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SIMULTANEOUS TG, DTG, DTA AND EGA TECHNIQUE FOR THE DETERMINATION OF CARBONATE, SULPHATE, PYRITE AND ORGANIC MATERIAL IN MINERALS, SOILS AND ROCKS

PART I. PRINCIPLES OF THE METHOD

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A simultaneous TG, DTG, DTA and EGA method was developed for the determination of carbonate, sulphate, pyrite and organic material in minerals. The method is based on the selective direct determination of SO_3 and CO_2 evolved from the heated sample, and on the indirect determination of H_2O. The thermogas-titrimetric adapter of the derivatograph collects the liberated gases (CO_2, SO_3, SO_2) quantitatively, absorbs them in water, and titrates them continuously and automatically with NaOH titrant. The changes in the volume of titrant consumed are recorded as a function of the temperature. In two parallel examinations, one titration is performed at pH 4, and the other at pH 9.3. The former measurement yields only the amount of SO_3 (SO_2), while the latter gives the joint amount of SO_3 (SO_2) and CO_2.

With the development of thermoanalytical measuring techniques the strange situation has arisen that the measurements can be performed with a significantly greater accuracy than the determination of the composition of multicomponent systems. For instance, although the weight change of a sample can be found by means of a thermobalance with an accuracy of $\pm 0.1\%$, the amounts or the individual components of minerals can often be determined only with an accuracy lower by several orders of magnitude. This fact can be attributed to three causes.

The most frequent and difficult problem is caused by the circumstance that the individual mineral components decompose closely after one another. Whereas in a favourable case the overlapping of the transitions only decreases the accuracy of the determination, under disadvantageous conditions it may totally frustrate even the identification of the components.

Such an unfavourable case is demonstrated in Fig. 1. These simultaneous TG, DTG and DTA curves illustrate the decomposition of siderite in nitrogen and oxygen atmospheres. It is well known that, due to the conditions of siderite formation, it may be contamined with varying amounts of pyrite and organic material. However, under given conditions these contaminants show similar heat and weight effects to those of siderite. For example, the decompositions of all three materials are endothermic processes in a nitrogen atmosphere, but exothermic in oxygen. All three decompositions involve weight loss, the processes taking place in the same temperature range and overlapping completely. Accordingly, from the curves in Fig. 1 neither the presence nor the absence of these contaminants can be stated.

However, the identification and determination of the accessory components is difficult even if their decompositions do not coincide with those of the main com-

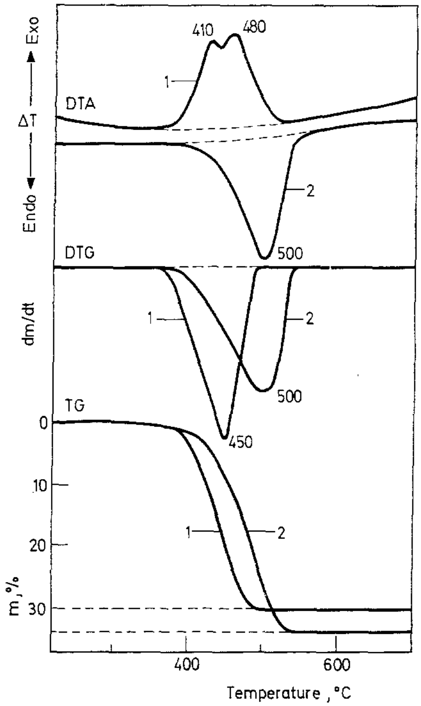

Fig. 1. Simultaneous TG, DTG and DTA curves of siderite in O_2 (1) and N_2 (2)

ponents. The TG and DTG curves indicate small, characterless, but not negligible weight changes between those of the individual identifiable components. The small weight effects of the accessory components easily melt into this weight change "background".

