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SIMULTANEOUS TG, DTG, DTA AND EGA EXAMINATION OF ARGILLACEOUS ROCK. Part II.

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With the new technique described in Part I of this paper, the authors investigated five Silurian shale samples and semiquantitatively determined their sulphate, sulphide, carbonate, illite and chlorite contents.

A special examination and evaluation process was recently developed (described in Part I) [1], which afforded new data that could not be obtained by means of conventional thermoanalytical methods. The results of the investigation of five Silurian shales with this technique are presented below.

Experimental

Materials

Five Silurian shale samples were used for the investigations (see Table 1). These samples are graptolite shales from deep bore-holes located on the Polish Lowland and have already been examined [2, 3] by X-ray, chemical (Table 2), microscopic and conventional thermal methods (DTA, TG, DTG).

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Table 1 List of samples investigated

Bore-hole	No. of sample	Depth, m	Type of shale
Lebork	L 11	3167.5	black shale, rich in organic matter
	L 150	1920.5	dark microlithofacies, rich in carbonate minerals
Mielnik	M 40	1104.3	light microfacies, but rich in pyrite and organic matter
	M 82	918.8	dark microlithofacies
Kaplonosy	K 37	548.0	grey-bluish shale, rich in carbonate minerals, detrital quartz of silty fraction, pyrite and organic matter

Except for sample K37, the samples used for the experiments represented two typical microlithofacies of Silurian shales: the light and dark ones [2]. The light microfacies was characterized in the first part of this paper. The shales of the dark microlithofacies are brown-black to black in colour and have a rough fracture because of the pyrite and organic matter content.

Sample K37 from the Kaplonosy bore-hole differs from those described above. This rock is slightly diagenized.

Experimental results

The thermoanalytical curves of the five samples in oxygen and nitrogen atmospheres are shown in the Figures. The results of the quantitative analyses are given in Tables 3-5.

The amounts of liberated gaseous decomposition products, measured by TG, thermogastitrimetry (TGT) and water detector (WD) methods, are shown in Table 3. Table 4 gives the components of the samples, the amounts of which were calculated in the manner described in the first part of this paper. In order to be able to compare the present results with those obtained earlier by conventional analytical methods [2] (Table 2). Table 5 was constructed. This lists the amounts of the gaseous decomposition products formed (H_2O, CO_2 and SO_3) and the observed weight changes (Δm).

Table 2 Percentage chemical compositions of samples

Component	Sample				
	L 11	L 150	M 40	M 82	K 37
1	2	3	4	5	6
SiO_2	56.81	51.69	52.18	46.22	46.54
TiO_2	0.63	0.61	0.53	0.72	0.76
Al_2O_3	12.37	15.49	16.47	12.68	13.20
Fe_2O_3	3.15	3.68	2.96	2.78	2.26
FeO	3.33	2.59	2.53	2.73	2.86
CaO	5.83	5.67	5.53	10.11	11.83
MgO	3.95	3.45	3.36	4.57	4.05
MnO	0.06	0.09	0.03	0.06	0.05
Na_2O	1.30	1.62	1.52	0.64	0.70
K_2O	2.99	3.28	4.53	3.33	3.52
$H_2O(-)$	0.30	0.86	1.04	0.81	0.83
CO_2	4.52	5.70	5.66	9.38	9.44
S	1.81	1.17	0.63	-	1.49
SO_3	0.41	1.40	0.14	0.90	0.49
P_2O_5	0.09	0.09	-	0.06	0.10
$H_2O(+)$ + C org.	3.57	2.66	3.85	5.33	2.74

As abbreviations in the discussion instead of "curve 3 in Figs 1, 3, 5, 7" for example we use "F 1, 3, 5, 7:3". Similarly, row I, column 3 of Table 3 is designated by "T3:I.3".

Discussion

Moisture

The moisture contents of the samples were calculated from the 20-200° sections of the WD (water detection) and IWD (integral water detection) curves (F1-10:4,7, T3:I.1, T3:II.1). Practically the same values were obtained from the corresponding parts of the TG curves (F 1:2, 9).

