

SIMULTANEOUS TG, DTG, DTA AND EGA EXAMINATION OF ARGILLACEOUS ROCKS. PART I

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The suggested new measuring technique is based on the fact that in the course of the decomposition of clays only three gaseous decomposition products, i.e. SO_3 (SO_2), CO_2 and H_2O are being formed. By thermogastitrimetry the liberation process of the two former products is traced, while by means of a water detector the water released is determined in a selective way. Thus the overlapping processes can be separated. Interpretation and evaluation of the curves can be further improved by performing the examinations in N_2 and O_2 atmospheres respectively, which offers a possibility to conduct the reactions into another direction.

It is well known that thermoanalytical methods in general are of little use for determining the mineral composition of argillaceous rocks. Difficulties in interpretation arise from a variety of causes, for example, the variation in chemical composition and crystalline structure of clay minerals, the relatively small weight and enthalpy changes involved, the presence of other components such as sulphides and organic material which oxidise during heating and the occurrence of secondary reactions between certain components causing unexpected weight and heat effects [1].

The present paper reports on a simultaneous TG, DTG, DTA and EGA measuring technique which enables eighteen individual characteristic curves to be partly simultaneously recorded (Figs 1 and 2). The enormous amount of information in these curves enhances the certainty of identification and the accuracy of the determination.

Experimental

Methods

The recommended thermoanalytical technique deviates from the conventional method. The analysis of argillous rocks can be reduced to the measurement of three gaseous decomposition products, i.e. to the determination of SO_3 (SO_2), CO_2 and H_2O . In the case of argillous rocks no other gaseous decomposition product develops. According to the new method the curves illustrating the process of the formation of SO_3 (SO_2), CO_2 (TGT_{SO_3} , TGT_{CO_2}) and H_2O (WD) resp. are traced by means of a derivatograph coupled with a thermogastitrimetric adapter (TGT) and a water detector (WD), respectively. The measurements are performed partly in a strongly oxidizing oxygen (Fig. 1) partly in an inert, nitrogen (Fig. 2) gas

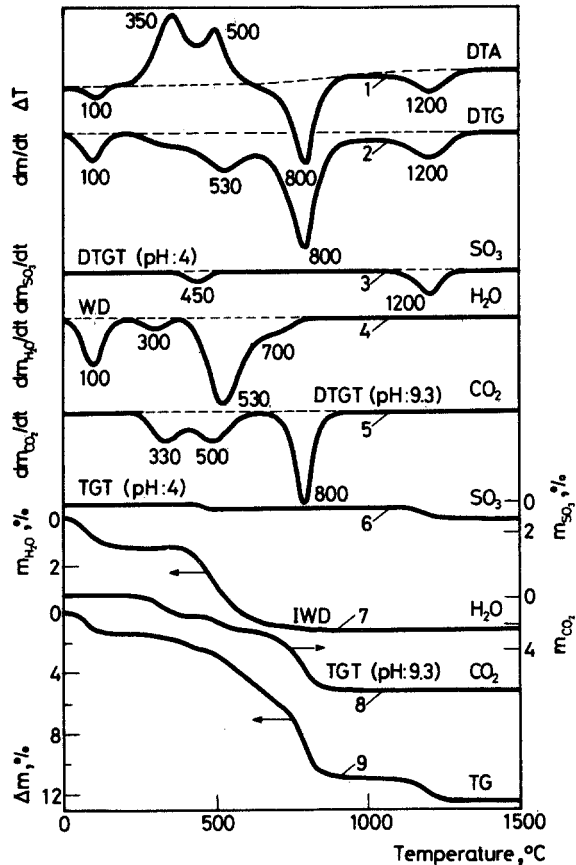


Fig. 1 Simultaneous TG, DTG, DTA and EGA examination of Silurian shale (Zebrač bore-hole) in O_2 atmosphere