The formation of the weight change "background" can be explained by the circumstance that the decomposition of the main components generally accelerates gradually and decays only slowly, and therefore the introductory stages of the transformation and the decay period of the subsequent ones overlap. The phenomenon may have yet another cause. In addition to their main and accessory components, mineral substances generally contain small amounts of further, not identifiable contaminants. The decomposition of these latter may also contribute in some way to the weight change "background".

Figure 2 shows how the weight effect of an accessory component melts into the weight change "background". Curves 1 were traced for a bauxite sample containing gibbsite (300°) and boehmite (520°). Between the decomposition processes of the two main components, as well as before and after them, a continuous small weight loss can be observed in the DTG curve. We obtained curves 2 and 3 by mixing 1.9 % of organic material and 15.3 % of siderite, respectively, with the bauxite samples before the experiments. The decomposition of these additives did not show any

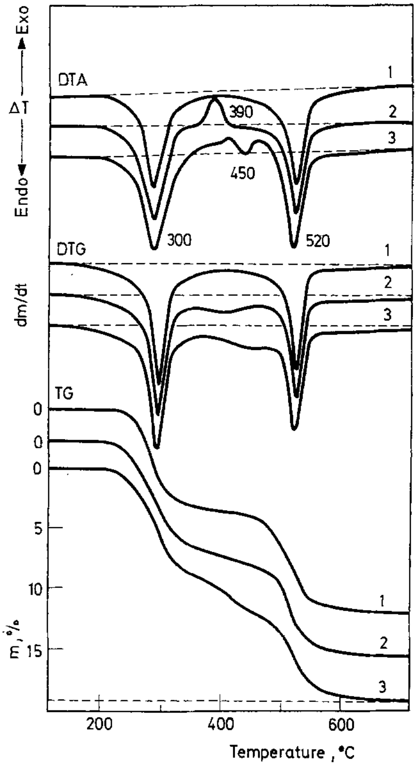

Fig. 2. Simultaneous TG, DTG and DTA curves of a bauxite (1), a mixture of bauxite and organic material (2), and a mixture of bauxite and siderite (3)

evaluable trace on the TG and DTG curves. The maxima at 390° and 450° in the DTA curve could be identified only in the certain knowledge of the composition of the sample.

Little significance has been attributed to the third error source so far. It is well known that certain mineral components may react with one another while still in the solid phase, before their decomposition. Therefore, the heat and weight effects characteristic of the decomposition of these components fail to emerge and their presence remains hidden.

It may also occur that the gaseous decomposition products of one of the components react with the other solid component. In this interaction unexpected weight and heat effects may appear, or compounds may be formed which were originally not present in the sample at all. This circumstance may lead to significant and multiple sources of error.

We experimentally proved [1], for example, that aluminium oxide or ferric oxide can both bind sulphur trioxide, and sulphur dioxide too in the presence of oxygen. The decomposition of the aluminium oxysulphate and ferric oxysulphate formed is

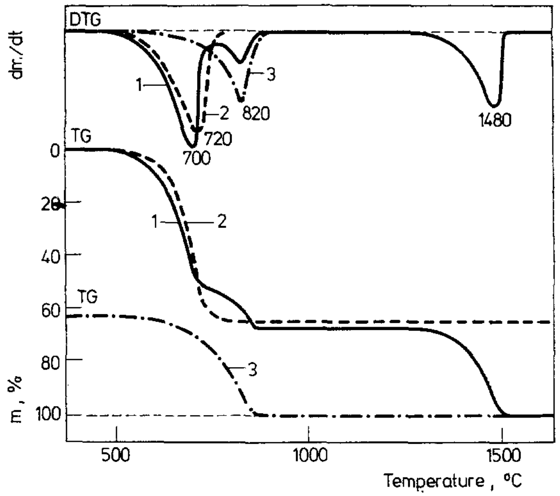

Fig. 3. Simultaneous TG and DTG curves of a mixture of pyrite and calcium carbonate (1), pyrite (2) and calcium carbonate (3)

complete only above 1000°. Silica or acid silicates may react with metal sulphates and metal carbonates below the decomposition temperatures of these latter.