Organic matter

The presence of organic matter was concluded from the fact that, due to its burning in oxygen atmosphere, a significant amount of heat was released in the range 200-500o (F 1, 3, 5, 7, 9:1). In the burning process, carbon dioxide was formed among others (F 1, 3, 5, 7, 9:5.8). In nitrogen atmosphere, however, there was no heat liberation (F 2, 4, 6, 8, 10:1) and carbon dioxide was not detected (F 2, 4, 6, 8, 10:5.8).

Table 3 Percentage amounts of gaseous decomposition products formed in O_2 and N_2 atmospheres, measured with a derivatograph combined with thermogastitrimetric equipment and a water detector

Temp. interval	20-200°C	200-450°C	200-500°C	450--770°C	500-640°C	650-1000°C	400-500°C	300-1500°C	20-1000°C	20-1500°C
Component	Moisture	Org. mat.		Illite-chlorite	Siderite	Calcite	Pyrite	Total S	Weight loss	
Curve calc. based on	WD	WD	TGT	WD	TGT	TGT	TGT	TGT	TG	TG
Measured gas product	H_2O	H_2O	CO_2	H_2O	CO_2	CO_2	SO_3	SO_3	Δm	$\Delta m'$
	1	2	3	4	5	6	7	8	9	10
Lebork I O_2	0.8	0.3	4.5	3.0	0.1	4.8	1.4	4.2	9.1	11.5
L 11 II N_2	0.7	0.1	0.1	3.1	0.1	5.2	0.1	2.2	9.9	12.1
Lebork I O_2	0.1	0.3	3.8	2.8	1.2	6.2	0.8	3.3	11.5	14.2
L 150 II N_2	0.8	0.1	0.1	2.5	1.3	6.4	0.1	2.0	12.4	14.8
Mielnik I O_2	1.3	0.7	1.2	2.6	0.8	5.4	0.5	2.8	10.5	13.0
M 40 II N_2	1.4	0.1	0.3	2.5	1.0	5.7	0.1	1.6	11.0	12.5
Mielnik I O_2	0.5	0.6	3.4	2.5	2.4	8.0	0.1	1.6	13.8	15.4
M 82 II N_2	0.8	0.1	0.1	2.4	2.2	7.8	0.1	1.4	14.7	16.2
Kaplonosy I O_2	1.0	0.8	4.0	1.7	1.0	9.0	0.5	3.6	14.8	17.8
K 37 II N_2	1.3	0.1	0.2	1.8	1.0	8.8	0.1	2.4	15.5	18.1

The carbon content of the bitumen-like organic matter was estimated as 80%, which, in oxygen atmosphere, can be converted quantitatively to carbon dioxide (T 3:I.3, T 4:2b). Thus, the organic matter contents of the samples could be calculated (T 4:2a). Water was also formed in the burning decomposition of the organic matter (T 3:I,II.2). Since the formation of water is not characteristic of the process, neither qualitative nor quantitative conclusions could be drawn. It should be noted, however, that experience shows the burning of the organic matter and the oxidation of the pyrite to take place in nearly the same temperature range. Thus, in the present case the DTA curves (F 1, 3, 5, 7, 9:1) are difficult to interpret, since they are the resultants of two different exothermic effects.

Table 4 Composition of Silurian shales, calculated from amounts of gaseous decomposition products, %

Components	Moisture	Org. mat.	Illite	Chlorite	Siderite	Calcite	Pyrite	Gypsum
Calculated from	H_2O	CO_2	H_2O	H_2O	CO_2	CO_2	SO_3	SO_3
	1	2	3	4	5	6	7	8
				%				
Lebork a	0.8	1.5	55.3	3.6	0.2	11.4	1.5	3.7
L 11 b	0.8	4.5	2.5	0.6	0.1	5.0	2.0	2.2
Lebork a	0.9	1.3	44.3	3.0	3.4	14.3	1.0	3.4
L 150 b	0.9	3.8	2.0	0.5	1.3	6.3	1.3	2.0
Mielnik a	1. 3	0.4	50.9	1.2	2.6	12.7	0.9	2.7
M 40 b	1. 3	1.2	2.3	0.2	1.0	5.6	1.2	1.6
Mielnik a	0.7	1. 2	50.9	0.6	5.7	18.0	0.2	2.4
M 82 b	0.7	3.4	2.3	0.1	2.2	7.9	0.2	1.4
Kaplonosy a	1.2	1.4	37.6	0.6	2.6	20.2	0.9	4.1
K 37 b	1.2	4.0	1.7	0.1	1.0	8.9	1.2	2.4

Siderite

Siderite is likely to occur in the sample, if carbon dioxide is formed in the range 500-650° in nitrogen atmosphere. The presence of siderite could be established in the samples (F 2, 4, 6, 8, 10:5.8), and the amount of carbon dioxide (T 3:II.5, T 4:5b) permitted calculation of the siderite contents of the samples (T 4:5a). It should be noted that in oxygen atmosphere the amount of carbon dioxide is less characteristic of the siderite content of the sample, since under unfavourable conditions the burning of the organic matter may shift even over 500°.

