Journal of Thermal Analysis, Vol. 13 (1978) 553–561

QUANTITATIVE THERMOGRAVIMETRY OF MULTICOMPONENT ZEOLITE-BEARING ROCKS

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(Received February 17, 1977; in revised form October 22, 1977)

A quantitative thermoanalytical determination of mixture compositions is extremely difficult if there is a partial or full overlapping of the temperature ranges of the thermal transformations, and a proximity of the quantitative characteristics of the weight changes is also observed. A method of quantitative analysis of such a system is offered, based on the calculation of differences in the regularity of rate variation of the thermal transformations of the separate mixture components. The principle of distinguishing temperature intervals with maximum differentiation of thermal effects and methods of calculation of the quantitative mixture composition is shown. Examples of determination of the mineral compositions of zeolite-bearing rock are given.

Quantitative thermogravimetry of natural and artificial mineral water-bearing mixtures can be based on the recording of weight change, generally connected with dehydration processes and dehydroxylation of minerals when heated. However, an estimate of each component is extremely difficult if there is a partial or full overlapping of the temperature ranges of the thermal transformations. A quantitative determination in this case becomes possible on the basis of calculating differences in the regularity of rate variation of such thermal transformations. It is possible to distinguish temperature ranges with the utmost differentiation of thermal effects and make a calculation of the contents of components via the thermogravimetric curves.

Apparatus and material

The methods suggested for the thermogravimetric determination of the mixture composition, the components of which are characterized by overlapping of the thermal transformations, can be seen in the appendix to the zeolite-bearing (clinoptilolite) rocks. The mineralogical composition of zeolitized tuffs is mainly represented by the zeolite, montmorillonite, quartz, and rarely by feldspar and relict volcanic glass. It turned out that the pure samples of these latter three minerals which we had at our disposal were practically thermally gravimetrically-inert (they do not undergo weight change during heating). Thermogravimetry was carried out on an OD-102 Derivatograph, using a Pt-Pt/Rh thermocouple (heating of 1 g of specimen up to 1000° at a rate of 10°/min).

Results and discussions

The clinoptilolite DTA curve records a continuous water loss by the mineral in the wide temperature range from 40 to 700° [1–4]. The weight loss amounts to 13.2% (Fig. 1). Montmorillonite is characterized by an intense endothermic effect (35–170°), which is associated with the release of interlayer water, and also by two small endothermic effects (450–555° and 610–695°), conditioned by thermal dissociation of OH^- groups with different binding energies from the octahedral layers [5–15]. Here, water is also released and the total loss of weight is 15.2% (Fig. 2).

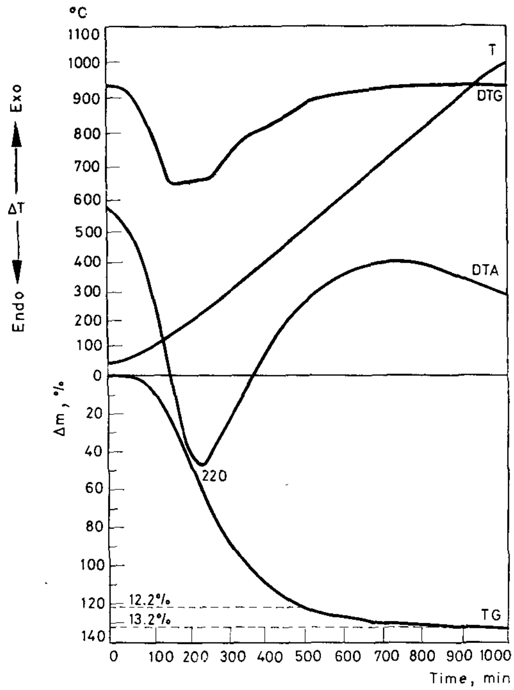

Fig. 1. TG, DTG and DTA curve of clinoptilolite

The coincidence of the temperature range of full dehydration, the overlapping of the corresponding thermal effects within it, and also the proximity of the weight change quantitative characteristics make difficult a quantitative estimate of mixtures such as these by the usual means (comparison of areas of thermal effects, calculation involving values of total loss of weight). The potentialities of the derivatograph, which, besides recording the thermogravimetric curve of a general change in the mass *m* of a sample also records the rate of this process d*m*/d*t*, allow this latter parameter to be used to determine the compositions of such mixtures.