A frequently occurring example is illustrated in Fig. 3. Mineral substances often contain metal sulphate or pyrite, and simultaneously alkaline earth metal carbonate too. Experience reveals that these compounds react with one another in the solid phase to form alkaline earth metal sulphate, which can be decomposed only at about 1400°.

We also proved this experimentally. We mixed equivalent amounts of ferric sulphate and calcium carbonate. Curves 1 in Fig. 3 are the TG and DTG curves for this mixture, while curves 2 and 3 were traced from the pure reaction partners. According to curve 1, half of the reaction partners reacted with one another to form calcium sulphate. We also observed that in the presence 3—5 times the equivalent amount of calcium carbonate, calcium sulphate was formed in an amount equivalent to the ferric sulphate, which means that the reaction took place quantitatively.

Due to these potential errors, conventional mineral analysis based on simultaneous TG, DTG and DTA examinations has reached the limit of its efficiency. Further development in this field can only be expected from the introduction of new measuring techniques. Motivated by these considerations, we have developed a method [2, 3] of which we give only a short description in the following. A detailed survey of the technique will be reported in the subsequent parts of this paper.

Method

Experience shows that other than heat-stable components or components which decompose with the release of water, mineral substances contain only carbonate, sulphate and sulphide minerals and possibly organic substances. Our method based on simultaneous TG, DTG, DTA and TGT (thermo-gas-titrimetry), operating up to 1500° [2, 3, 4], is suitable for the detection and determination of these latter components. The technique is based on the direct determination of CO_2 and SO_3 (SO_2) and on the indirect determination of H_2O.

The type of derivatograph suitable for the TGT measurements is already known [3], but we think it expedient to recall here at least the essence of TGT measurements. The O_2 or N_2 used as carrier gas transports the CO_2 and SO_3 (SO_2) evolved in the course of the TG, DTG and DTA measurements into water. The pH of the water therefore changes and this is sensed by a glass and reference electrode couple. As soon as the pH of the solution begins to deviate from the preselected value, the automatic burette begins to operate, adding NaOH titrant to the absorption liquid so that the pH of this stays constant (pH-stat). The volume of titrant consumed, recorded as a function of the temperature, yields the TGT curve.

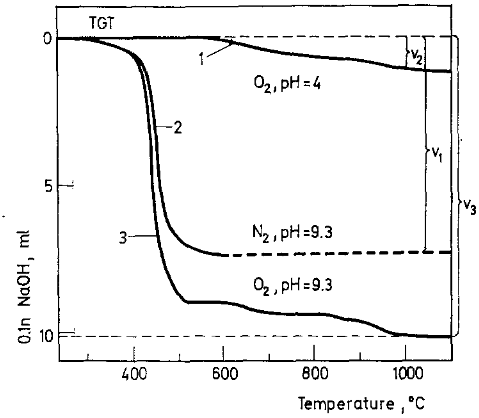

Fig. 4. TGT curves of a mixture of siderite, pyrite and organic material in O_2 (1, 3) and N_2 (2) at pH 4 (1) and pH 9.3 (2, 3)

Principle of evaluation of TGT curves

The TGT curve traced in the presence of H_2O_2 at pH 4 (Figs 4 and 5) indicates only the joint amount of SO_3 and SO_2, for the CO_2 is not absorbed at pH 4. In the next experiment, carried out at pH 9.3, the CO_2 too is absorbed and is also titrated as a monobasic acid. By difference calculation from the two different kinds of TGT curves, a curve representing the changes in the amount of CO_2 can be drawn (Fig. 6).

The curve denoted by SO_3 (Fig. 6) illustrates the decomposition processes of sulphide and sulphate minerals, while the curve denoted by CO_2 represents the burning process of the organic material and the dissociation of carbonates.