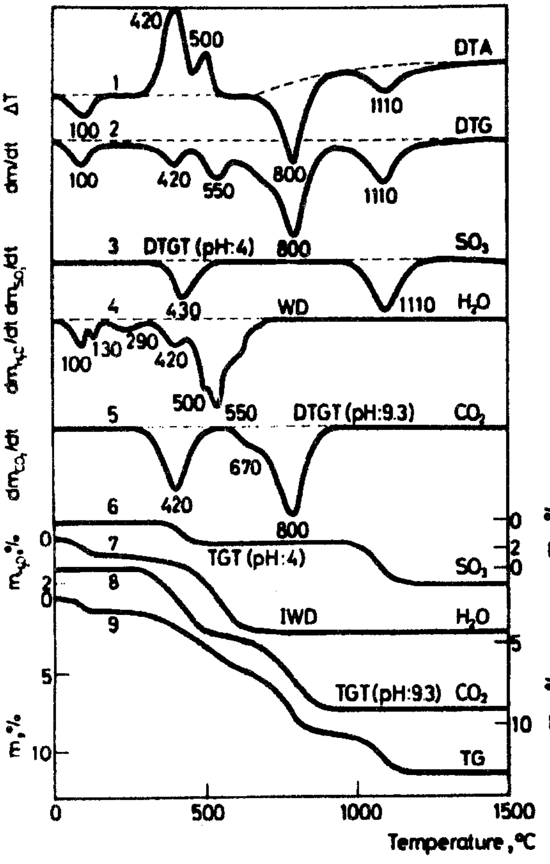

Fig. 1 Thermoanalytical curves of sample L 11 in O_2 atmosphere

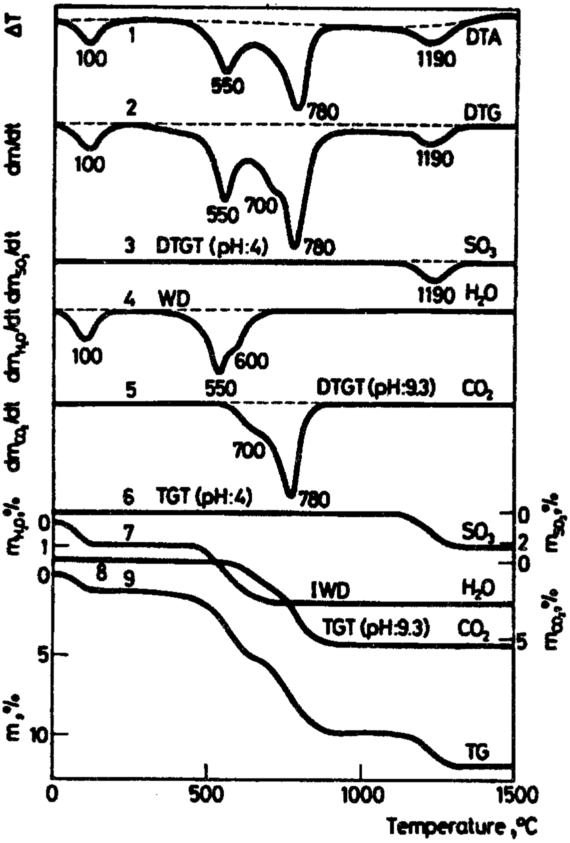

Fig 2 Thermoanalytical curves of sample L 11 in N_2 atmosphere

Calcite - dolomite -ankerite

The decomposition of calcite-dolomite-ankerite takes place in the temperature range 600-1000°. According to the DTA, DTG and DTGT curves (F 1-10:1,2,5), samples L11, L150 and M40 contained dolomite and possibly ankerite, while in samples M82 and K37 calcite predominated. However, it was not possible to determine the extent of substitution of Ca^{2+} by Mg^{2+} and Fe^{2+} in the carbonates in question. For the sake of simplicity, the amount of carbon dioxide evolved (T3:I,II,6; T4:6b) was converted to calcite (T4:6a). Since no other component of the sample underwent decomposition in this temperature range, the amount of calcite could also be determined with fairly high precision from the TG curves (F 1-10:9).