If the system studied consists of two components only and is considered as a mechanical mixture where interaction between the components does not matter, its composition may be determined simply via the equations:

$$\frac{\mathrm{d}m_x}{\mathrm{d}t} X + \frac{\mathrm{d}m_y}{\mathrm{d}t} Y = \frac{\mathrm{d}m_{xy}}{\mathrm{d}t} \tag{1}$$

$$X + Y = 1$$

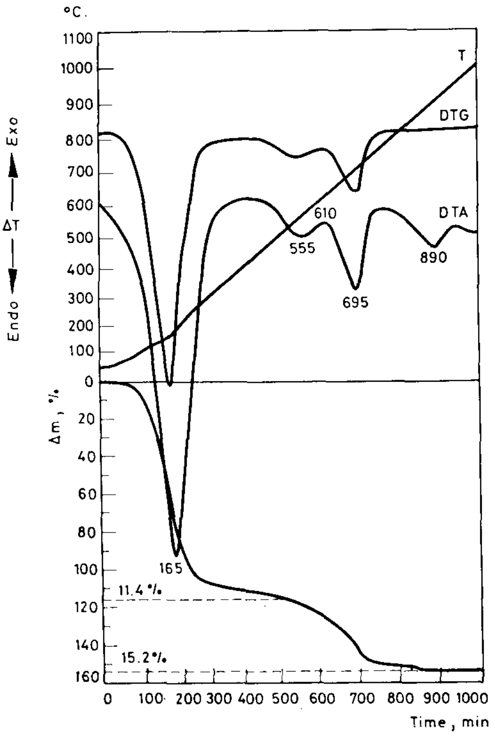

Fig. 2. TG, DTG and DTA curve of montmorillonite

where: $\mathrm{d}m_x/\mathrm{d}m$ and $\mathrm{d}m_y/\mathrm{d}t$ = derivatives of the change in mass m of the reference components at time t;
$\mathrm{d}m_{xy}/\mathrm{d}t$ = the same for the mixture (sample to be analyzed);
X and Y = contents of mixture components in unit fractions.

The determination of mixture components is in principle possible at any temperature where there is a change of mass.

In this case the system considered contains thermally-inert components too. Then, the equations are:

$$\begin{aligned} \frac{\mathrm{d}m_x^{T_1}}{\mathrm{d}t}X + \frac{\mathrm{d}m_y^{T_1}}{\mathrm{d}t}Y &= \frac{\mathrm{d}m_{xy}^{T_1}}{\mathrm{d}t} \\ \frac{\mathrm{d}m_x^{T_2}}{\mathrm{d}t}X + \frac{\mathrm{d}m_y^{T_2}}{\mathrm{d}t}Y &= \frac{\mathrm{d}m_{xy}^{T_2}}{\mathrm{d}t} \\ X + Y + Z &= 1 \end{aligned} \tag{2}$$

where: X and Y = contents of thermally-active components;
Z = total content of thermally-inert components;
T_1 and T_2 = temperatures which correspond to the $\mathrm{d}m/\mathrm{d}t$ values to be measured.

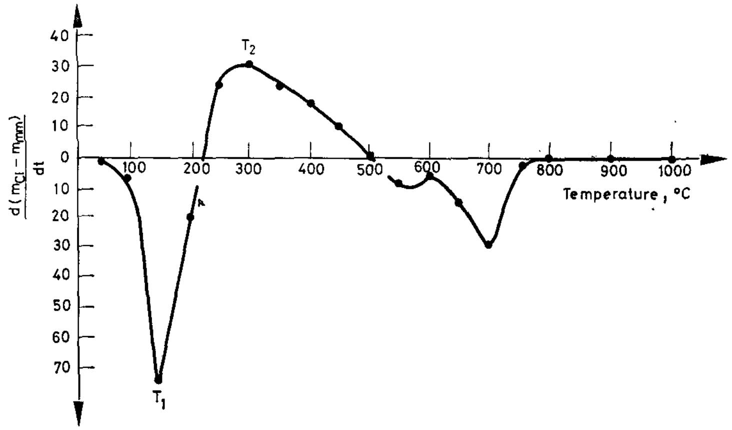

Fig. 3. Dependence of rate difference of clinoptilolite mass change and montmorillonite upon temperature.