If the experiment is repeated at pH 9.3 in N_2 up to 600°, the amount of the organic material and that of carbonates can be determined separately by difference calculation from the TGT curves traced at pH 9.3 in O_2 (curves 2 and 3 in Figs 4 and 5).

$$\begin{tikzcd} & CO_2,\ H_2O \\ \text{Org. mat.} \arrow[ru, "O_2"] \arrow[rd, "N_2"'] & \\ & CO,\ H_2O,\ H_2,\ C_nH_m,\ \text{coke, tar}\ [CO_2] \end{tikzcd} \tag{1}$$

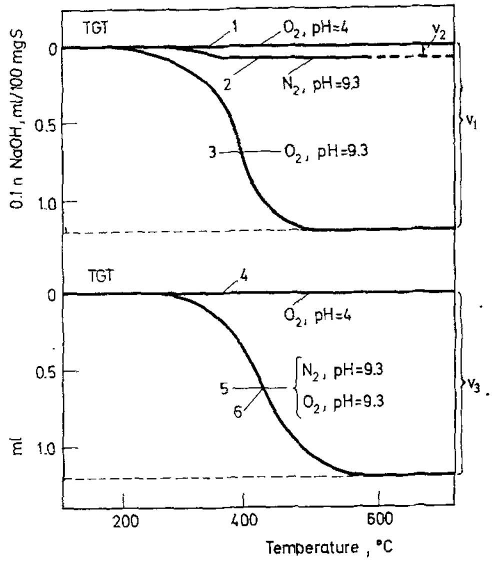

Fig. 5. TGT curves of mixtures of bauxite and organic material (1, 2, 3) and of bauxite and siderite (4, 5, 6) in O_2 (1, 3, 4, 6) and N_2 (2, 5) at pH 4 (1, 4) and pH 9.3 (2, 3, 5, 6)

In N_2 the amount of CO_2 formed in the decomposition of organic compounds is negligible. However, it is to be noted that oxyen-containing compounds [$Fe_2(SO_4)_3$, Fe_2O_3] may oxidize the tar and coke above 600°, and in this way CO_2 can be formed at higher temperatures.

Sulphide and sulphate minerals can theoretically be separated by changing the atmosphere:

$$\begin{tikzcd} & Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3\,SO_3 \\ FeS_2 \arrow[ru, "O_2"] \arrow[rd, "N_1"'] & \\ & FeS + S \end{tikzcd}$$

However, in practice this cannot be accomplished because the components react with one another above 600°:

$$4\,FeS + 3\,Fe_2(SO_4)_3 = 10\,FeO + 13\,SO_2 \qquad (3)$$

Metal oxides (Fe_2O_3) can also lead to oxidation.

From the TG and TGT curves, difference calculation allows construction of a curve which indicates solely the departure of H_2O. By means of this curve the

