

STUDY OF THE QUANTITATIVE DETERMINATION OF THE PHASES IN THE SYSTEM $\text{CaSO}_4-\text{H}_2\text{O}$

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The quantitative determination of anhydrite, basanite and gypsum was studied in a wide range of concentrations. It was estimated that adequate accuracy can be attained when combined thermal and X-ray diffraction analysis was used. The detectability and range of application of particular methods depending upon the phase content are presented.

In order to determine the phase composition quantitatively in a rapid and reliable way, a method common for thermal and X-ray analysis, that combines the advantages of both but exhibits none of their shortcomings, has been elaborated. According to some authors, X-ray analysis is characterized by a large scatter of the results in the case of the gypsum-basanite system within a range of from 30 to 70% of one of the phases. Errors occurring during the determination of data are due to the fact that basanite dehydrated to a considerable degree does not change its crystallographic structure [1]. Although thermal analysis makes it possible to distinguish the α and β forms of basanite from each other, it does not render sufficiently accurate results in the determination of small contents of hydrate phases within the other, unless special conditions of measurement are employed. The method described in this paper has been repeatedly applied for engineering and research purposes and is characterized by the good reproducibility of the results.

Experimental

Thermal analysis was carried out with a Derivatograph (MOM). The heating rate was about $3^\circ/\text{min}$, and the weighted sample was 1500 mg. The sensitivity of 500 mg made it possible to determine the losses in mass of the sample with an accuracy of 0.33%

Diffraction patterns were obtained by means of a TUR-M-61 apparatus. CuK_α radiation with a Ni filter was used with a suitably selected system of slits. The working parameters of the Cu tube were: 18 mA, 35 kV. The speed of rotation of the goniometer depended on the range of the determined parameters.

For preparation of the calibration curves, chemically pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used, from which $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ was obtained. The specimens obtained were

tested by X-ray and thermal methods. Figure 1 shows the DTA curve for gypsum, the course of which is equivalent to that given in numerous publications on that compound [2]. This two-stage curve corresponds to a double-step dehydration. The point of inflection of the TG curve can be unequivocally described employing

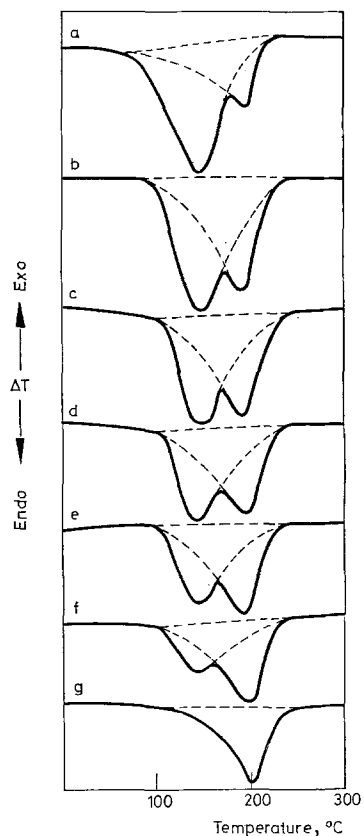


Fig. 1. DTA curves for gypsum, basanite and mixtures. a — gypsum; b — 1 : 4; c — 2 : 3; d — 1 : 1; e — 3 : 2; f — 4 : 1; g — basanite

the DTG curve. The loss in mass right from the beginning up to the point of inflection amounted to 16.33%, beyond which it decreased down to 3.33%. From a comparison of the two figures, it follows that the above-mentioned parameter cannot serve as the basis for further quantitative calculations and that the dehydration steps overlap one another.

Basanite, as can be seen in Fig. 1g, shows an asymmetrical dehydration peak. The total loss in mass is equal in this case to 6.26%; this differs from the stoichiometric value by 0.01%, which indicates the appropriate purity of the sample.

In the investigations on the $\text{CaSO}_4\text{-H}_2\text{O}$ system, homogeneous mixtures with the following compositions were used: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ equal to 1 : 4; 2 : 3; 1 : 1; 3 : 2 and 4 : 1. Further mixtures with small contents of one of the phases in one or two other phases were prepared in order to determine the composition by means of X-ray analysis, the identification factor being another parameter to be determined. The obtained results are shown in Figs 1b–f. All the curves exhibit two endothermic effects. The method of separation of these two overlapping effects accepted by the authors is also shown in Fig. 1. The surface areas of these effects are variable, which is evident from this illustration.