Solution of these equations is possible in the knowledge of $\mathrm{d}m/\mathrm{d}t$ values for at least two temperatures (if these values are sufficient to obtain inhomogenous equations). Selection of these temperatures is made on the basis of considering the dependence $\mathrm{d}(m_x - m_y)/\mathrm{d}t$ under the following conditions: difference values of rate of mass change by both components are sufficiently high (curve deflection from the axis of X) and as different as possible (deflection sign). Such a dependence for the clinoptilolite-montmorillonite system permits choice of the following temperature values: $T_1 = 150°$, $T_2 = 300°$ (Fig. 3).

Equations (1) and (2) may be solved algebraically, for which it is necessary to know the numerical values $\mathrm{d}m_{cl}^{T_1}/\mathrm{d}t$, $\mathrm{d}m_{mm}^{T_1}/\mathrm{d}t$, $\mathrm{d}m_{cl}^{T_2}/\mathrm{d}t$ and $\mathrm{d}m_{mm}^{T_2}/\mathrm{d}t$. The diagrammatic solution, the use of which is rational for the zeolite + thermally-inert components system, is made by means of constructing a calibration curve in the coordinates: composition *vs.* $\mathrm{d}m/\mathrm{d}t$.

Let us consider the course of the thermogravimetric curve on the example of sample 640 (Table 1). Its curves are given in Fig. 4. In order to calculate we use the DTG curve. We measure $dm^{T_1}_{xy}/dt$ and $dm^{T_2}_{xy}/dt$ values as the deflections in millimeters of the DTG curve from its base line at points T_1 and T_2, which correspond to values of 150° and 300° (according to Fig. 3). They are equal to 81 and 40 mm, respectively. In the same way we measure the values $dm^{T_1}_{x}/dt = 104$ mm and $dm^{T_2}_{x}/dt = 57$ mm (clinoptilolite) and $dm^{T_1}_{y}/dt = 200$ mm and $dm^{T_2}_{y}/dt = 6$ mm (montmorillonite) on the reference montmorillonite (Taganka, Kazakh Republic, USSR) and on the reference clinoptilolite (Dzegvi, Republic of Georgia, USSR) thermal curves.

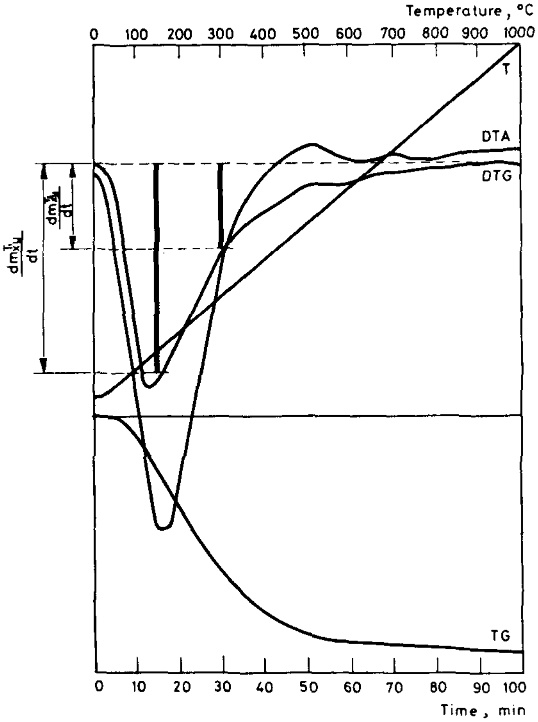

Fig. 4. TG, DTG and DTA curve of clinoptilolite tuff sample N640 (Noemberyan, Armenia) with indication of components to be measured