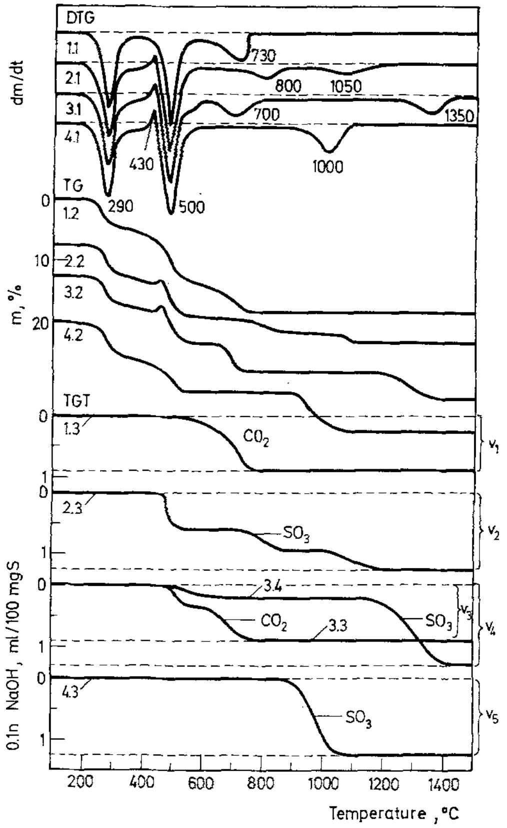

Fig. 6. Simultaneous TG, DTG and TGT curves of mixtures of bauxite and calcite (1,1, 1,2, 1,3), bauxite and pyrite (2,1, 2,2, 2,3), bauxite, pyrite and calcium carbonate (3,1, 3,2, 3,3), and bauxite, pyrite and magnesium oxide (4,1, 4,2, 4,3)

amounts of minerals decomposing with H_2O release can be determined with greater accuracy than from the TG curve [4].

We have observed that the interpretation of the curves becomes easier and their evaluation more accurate if excess MgO is mixed with the sample. This binds the total amount of SO_3 (SO_2) in the moment of its formation in the form of $MgSO_4$ and hinders weight change in the sample in a broad temperature interval (560–1200° in curves 2,1, 2,2 and 2,3 in Fig. 6). $MgSO_4$ can be decomposed, however, above 1000° (curves 4,1, 4,2 and 4,3 in Fig. 6).

Experimental

Materials

Siderite: As can be seen, from Table 1 the siderite selected as model substance was of nearly ideal purity from the point of view of the measuring technique; it did not contain either pyrite of sulphate-containing mineral or organic material, and its alkaline earth metal content was only minimal.

Table 1

Composition of the siderite

FeO	54.5%	CaO	0.3%
Fe_2O_3	1.2	MgO	0.7
CO_2	33.1	MnO	1.5
S	0.1	Al_2O_3	0.5
org. mat.	—	SiO_2	1.2

Siderite calculated of CO_2: 87.2%

Table 2

Composition of the bauxit

Al_2O_3	50.5%	CaO	0.3%
Fe_2O_3	22.7	MgO	0.2
H_2O	15.5	S	0.1
SiO_2	1.1	CO_2	0.4
MnO	0.1	org. mat.	—

Bauxite: In the selection of the bauxite sample (Table 2) we started from the same point of view as above.

Pyrite: The sample was scarcely oxidized, it was relatively pure, and it contained 46.9% S and 87.9% FeS_2 respectively.

Organic material: In order to be able to state the accuracy of the method regarding the determination of the organic material, we needed a model substance whose decomposition in oxygen and oxygen-free atmospheres takes place similarly to that of natural organic material contaminants of minerals. For this purpose we found brown coal to be the most suitable. We determined the elementary carbon content of a brown coal sample (78.3% C). We mixed a known amount of this with the samples examined (Figs 2 and 4).

The compositions of the siderite, bauxite, pyrite and brown coal samples were determined by conventional standard methods.

Calcium carbonate of analytical purity. This preparation was of stoichiometric composition.

Magnesium oxide of analytical purity. Directly before use, the compound was heated to 1000°C in order to remove any bound carbon dioxide and water content.

Experimental conditions

Figure 1 illustrates the simultaneous TG, DTG and DTA curves of the original siderite sample (Table 1) free from pyrite, metal sulphate and organic material. The examinations were carried out partly in oxygen (curves 1) and partly in nitrogen (curves 2), using open crucibles. The heating rate here and also in the following measurements was 5°/min and the rate of the gas flow was 10 l/hour.

Figure 2 shows the simultaneous TG, DTG and DTA curves of the original pure (Table 2) bauxite (curves 1), of bauxite mixed with 1.9% brown coal (curves 2) or 15.3% siderite (curves 3). These experiments were carried out in oxygen, using open crucibles.

The TG and DTG curves of pure, water free ferric sulphate (curves 2), pure calcium carbonate (curves 3) and a mixture of nearly equivalent amounts 1 : 1.3 ratio of these two compounds (curves 1) are shown in Fig. 3.