Table 1 shows the absolute value of the surface area of each effect, as well as the ratios of the areas of these effects.

Table 1

Surface areas and indexes (ratios) of surface areas of hydrate mixtures

Compositions	Surface areas (cm^2)		Indexes of surface areas
	I	II	I : II
Gypsum	38.57	21.17	1.82
80 % gypsum + 20 % basanite	37.05	31.40	1.18
60 % gypsum + 40 % basanite	30.22	28.55	1.06
50 % gypsum + 50 % basanite	24.15	24.55	0.98
40 % gypsum + 60 % basanite	19.62	20.95	0.94
20 % gypsum + 80 % basanite	14.70	18.15	0.81
Basanite	—	18.97	0.0

Based on the assumption that the extent of each effect constitutes a certain measure of the absorbed heat, and thus is a measure of the amount of water discharged from the sample, it was assumed that the measurement of the surface areas of all effects and their comparison could be considered as an index of the hydrate content of the sample.

Results and discussion

The straight line shown in Fig. 2 was plotted on the basis of the index taken from Table 1. As the sample may also exhibit the presence of the anhydrous phase, the straight line will not serve as the basis for direct quantitative calculations. Such calculations will also require data taken from the TG curve. Each ratio of the surface areas of effects obtained by planimetry is strictly connected with a definite ratio of the hydrate phase contents, to which a suitable loss in mass further corresponds.

Lack of conformability between the actual loss in mass and the calculated one is an indication of the presence of anhydrite in the sample. If due attention to the

share of this in the sample is given in the calculation procedures, a full determination of the phase composition will be possible. As can be concluded from Fig. 2 the calibration line covers the participation of a hydrate within a range from 20 to 80%. It was proved that the error of this method increases with a fall in content of some of the hydrates. It is within the range from 0 to 20% that the X-ray analysis renders the best results. The result of such a calibration for this range is shown in Fig. 3, by way of example.

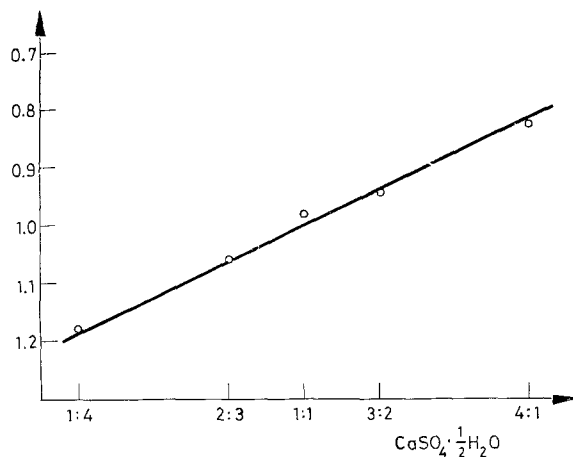


Fig. 2. Index of surface areas as a function of the hydrate composition

A number of experiments were carried out in order to determine the identification limit for the thermal, as well as for the X-ray analysis. The obtained results are summarized in Table 2.

Table 2
Identification limits

Methods	Principal phase	Mixture	Identification limit, %
Thermal analysis	basanite	gypsum	5
	anhydrite	basanite	3
	anhydrite	gypsum	1
X-ray	gypsum	basanite	3
	gypsum	anhydrite	2
	basanite	gypsum	1
	basanite	anhydrite	4
	anhydrite	gypsum	1
	anhydrite	basanite	3

With regard to the requirements put to the authors, the identification limits were sufficient, stressing the possibility of their reduction within the scope of the thermal, as well as X-ray analysis.