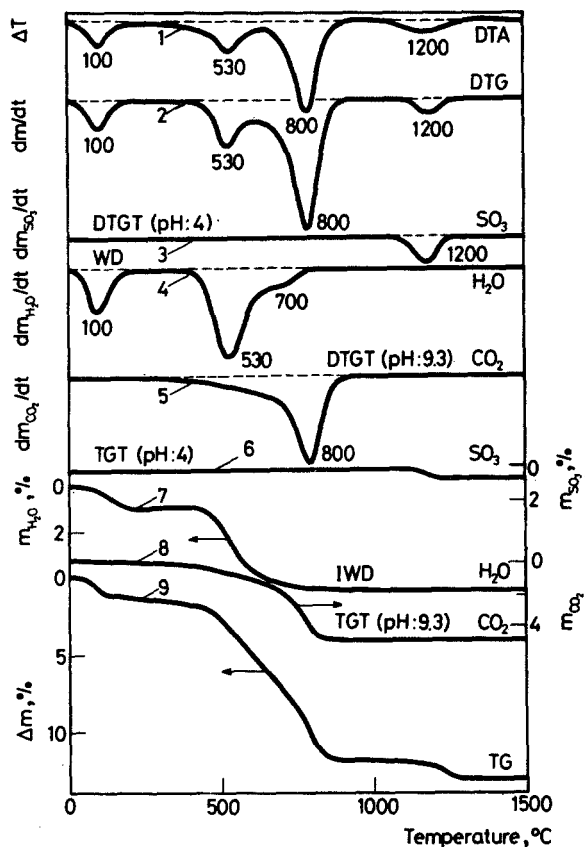


Fig. 2 Simultaneous TG, DTG, DTA and EGA examination of Silurian shale (Zebrač bore-hole) in N_2 atmosphere

atmosphere. Also the derived curves of SO_3 and CO_2 formation ($DTGT_{SO_3}$, $DTGT_{CO_2}$) as well as the integral curve of H_2O (IWD) release are produced. Based on these curves the identification of the mineral components and their determination takes place according to similar principles as in the case of TG and DTG curves. In the present case the TG, DTG and DTA curves were simultaneously recorded to enable the great number of data published in the past decades concerning the composition of argils to be utilized.

An advantage of the method lies in the possibility that the decomposition processes leading to the formation of SO_3 , CO_2 and H_2O can be separated, thus offering a better resolution and significant increase in selectivity in both qualitative and quantitative analyses in contrast to the TG and DTG curves.

TG, DTG, DTA and EGA examinations were performed by a Derivatograph

1500 (produced by the Hungarian Optical Works, Budapest) coupled with a thermogastitrimetric adapter on the one hand, and with the so-called Aquograph water detector on the other. The way of operation of the former [3–5] as well as of the latter [6, 7] has been described earlier in detail.

Materials

A sample of Silurian shale from the deep borehole (1450 m) at Zebrak, Poland was investigated. It represents the “light microlithofacies” of Silurian shales [8, 9]. It consists mainly of clay minerals, a small amount of quartz, feldspars and muscovite, variable amounts of carbonate minerals (calcite, dolomite, siderite), pyrite, sulphate minerals (gypsum, barite, celestine) and traces of organic matter.

Thermal [9], X-ray [9] and chemical [8] analyses (Table 1) have been carried out earlier.

Table 1 Chemical composition of the sample Ž 13 (A. Langier-Kuźniarowa, 1967)

	%, weight		%, weight
SiO ₂	49.34	Na ₂ O	1.66
TiO ₂	0.72	K ₂ O	4.05
Al ₂ O ₃	17.59	H ₂ O (–)	1.75
Fe ₂ O ₃	3.60	CO ₂	4.41
FeO	3.87	S	0.26
CaO	5.03	SO ₃	0.14
MgO	3.68	H ₂ O (+) + C org.	4.62
MnO	0.06		

Experimental results

The results of the examinations of Silurian rock of Zebrak, selected as model substance, are illustrated in Figs 1 and 2 (performed in O₂ and N₂ atmospheres) resp. and summarized in Tables 2, 3 and 4. In Table 2 the amounts of the liberated gaseous decomposition products measured by TG, TGT and WD methods are shown. In Table 3 the components of the sample are given whose amounts were calculated in the way to be described in detail in the next chapter. In order to be able to compare the earlier [9] results (Table 1) obtained by means of conventional analytical methods to those obtained by the methods outlined here, Table 4 was constructed. Here the amounts of the gaseous decomposition products (SO₃, CO₂, H₂O) and the magnitudes of the observed weight changes (Δm) are listed.