The accuracy of the method was checked with model experiments (Fig. 4). To 92.3 wt.% of the siderite sample we added 3.4 wt.% of brown coal and 4.3 wt.% of pyrite, and performed parallel TGT measurements partly in oxygen at pH 4 (curve 1) and pH 9.3 (curve 3), and partly in nitrogen at pH 9.3 (curve 2). In the latter examination we raised the temperature only to 600° to avoid the oxidation of coke and tar. In order to check the reproducibility, we repeated every measurement seven times. The results of these examinations are shown in Tables 3, 4 and 5. Here, for each parallel measurement we have shown the amount of 0.1 *N* NaOH titrant consumed for 100 mg of sample, and also the found and calculated amounts of siderite and $FeCO_3$ (Table 3), pyrite and FeS_2 (Table 4) and brown coal and elementary carbon (Table 5). As mentioned earlier the latter can be determined from the results of three titrations by means of difference calculation $(v_3-v_1-v_2)$. We also traced the simultaneous TG, DTG and DTA curves for the decomposition

Table 3

Determination of siderite content of a mixture of siderite-pyrite and org. mat.

0.1 n NaOH / 100 mg sample		Found		Calculated	
v_1		$FeCO_3$		$FeCO_3$	siderite
ml	ml	%	%	%	%
6.81	6.89	78.9	79.8	80.5	92.3
6.89		79.8			
6.91		80.1			
6.86		79.5			
6.93		80.3			
6.86		79.5			
6.95		80.5			

Table 4

Determination of pyrite content of a mixture of siderite-pyrite and org. mat.

$\frac{0.1\text{ n NaOH}}{100\text{ mg sample}}$		Found		Calculated	
v_2		Fe_2S		FeS_2	pyrite
ml	ml	%	%	%	%
1.23		3.7			
1.11		3.3			
1.21		3.6			
1.17	1.19	3.5	3.5	3.8	4.3
1.25		3.7			
1.15		3.4			
1.21		3.6			

of the mixture. The shapes of these curves were very similar to those of the curves in Fig. 1, and therefore they are not given here.

The TGT curves relating to the simultaneous TG, DTG and DTA curves in Fig. 2 are illustrated in Fig. 5. Curves 1 – 3 were traced for mixtures of bauxite and brown coal and curves 4 – 6 for mixtures of bauxite and siderite, partly in O_2 at pH 9.3 and partly in N_2 at pH 9.3. The numerical results of these measurements are shown in Table 6.

The simultaneous TG and DTG curves in Fig. 6 show the way in which the known decomposition process of pure bauxite (curves 1 in Fig. 2) changed if known

Table 5

Determination of carbon content of a mixture of siderite-pyrite and org. mat.

$\frac{0.1\text{ n NaOH}}{100\text{ mg sample}}$		Found		Calculated	
$v_3-v_1-v_2$		C		C	brown coal
ml	ml	%	%	%	%
10.07 – 6.81 – 1.23 = 2.03		2.4			
10.09 – 6.89 – 1.11 = 2.09		2.5			
10.01 – 6.91 – 1.21 = 1.88		2.3			
10.11 – 6.86 – 1.17 = 2.08	1.97	2.5	2.4	2.7	3.4
10.00 – 6.93 – 1.25 = 1.82		2.2			
10.12 – 6.86 – 1.15 = 2.11		2.5			
9.95 – 6.95 – 1.21 = 1.79		2.1			

