartz content ranging from 10 to 50% were analyzed thermally. The results are presented in Table 3. The presence of quartz does not affect the results significantly. The percentage error varies between - 4.12 to 0.71.

Iron Oxide. Gypsum containing up to 10% iron oxide can be safely determined by the present method (Table 3).

Halite. Large masses of gypsum are formed by sedimentation in drying saline lacustrine and marine basins, where gypsum is formed along with halite. There is an increase in percentage error with increase in the halite content.

It seems that some of the halite reacts with gypsum as follows:



On recalculation it was found that 43-27% of the NaCl may have reacted with gypsum, thus decreasing its content from the initial amount. However, samples containing up to 7.5% NaCl may be safely estimated (Table 3).

Calcite and Dolomite. Calcite and dolomite often occur as an impurity in gypsum. The effect of

these minerals up to 30% are not significant (Table 3).

Illitic Clays. The effect of illitic clays in gypsum is rather interesting. The negative percentage error decreases with an increase in the amount of clay. Thus even in a low percentage of clay interferes with the estimation of gypsum.

Anhydrite. A small amount of anhydrite is a common impurity of gypsum. The percentage error in the presence of 20% anhydrite is +3.40. The effect of the presence of anhydrite is thus not significant.

Conclusions

The ratios of areas of the endothermic peaks of gypsum (150° and 175° peaks taken as unit) plotted against concentration gives a sensibly linear relationship, thus allowing quantitative estimation of gypsum. Variations in the results due to quartz, iron oxide, halites, calcite, dolomite and anhydrite are not significant. However, the presence of illite can interfere with the quantitative estimation.

References

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