In the course of the discussion beside the abbreviations (e.g. TG, IWD, etc.) used so far, further ones are applied in connection with the Figures and Tables. E.g.

Table 2 The amounts of gaseous decomposition products formed in O₂ and N₂ atmospheres (measured by TG, TGT and WD methods)

Temp. interval	20-200°	200-430°	430-800°	430-800°	430-650°	650-1000°	380-520°	500-1000°	1000-1500°	300-1500°	20-1000°	20-1500°
Components	humidity	org. material	illite-chlorite	siderite	calcite	pyrite	metal sulphates	gypsum	total S content	weight loss	TG	TG
Calculation based on curve	WD	WD	WD	TGT	TGT	TGT	TGT	TGT	TGT	TGT	TG	TG
Measured gas products resp. weight change	H ₂ O	H ₂ O	CO ₂	H ₂ O	CO ₂	CO ₂	SO ₃	SO ₃	SO ₃	SO ₃	Δm	Δm
O ₂ I %	1	2	3	4	5	6	7	8	9	10	11	12
N ₂ I %	1.3*	0.2	2.0*	3.5*	0.2	4.2*	0.4	—	0.7	1.1*	11.3	12.3
O ₂ II %	1.2	<0.1	0.2	3.6	0.3*	4.3	<0.1	—	0.5	0.7*	12.4	13.0

* Data upon which the calculation of the composition of the sample (Table 4) is based.

Table 3 Composition of Silurian shale (Zebrak, Poland) calculated of amounts of gaseous decomposition products

		1	2	3	4	5	6	7	8	9
Components		mois- ture	org. mat.	illite	chlorite	sider- ite	calcite	pyrite	iron(III) sulphate	gypsum
I	%	1.3	0.7	42.0	12.3	0.8	9.5	0.3	—	1.2
Calculated of		H ₂ O	CO ₂	H ₂ O	H ₂ O	CO ₂	CO ₂	SO ₃	SO ₃	SO ₃
II	%	1.3	2.0	1.9	1.6	0.3	4.2	0.4	—	0.7

instead of curve 3 in Fig. 2 “F2: 3” or “row I, column 3 of Table 2 “T2, 13” are given.

Discussion

This time the interpretation and evaluation of Figs 1 and 2 deviate from the conventional practice.

Moisture

Water bound by adsorption departed in the 20–200° temperature interval. This was determined on the basis of the WD curves (F1: 4, 7, F2: 4, 7). The numerical results obtained can be seen in Tables 2, 3 and 4 (T2: I.1, T2: II.1, T3: II.1, T4: 8).

Organic material

Most part of the organic material of the sample burned off in O₂ at 200–430 °C, the hydrogen forming water (T2: I.2) and the carbon forming carbon dioxide (T2: I.3). In N₂, CO₂ is also formed but only in a small and negligible amount (T2: II.3).

The liberation of significant heat observed in O₂ atmosphere (350° peak at F1: 1 curve) was missing in N₂ atmosphere. The decomposition of organic material in N₂ atmosphere is endothermic. In the present case this latter heat effect was small and that is the reason why this did not influence the course of the DTA curve (F2: 1). The small effect of the weight change practically did not exert any influence on the TG and DTG curves (F2: 9, 2) either. The small amount of the liberated water and carbon dioxide was effectless upon curves 4, 5, 7, 8 in Fig. 2.

The fact that the course of the thermoanalytical curves changed when the sample was examined in N₂ atmosphere instead of O₂, offers a possibility for the identification of the organic material.