Table 6

Determination of accessory components of bauxite

Components determined		TG, DTG, DTA curves		TGT curves		0.1 n NaOH / 100 mg sample		Found		Calculated	
								CO_2	SO_3	CO_2	SO_3
	%	fig	curve	fig	curve	v	ml	%	%	%	%
Org. mat. (elementary C)	1.9 (1.5)	2	2	5	3	v_1	1.18	5.2	—	5.5	—
Siderite ($FeCO_3$)	15.3 (13.3)	2	3	5	5	v_3	1.22	5.4	—	5.1	—
Calcite ($CaCO_3$)	8.2	6	1.1 1.2	6	1.3	v_1	0.87	3.8	—	3.6	—
Pyrite (FeS_2)	4.6 (4.0)	6	2.1 2.2	6	2.3	v_2	1.24	—	5.0	—	5.4
Pyrite (FeS_2)	4.7 (4.1)	6	3.1 3.2	6	3.4	v_4	1.30	—	5.2	—	5.5
Calcite ($CaCO_3$)	9.6				3.3	v_3	0.91	4.0	—	4.2	—
Pyrite (FeS_2) [MgO]	4.3 (3.8)	6	4.1 4.2	6	4.3	v_5	1.25	—	5.0	—	5.1

amounts (Table 6) of calcite (curves 1,1 and 1,2), pyrite (curves 2,1 and 2,2), pyrite and calcite (curves 3,1 and 3,2), or pyrite and magnesium oxide (curves 4,1 and 4,2) were previously mixed with the bauxite sample. From the simultaneously traced TGT curves, the amounts of liberated carbon dioxide, sulphur trioxide and sulphur dioxide can be read, and the temperature range in which the liberation of the gases occurred can also be determined (curves 1,3, 2,3, 3,3, 3,4 and 4,3). The results of the TGT examinations are summarized in Table 6. Here, in addition to the amount of 0.1 *N* NaOH titrant consumed for 100 mg of the sample, the found and calculated amounts of CO_2 and SO_3 are given as percentages, as well as the amounts of the components mixed with the bauxite.

Results and discussion

Figures 1 and 4 and the data in Tables 3, 4 and 5 reveal that the method described allows determination of the composition of the sample even in those cases when the simultaneous TG, DTG and DTA method fails due to the total overlapping of the decomposition processes.

The standard deviation of the parallel examinations proved the reproducibility of the measurements.

Comparison of Tables 3, 4 and 5 shows that the magnitudes of the absolute errors in the determination of the accessory and main components are similar, but of course those of the relative errors are not.

The accuracy of the determination of the accessory components remains acceptable even if the result is calculated from the data of several measurements by means of difference calculation (Table 5), despite the fact that the individual errors of the measurements accumulate due to this.

In order to illustrate the principle and practical performance of the method, a few characteristic examples are shown in Figs 2, 5 and 6 and in Table 6.

The principle of the determination of the organic material can be read from curves 1 – 3 in Fig. 5. In the present case the composition of the sample was known, but in the event of an unknown composition we would have reasoned in the following way. According to curve 1 no titrant was consumed up to 1500°, so no SO_3 and SO_2 were liberated. From this we could have drawn the conclusion that the sample did not contain pyrite or sulphate-containing mineral.

Thereafter, we would have stated that the consumed titrant (v_2) indicated by curve 3 was totally caused by the organic material impurities. This could have been supported by curve 2 traced in N_2. With the change of the atmosphere, only the decomposition of organic materials (reaction 2) can be influenced, and not that of carbonate minerals.

The fact that according to curve 2 a small amount of titrant was consumed after all, can be attributed to the circumstance that organic materials occurring in minerals also contain oxygen; upon heating this would depart as CO, but a small amount of CO_2 can also be formed (reaction 2). Our observations indicate that the amount of the latter is not greater than 5 – 10% of the amount of CO_2 formed in an O_2 atmosphere.

Consequently, if curve 2 indicates a CO_2 amount below this limit (10%) it can be neglected, while if the curve indicates a greater amount, then in the given temperature range a carbonate mineral (e.g. siderite) also decomposed. The amount of the latter can be determined by difference calculation performed on the basis of curves 2 and 3 on the analogy of the example of siderite (Table 5).