Table 5a Amounts of gaseous decomposition products, determined by conventional and thermoanalytical methods

Sample	Determined by conventional method						
	H_2O (-)	H_2O (+) (+org. mat.)	CO_2 (CO_3^{2-})	SO_3 (S^{2-})	SO_3 (SO_4^{2-})	SO_3 total	Δm 20-1000 °C
	1	2	3	4 %	5	6	7
Lebork L 11	0.3	3.6	4.5	4.5	0.4	4.9	13.0
Lebork L 150	0.9	2.7	5.7	3.0	1.4	4.4	12.8
Mielnik M 40	1.0	3.9	5.7	1.5	0.1	1.6	11.2
Mielnik M 82	0.8	5.3	9.4	-	0.9	0.9	15.6
Kaplonosy K 37	0.8	2.7	9.4	3.8	0.5	4.3	16.9

Total sulphur content

The various side-reactions that occur (see Part I of the paper [1]) mean that a reliable and accurate quantitative determination of sulphur by this method is possible only for the total sulphur content only. The total sulphur content is the sum of sulphur bound in the form of sulphides and sulphates (T3:I.8, T5:1.3). The total sulphur content can be obtained by the determination of SO_3 or SO_2 released in the range 300-1500° by means of the TGT method.

Pyrite

In nitrogen atmosphere, pyrite undergoes disprortionation upon heating. Theoretically, this process takes place without SO_2 or SO_3 formation. Therefore, the amount of pyrite in the samples (T4:7a; T4:7b) can be obtained via the difference between the total sulphur (T3: I.8; T5:1.3) measured in oxygen atmosphere and the sulphur bound in the form of sulphates originally present in the samples (T3:II.8; T5:1.2) measured in a nitrogen atmosphere.