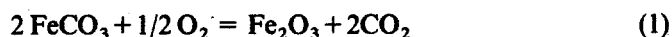
Table 4 The amounts of gaseous decomposition products determined by conventional and thermoanalytical method

		Determined by											
		conventional methods					thermoanalytical method						
H ₂ O (-)	H ₂ O (+)	CO ₂	SO ₃ (S ²⁻)	SO ₃ (SO ₄ ²⁻)	Δm total (20-1000°)	H ₂ O (-)	H ₂ O (+)	CO ₂	SO ₃ (S ²⁻)	SO ₃ (SO ₄ ²⁻)	SO ₃ total (20-1000°)	Δm	Δm
1	2	3	4	5	7	8	9	10	11	12	13	14	15
% 1.8	4.6	4.4	0.8	0.1	0.9	1.3	4.2	4.5	0.4	0.7	1.1	11.3	12.3
							(+ org. mat.)	(CO ₃ ²⁻)	(S ²⁻)	(SO ₄ ²⁻)			

So it could be stated that in O₂ atmosphere the 200–430° section of curves 8 and 5 and the maxima at 350° in curve 1 in Fig. 1 were due to the burning of the organic material. With an approaching accuracy the amount of the organic material was also calculated (T2: I.3, T3: II.2) from the amount of carbon dioxide measured in the presence of O₂. It was supposed that the organic material contained about 80% of carbon. Calculating in this way the organic material was found to be 0.7% (T3: I.2).

Siderite

In O₂ the decomposition of siderite is exothermic.



and in N₂ endothermic:



Both reactions take place at about 500°. It is advisable to calculate the amount of siderite from the amount of CO₂ which is measured in N₂ atmosphere. The burning of the rest of the organic material in O₂ may rise over 430° what cannot happen in N₂. Over 650° the decomposition of dolomite and calcite begins.

In the present case in both O₂ and N₂ atmospheres the amount of CO₂ released was nearly identical (T2: I.5, T2: II.5).

Between 430–650° in N₂ atm. we measured only 0.3 mg CO₂ (T2: II.5, F2: 5.8). From these it follows that if the sample contained siderite at all, it was certainly less than 0.8% (T3: I.5).

Calcite

The sample also contained a significant amount of alkaline earth carbonate minerals as curves 1, 2, 5 and 8 of Figs 1 and 2 prove. The amount of carbon dioxide directly determined by means of the TGT method (T2: I.6, T2: II.6, T4: 10) was 4.2%. This was in good agreement with that obtained on the basis of the weight loss shown between 650–1000° in the TG curves.

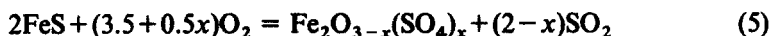
From the course of curves 2, 3 or 5 of both Figs one cannot state whether the sample contained only calcium carbonate (T1: I.6) as it has been supposed in the calculations for the sake of simplicity, or other carbonate minerals e.g. dolomite too. Similarly to calcite the decomposition of a small amount of dolomite is a one-step process and it would also cause only a single peak instead of a double one in the DTA, DTG or DTGT curves, resp.

Sulphur compounds and their reactions

The pyrite often presents first disproportionates at 400–500°

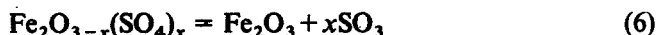


This is an endothermic process. The sulphur immediately burns off (Eq. (4)) and the iron(II) sulphide oxidizes (Eq. (5)) in O₂ atmosphere between 400–500° while a large amount of heat is set free.

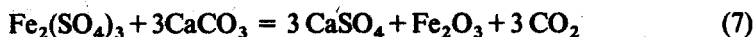


The value of "x", in other words the sulphate content of the iron(III) oxysulphate, depends on the experimental conditions [10].