If we had obtained curves 4 – 6 for a sample of unknown composition, then by similar speculation we could have stated that the sample did not contain either pyrite and sulphate-containing mineral or organic material, but that it contained a carbonate mineral which from its decomposition temperature would be identified as siderite.

As in every thermoanalytical examination, in TGT too the temperature range in which gas formation occurs provides important information regarding the identification of the components. We can distinguish for instance between the decompositions of siderite (curve 5 in Fig. 5) and calcite (curve 1,3 in Fig. 6), or between those of magnesium sulphate (curve 4,3 in Fig. 6) and calcium sulphate (curve 3,4 in Fig. 6).

The shapes of curves 2,1, 2,2 and 2,3 in Fig. 6 prove that in fact secondary reactions may take place between pyrite or sulphate-containing compounds and MgO, CaO, Al_2O_3 and Fe_2O_3. The stage of curve 2,3 at about 500° can only be connected with the oxidation of pyrite. The stage at about 850° indicates not only the decomposition of the intermediate product ($Fe_2O_{3-x}(SO_4)_x$) of pyrite, but (judging from the high decomposition temperature) also that of the secondary $Al_2O_{3-x}(SO_4)_x$. It can be supposed that at about 1100° the decomposition of $MgSO_4$ and $CaSO_4$ took place, these also having been formed secondarily from the interaction between pyrite and the CaO and MgO contaminants of bauxite (Table 2).

In the case of curves 3,1, 3,2 and 3,3 in Fig. 6, the sample contained only a little more $CaCO_3$ than pyrite, as concerns the equivalent amount. Despite this, under the given conditions their reaction was nearly complete.

Secondary reactions undoubtedly interfere and cause many errors. However, with appropriate arrangements they may contribute to the reliability of the detection and accuracy of the determination. For example, if we add a great excess of MgO (10 times the equivalent amount) of the sample, then the course of the TG–DTG curves can be freed from the effects of the oxidation of sulphide minerals and the uncertain decomposition processes of sulphate-containing compounds, and thus their interpretation will be easier and their quantitative evaluation more accurate.

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Zusammenfassung — Autoren entwickelten eine Methode zur simultanen TG, DTG, DTA und EGA zur Bestimmung von Karbonaten, Sulfaten Pyrit und organischem Material in Mineralen. Die Methode basiert auf der selektiven direkten Bestimmung des beim Erhitzen der Probe entwickelten SO_3 bzw. CO_2 und der indirekten Bestimmung von Wasser. Die in Freiheit gesetzten Gase (CO_2, SO_3, SO_2) werden im gastitrimetrischen Adapter des Derivatographen gesammelt, in Wasser absorbiert und kontinuierlich und automatisch mit NaOH titriert. Das Volumen der verbrauchten Titrierflüssigkeit wird in Abhängigkeit von der Temperatur registriert. In zwei Parallelversuchen wird eine Titration bei pH 4, die andere bei pH 9.3 ausgeführt. Die erstere Messung ergibt nur die Menge an SO_3 (SO_2), während bei der letzteren die Gesamtmenge an SO_3 (SO_2) und CO_2 erhalten wird.

Резюме — Разработан совмещенный метод ТГ, ДТГ, ДТА и АВГ (анализ выделяющегося газа) для определения карбоната, сульфата, пирита и органического вещества в минералах. Метод основан на прямом селективном определении SO_3 и CO_2, выделяющихся из нагретого образца, и на косвенном определении воды. Термогазо-титриметрическая приставка к дериватографу позволяет количественно собирать выделяющиеся газы (CO_2, SO_3, SO_2), поглощать их водой и титровать их непрерывно автоматическим методом с помощью едкого натра. Изменения объёма израсходованного титранта регистрируются в зависимости от температуры. Проводится два параллельных титрования: одно титрование проводится при $pH = 4$, а другое — при $pH = 9.3$. Данные первого титрования дают только количество $SO_3(SO_2)$, а второго — совместные количества $SO_3(SO_2)$ и CO_2.