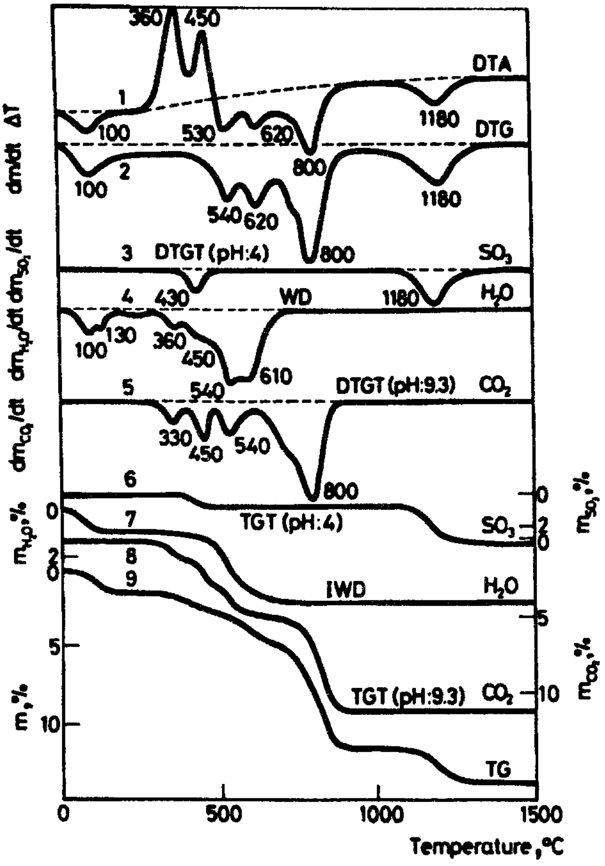

Fig. 3 Thermoanalytical curves of sample L 150 in O_2 atmosphere

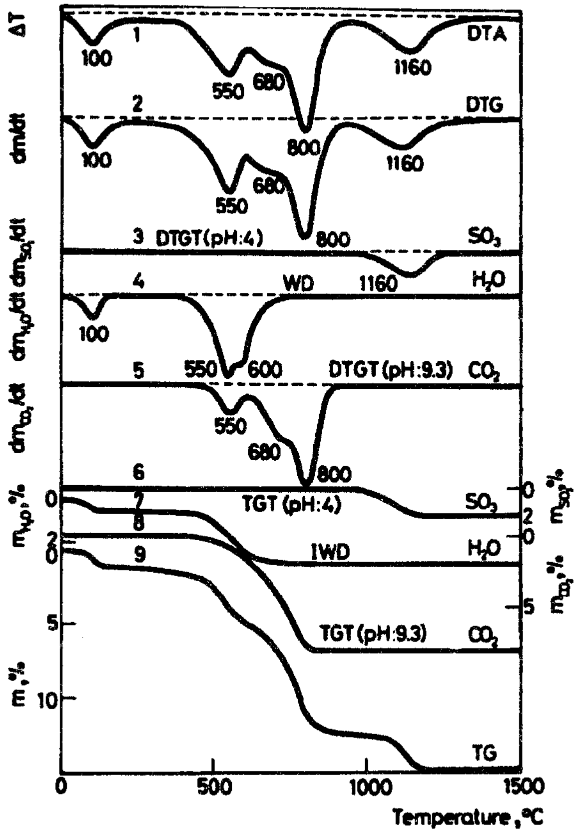

Fig. 4 Thermoanalytical curves of sample L 150 in N_2 atmosphere

Sulphur bound in metal sulphates

The samples usually contain metal sulphates as well. The presence of iron(II) and iron(III) sulphates is most probable. The latter decomposes between 500° and 1000°. The TGT curves (F 1-10:3.6), however, revealed SO_3 formation at around 1200° only. This phenomenon can be explained as follows [4]. If the sample contains alkaline earth metal carbonates (e.g. $CaCO_3$) as well, then at the temperature of their dissociation they react with the metal sulphates to produce alkaline earth metal sulphates (e.g. $CaSO_4$) as a result of an exchange reaction. The metal sulphates thus formed decompose only in the range 1000-1500°. Therefore, it is reasonable to presume that only a portion of the $CaSO_4$ (T4:8a) was present in the sample originally; the major part of it was formed in secondary reactions from iron(II) and iron(III) sulphates during the investigation (T4:8a).

Thus, the amount of SO_3 formed in nitrogen atmosphere in the range 300-1500° (T4:8b; T5:12) is directly proportional to the sulphur content of the sample bound in the form of sulphates.

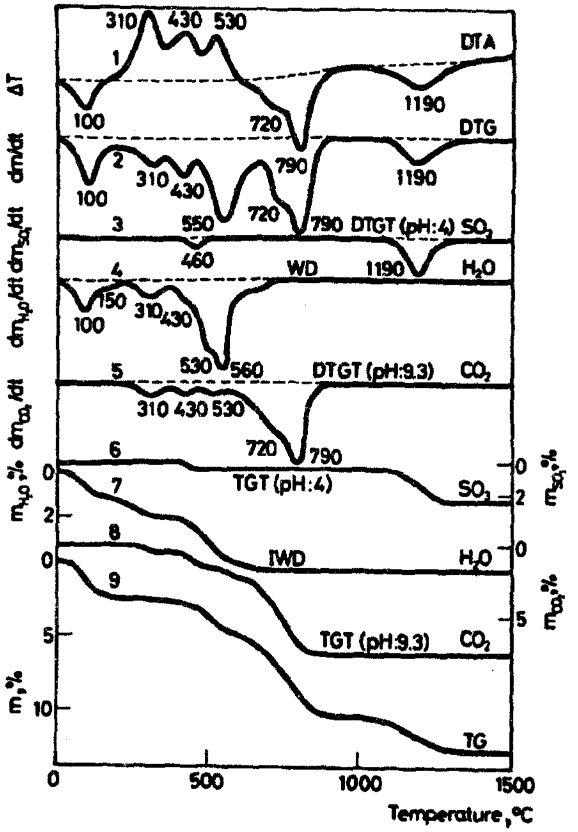

Fig. 5 Thermoanalytical curves of sample M 40 in O_2 atmosphere

Illite, chlorite

X-ray investigations have shown that the main components of the samples are illite and clinochlore. This is supported by the WD curves (F 2, 4, 6, 8, 10:4). According to the literature, the dehydroxylation of illite takes place at about 550°, while clinochlore decomposes at a higher temperature (600-720°), depending on the amount and nature of cations included in its structure.