This oxidation process is indicated in the present case by the step between 400–500° in the TGT curve (F1: 6), the DTGT peak at 450° (F1: 3) and DTA maxima at 500° (F1: 1) in Fig. 1. The whole process is connected only with a small weight change. The iron(III) oxysulphate intermediate decomposes between 700–1000°:



If the sample contains magnesite, dolomite or calcite then these would react (Eq. (7)) with the Fe₂(SO₄)₃ being present originally in the sample or with the Fe₂O_{3-x}(SO₄)_x transitionally formed from pyrite between 600–800° and calcium- or magnesium sulphates would be formed [1].



The CaSO₄ decomposes (Eq. (8)) only above 1000°.



The fact that in the present case the above reactions had taken place, proves that no SO₃ was released simultaneously at about 1200° and in O₂ atmosphere. That means that 1.2% CaSO₄ decomposed in this temperature range. But only one part of this CaSO₄ was present originally in the sample, the other part of it was being formed in secondary reactions (Eq. (7)) taking place between metal sulphates and carbonates. Since MgSO₄, SrSO₄ and BaSO₄ also decompose in the temperature interval between 1000–1500°, their original presence in the shale investigated cannot be excluded. Anyhow, the 1200° peaks of curve 3 in Figs 1 and 2 prove that the main component was CaSO₄.

Total sulphur content

From the above said it follows that only the total sulphur content of the sample (T2: I.10, T4: 13) can be determined with certainty and accurately in measurements carried out in the presence of O₂ and between 300–1500°. The total sulphur content is independent of the condition in what way and temperature interval the oxidation of pyrite takes place and whether secondary reactions, similar to reactions 7, 9 and 10 occur or not.

The error of the determination depends solely on the accuracy of the TGT measurement, which is, even in the case of minute sulphur contents smaller than ± 10% [1]. Accordingly, in the present case we stated that the total sulphur content (T2: I.10, T4: 13) of the sample investigated expressed in SO₃ was 1.1 ± 0.1%. This value is in a satisfactory agreement with the amount of the sulphur determined in the conventional way (T4: 6).

Pyrite

In nitrogen atmosphere the pyrite only disproportionates (Eq. (3)) and theoretically no SO₂ or SO₃ is being formed. This circumstance offers in principle a possibility to state whether the sample investigated contained only sulphate or sulphide too.

However, in general the formation of a small amount of SO₂ cannot be excluded even in the absence of O₂. Mineral substances often contain also components rich in oxygen like Fe₂(SO₄)₃, Fe₂O₃ etc. One part of these compounds may react with metal sulphides and in a small amount also SO₂ may be formed:



According to our earlier experience the error caused by such secondary reactions is usually small as it is also in the present case (T2: II.7).

We calculated the pyrite content of the sample too, but we were aware that this calculation will eventually be only semiquantitative. The amount of pyrite (T3: I.7) was calculated from the difference (T3: 2.7) of the total amounts of sulphur trioxide measured in oxygen (T2: I.10) and in nitrogen atmospheres (T2: II.10) between 300–1500°. We found that the pyrite content of this sample was about 0.3% FeS₂.

Illite and chlorite

The results of earlier X-ray analysis [8] proved that the main components of the sample were illite and chlorite. The 530° peaks in the DTA and DTG curves (F1: 2, F2: 1, 2) and the 530° and 700° peaks in the WD curves (F1: 4, F2: 4) confirmed this

statement. According to the literature the dehydroxylation of illite takes place at about 550°, while that of chlorites, depending on the kind of the cation (Fe, Mg etc.), between 500 and 800°. However, on the basis of the H₂O curves recorded by the WD method (F2: 4, 7) we were able to state with certainty that water departed from the sample in the 430–800° temperature interval. From the curves we could even read the amount of the water (T2: I.4, T2: II.4).

By the fact that we measured nearly the same water amounts, independently of the kind of atmosphere it was proved that the burning of the rest of the organic material did not move over 430°.

The course of curve 4 in Figs 1 and 2 shows that the decomposition of the two clay minerals strongly overlap. Consequently, the absolute amount of the two clay minerals can only be determined if first the ratio of their relative quantity is stated in another way.