Let us introduce the data into Eq. (2):

$$104X + 200\ Y = 81$$
$$57X + \ \ 6\ Y = 40$$

where X and Y = concentrations of clinoptilolite and montmorillonite, respectively. By solving the equation, we obtain: $X = 0.70$; $Y = 0.04$. So, the clinoptilolite

Table 1

Results of determination of compositions of clinoptilolite tuffs from Noemberyan deposit

Sample	Composition, weight %								
	X-ray method			DTG method			LSM defined		
	cl	*mm*	*z*	*cl*	*mm*	*z*	*cl*	*mm*	*z*
600a	82	9	15	77	0	23	83	5	15
608	28	23	50	25	45	26	33	21	43
609	63	7	30	62	12	26	56	17	28
613	73	9	18	68	8	24	74	8	19
614	79	10	10	60	14	26	78	11	14
622	77	6	27	48	13	39	71	6	27
626	26	13	61	17	10	73	22	12	66
627	50	7	43	42	20	38	48	10	41
631	37	15	48	26	16	58	34	15	52
633	71	0	30	39	18	43	66	4	33
634	58	8	34	41	15	44	55	9	37
640	73	4	23	70	4	26	73	3	24
645	64	26	15	47	21	32	60	25	18
646	43	25	32	33	22	45	40	25	36
648	59	27	15	36	25	39	55	27	21
651	50	21	29	41	26	33	48	23	30

cl = clinoptilolite, *mm* = montmorillonite, *z* = sum of thermally-inert phases.

Table 2

Results of determination of compositions of samples of Transcarpathian clinoptilolite tuffs

Sample	Composition weight %									
	X-ray method						DTG method		Least squares method (LSM)	
	All-Union Research Institute of the Geology of Non-Ore Useful Minerals, Kazan		Institute of Geological Science of the Ukraine Soviet Socialist Republic Academy of Science, Kiev		Central Complex Laboratory of Kiev Geology Trust, Kiev					
	cl	*z*	*cl*	*z*	*cl*	*z*	*cl*	*z*	*cl*	*z*
10/2	80	20	80	20	—	—	66	34	72	28
11/2	26	74	15	85	—	—	17	83	20	80
48	94	6	90	10	76	24	82	18	87	14
51	79	21	60	40	53	47	63	37	70	30
67	79	21	70	30	—	—	61	39	70	31

cl = clinoptilolite, *z* = sum of thermally-inert phases.

content is 70% and that of montmorillonite is 4%. The residual 26% is the content of the thermally gravimetrically-inert component.

By the DTG method mentioned above, a quantitative analysis was made of natural specimens of zeolitized tuffs from Armenia, Azerbaijan, Turkmenistan and the Transcarpathians (in all 52 samples). In Table 1 the thermogravimetric data of the clinoptilolite tuffs of the Transcarpathians are compared with the results of X-ray studies made by different organizations. The comparison of the results of the analysis by DTG and X-ray methods by means of Student's ratio (t criterion) shows the presence of a divergence: $t = 5.40$ at $t_{0.05}(15) = 2.13$; a more precise determination of the values of the concentrations of the mixture components by the least squares method (LSM) permits the convergence to be improved (Table 2).

This method of quantitative determination described above may also be extended to systems with a large number of thermally gravimetrically-active components. If the system contains $X + Y + V + \ldots + N$ thermally-active components, then the equations are as follows:

$$\frac{dm_x^{T_1}}{dt} X + \frac{dm_y^{T_1}}{dt} Y + \frac{dm_v^{T_1}}{dt} V + \ldots + \frac{dm_n^{T_1}}{dt} N = \frac{dm_{xyv}^{T_1} \ldots {}_n}{dt}$$

$$\frac{dm_x^{T_2}}{dt} X + \frac{dm_y^{T_2}}{dt} Y + \frac{dm_v^{T_2}}{dt} V + \ldots + \frac{dm_n^{T_2}}{dt} N = \frac{dm_{xyv}^{T_2} \ldots {}_n}{dt}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\frac{dm_x^{T_n}}{dt} X + \frac{dm_y^{T_n}}{dt} Y + \frac{dm_v^{T_n}}{dt} V + \ldots + \frac{dm_n^{T_n}}{dt} N = \frac{dm_{xyv}^{T_n} \ldots {}_n}{dt}$$

$$X + Y + V + \ldots + N + Z = 1$$

where Z = sum of all thermally-inert components. Hence, as many equations are required as there are unknown thermally-active components, and one normalizing equation is added. The general number of equations is equal to $N + 1$. In this case, the knowledge of $dm_{xyv} \ldots {}_n/dt$ values at N points is necessary.