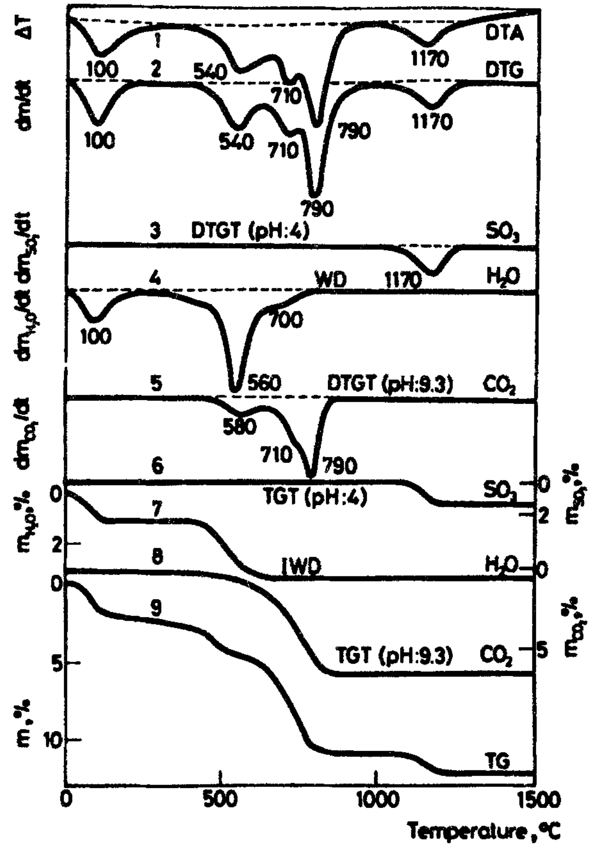

Fig. 6 Thermoanalytical curves of sample M 40 in N2 atmosphere

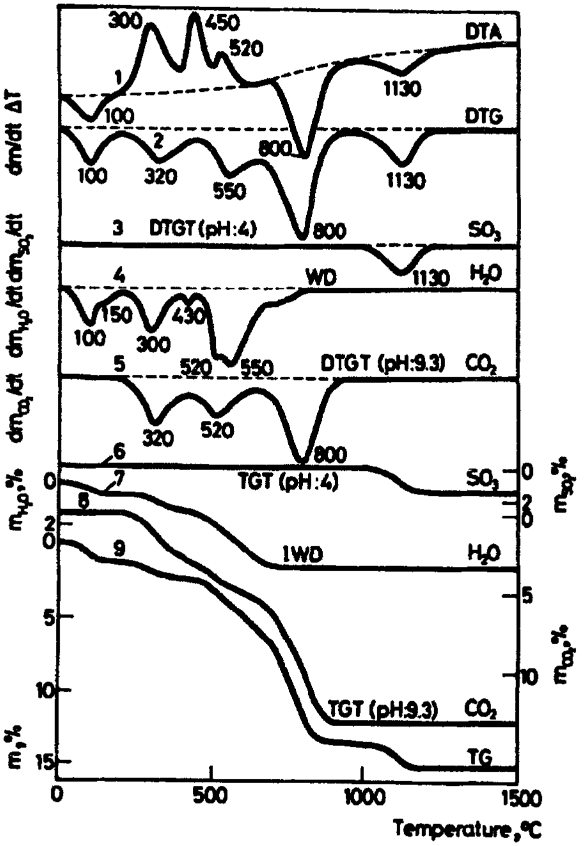

Fig. 7 Thermoanalytical curves of sample M 82 in O_2 atmosphere

As for the quantitative determination of illite and chlorite, some assumptions were made. Therefore, the corresponding data in Table 4 (T4:3a; T4:4a) can be considered only as semiquantitative ones.