One can start e.g. from the course of the WD curve (F1: 4) and from the ratio of the two peak areas (530 and 700°) respectively, as we did it in the present case too. We estimated the percentage ratio of illite: chlorite to be 70:30. Of course we took into consideration that the water amounts released during the decomposition of the two clay minerals strongly differ (see their formulae below).

Although it is well known that the composition of these two clay minerals strongly depends on the conditions of their formation, we supposed that the composition of illite corresponded to the idealized formula $KAl_2[Si_3AlO_{10}](OH)_2$ while that of clinocllore to $Mg_6[Si_3AlO_{10}](OH)_8$. Based on stoichiometric calculations it turned out that the 3.5% water departed between 430–800° (T2: I.4) corresponded to 35% illite (T3: I.3) and 15% chlorite (T3: I.4). It must, however, be emphasized that the above mentioned values are only approximate ones due to a series of suppositions and neglections used in the calculations.

One may approach the reality perhaps better if one starts from the results of X-ray analysis. In this case even the accuracy of the two methods can mutually be controlled.

Conclusion

From the results it follows that the proposed method is suitable for the qualitative and quantitative examination of shales, furthermore in general for that of rocks, ores, minerals and soils.

Although—with regard to the only approximate character of the applied chemical formulae of the mineral components, especially of clay minerals, and to the above mentioned influence of experimental conditions and overlapping thermal effects, the final results are only of semiquantitative character.

References

- 1 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 25 (1982) 327.
- 2 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Investigations by Means of the Derivatograph, in Wilson Wilson's Comprehensive Analytical Chemistry ed. G. Svehla, Vol. XII. adv. ed. W. W. Wendlandt, Elsevier Sci. Publ. Amsterdam, 1981.
- 3 J. Paulik and F. Paulik, Thermochem. Acta, 3 (1971) 13.
- 4 F. Paulik, J. Paulik and M. Arnold, J. Thermal Anal., 29 (1984) 333.
- 5 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 29 (1984) 345.
- 6 J. Kristóf, J. Inczédy, J. Paulik and F. Paulik, J. Thermal Anal., 15 (1979) 151.
- 7 J. Kristóf, J. Inczédy, F. Paulik and J. Paulik, Thermochem. Acta, 56 (1982) 285.
- 8 G. Bárdossy and A. Langier-Kuzniarowa, Report XXII. Sess. Intern. Geol. Congress. India, Calcutta, (1964) Sec. XV, 96.
- 9 A. Langier-Kuzniarowa, Biul. Inst. Geol. Warszawa, 197 (1967) 115.
- 10 F. Paulik, J. Paulik, M. Arnold, J. Thermal Anal., 25 (1982) 313.

Zusammenfassung – Das empfohlene neue Meßverfahren basiert auf der Tatsache, daß im Verlauf der Zersetzung von Tonerde nur drei verschiedene gasförmige Produkte gebildet werden: SO_3 (SO_2), CO_2 und H_2O . Der Prozeß der Freisetzung der beiden ersteren Produkte wird durch Thermogastitrimetrie verfolgt, das freigesetzte Wasser wird selektiv über einen Wasserdetektor bestimmt. Die einander überlagerten Prozesse können somit separat betrachtet werden. Interpretation und Auswertung der Kurven können weiter verbessert werden, indem die Untersuchung auch in Stickstoff- und Sauerstoffatmosphäre durchgeführt wird, was die Möglichkeit darbietet, den Verlauf der Reaktion in eine andere Richtung zu leiten.

Резюме — Предложен новый метод измерения, основанный на том, что в процессе разложения глины образуются только три газообразных продукта разложения, как например, трехокись серы (двуокись серы), двуокись углерода и вода. Первые два продукта определяются с помощью термогазитриметрии, а выделяющаяся вода определяется селективно датчиком воды. Следовательно эти перекрывающиеся процессы могут быть разделены. Интерпретация и оценка кривых может быть улучшена путем проведения экспериментов в атмосфере, соответственно, азота и кислорода, что дает возможность проводить процесс реакций в какое-либо другое направление.