Conclusion

The suppositions involved in the method of calculation described above are true under conditions of constancy of weight and rate of heating of reference samples and samples to be tested. In the case of different specimens, conversion coefficients for dm/dt values are introduced. The determination is not hampered by any thermally-active component which possesses constancy of mass at the selected temperature values, because the sample is taken into account in the sum of the thermally-inert components. If there arises a need for a quick determination, an important advantage lies in the possibility of performing the heating of samples up to relatively low temperatures (350–400°). As a result, the accuracy of dm/dt determination is increased due to the better reproducibility of the recording apparatus in the range of moderate temperatures.

The method described above has shown a good coincidence with the X-ray test data. For instance, when 11 specimens of zeolite-bearing tuffs which contain a zeolite phase as the thermally-active component are analyzed, the correlation ratio between the X-ray and thermal data amounts to 0.93. When 21 specimens ofzeolite-bearing tuffs, which contain zeolite and montmorillonite as their thermally-active phases are analyzed, the correlation ratio if the zeolite content is determined is 0.88; the correlation ratio if the montmorillonite content is determined is 0.64 (Table 3).

Table 3

Comparison of results of X-ray and thermogravimetric analyses

Number of samples analyzed	Correlation ratio on:	
	zeolite	montmorillonite
11	0.93	–
21	0.88	0.64

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Résumé — La détermination quantitative de la composition d'un mélange est très difficile par les méthodes thermoanalytiques si les intervalles de température où s'effectuent les transformations se chevauchent partiellement ou totalement et si les variations pondérales sont proches les unes des autres. Pour effectuer l'analyse quantitative d'un tel système, on présente ici une méthode qui repose sur le calcul des modifications de la vitesse de transformation des composants individuels du mélange. On décrit le principe suivant lequel on effectue la distinction des intervalles de température avec une différenciation maximale des effets thermiques ainsi que les méthodes permettant de calculer la composition du mélange. Le dosage des constituants présents dans des roches à zéolites est donné comme exemple.

Zusammenfassung — Eine quantitative thermoanalytische Beschreibung der Zusammensetzung eines Gemisches ist äusserst schwer, wenn die Temperaturbereiche der thermischen Zersetzungen teilweise oder vollständig überlappen und auch die quantitativen Charakteristika der Gewichtsänderungen nahe bei einander liegen. Eine Methode der quantitativen Analyse eines solchen Systems wird gezeigt, die auf der Berechnung der Unterschiede der Regelmässigkeit der Geschwindigkeitsänderung bei der thermischen Umsetzung der einzelnen Komponenten des Gemisches beruht. Das Prinzip der Unterscheidung von Temperaturbereichen unter maximaler Differenzierung der thermischen Effekte, sowie die Methode zur Berechnung der quantitativen Zusammensetzung des Gemisches werden beschrieben. Beispiele zur Bestimmung der Zusammensetzung der Mineralstoffe in zeolithaltigem Gestein werden gegeben.

Резюме — Количественное термоаналитическое определение состава смеси является чрезвычайно трудным, если происходит частичное или полное перекрывание температурной области термических превращений, а также если наблюдается близость количественных характеристик изменения веса. Предложен метод количественного анализа такой системы, основанный на вычислении различий в закономерностях изменения скорости термического превращения отдельных компонентов смеси. Показаны основные характерные температурные интервалы с максимумом дифференциации термических эффектов и методы вычисления количественного состава смеси. Представлены примеры определения минерального состава цеолита природного происхождения.