On the basis of the conducted investigations, the following procedure for the analysis of calcium sulphate with an unknown phase composition is suggested. The preparation of samples is brought down to the operation of rinsing them with acetone and to a preliminary drying procedure at a temperature below 70° , with

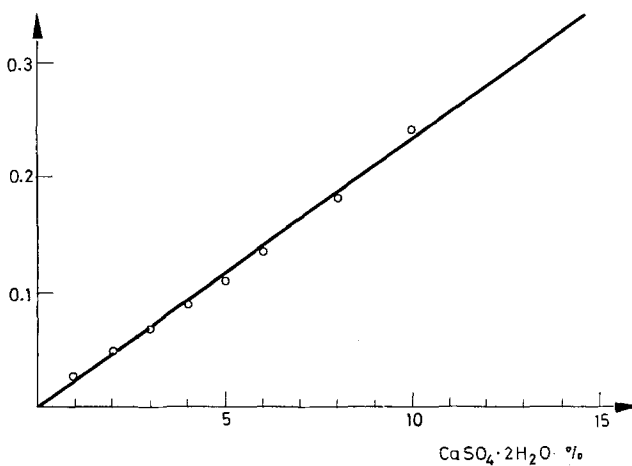


Fig. 3. $I_{4.29}/I_{3.02}$ for the basanite—gypsum system

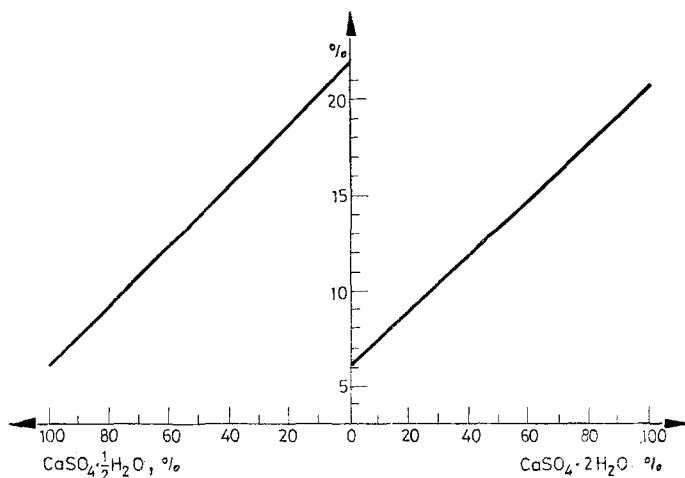


Fig. 4. Nomogram for establishing the phase composition in the gypsum—basanite system

a possible size reduction to be considered. Each sample is then subjected to X-ray analysis. Discovery of a unary system will certainly require further experiments to be carried out on the samples. The presence of a binary system within a range from 1 to 20% of one of the phases will render X-ray analysis sufficient for quantitative determinations. In the case of a binary system where one of the phases exceeds 20%, a thermobalance must be used to determine the losses in mass.

If one of the components is anhydrite, the composition can easily be calculated.

In the case of the gypsum—basanite system, the loss in mass serves as the basis for rapid determination of the composition of those two hydrates, using the nomogram shown in Fig. 4. The presence of a ternary system makes a complete thermal analysis indispensable. In this case, an area integration of the peaks must first of all be performed, followed by calculation of the surface area ratio, from which the ratio of hydrates present in the sample will be calculated.

Further calculations will enable the phase composition to be established. The fact of a lower accuracy index in the analysis of a ternary system must also be taken into account. The method described above is restricted to samples consisting of calcium sulphate phases without admixtures of other substances. This can be considered the main disadvantage of this method, although in practice such limited tasks are often imposed upon the analytical chemist.

References

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2. A. LANGIER-KUZNIAROWA, *Termogramy mineralow ilastych*, Warszawa, 1967.

RÉSUMÉ — On a cherché à doser dans un large intervalle de concentration l'anhydrite, la basanite et le plâtre. Dans ce but, on a fait appel à une méthode mixte par analyse thermique et diffraction des rayons X. Les résultats montrent que le seuil de détection et l'intervalle d'utilisation dépendent de la teneur de ces phases.

ZUSAMMENFASSUNG — Die quantitative Bestimmung von Anhydrit, Basanit und Gips wurde in einem weiten Konzentrationsbereich untersucht. Es wurde angenommen, daß durch eine kombinierte thermische und Röntgendiffraktionsanalyse eine entsprechende Genauigkeit erzielt werden kann. Die Nachweisgrenze sowie der Anwendungsbereich bestimmter Methoden sind vom Phaseninhalt abhängig.

Резюме — Количественное определение ангидрита, басанита и гипса было изучено в широкой области концентраций. Было установлено, что адекватная точность может быть достигнута при использовании термического и рентгено-дифракционного анализа. Показано, что область обнаруживаемости и применения частных методов зависит в фазового содержания.