For instance, illite and clinochlore were presumed to have ideal compositions (illite: $KAl_2[Si_3AlO_{10}](OH)_2$; clinochlore: $Mg_6[Si_3AlO_{10}](OH)_8$. On the other hand, the dehydroxylation curves of the two minerals closely overlapped. In spite of the fact that the total amount of water released in the overlapping dehydroxylation processes could be measured directly by the water detector with fairly high precision, the amounts of water released from the individual components could only be estimated. On the basis of the

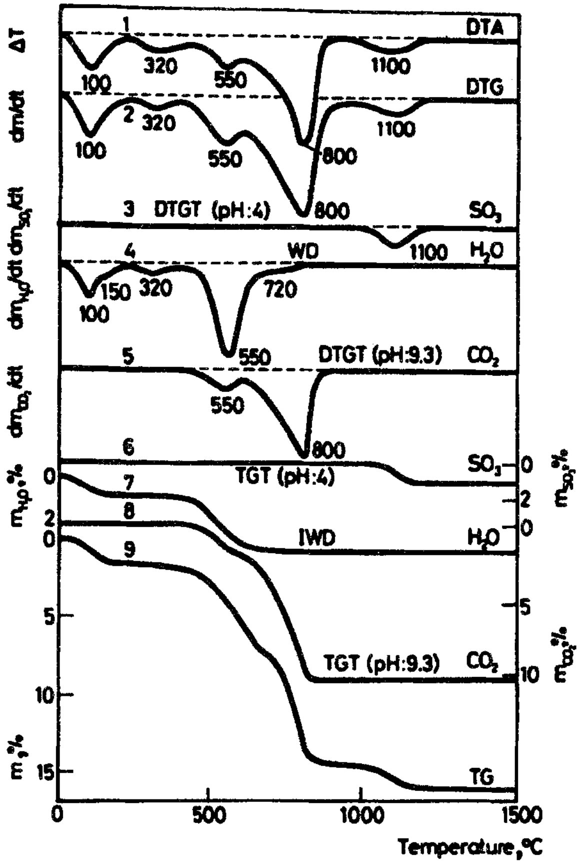

Fig. 8 Thermoanalytical curves of sample M 82 in N2 atmosphere

WD curves, the percentage distribution of structural water between illite and chlorite for samples L11, L150, M40, M82 and K37 was estimated as 80-20, 80-20, 90-10, 95-5 and 95-5, respectively. The error in the estimation was further increased by the fact that (according to the stoichiometry) the amount of water released from chlorite was four times higher than that from illite.

Since the burning of the organic matter may not be completed until 400°, the WD curves recorded in nitrogen atmosphere were used for the quantitative determination of structural water (T3:II.4; T4:3b; T4:4b).

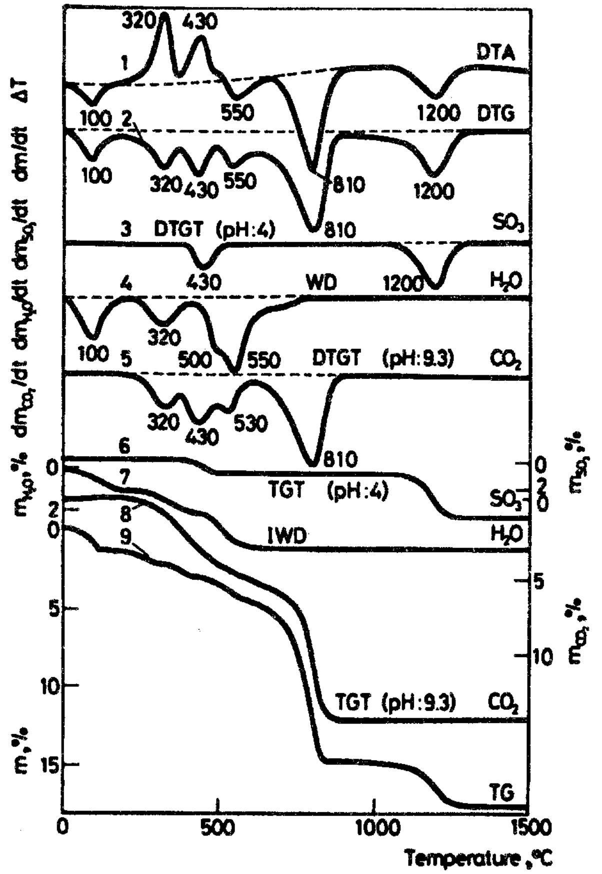

Fig. 9 Thermoanalytical curves of sample K 37 in O_2 atmosphere

Conclusions

The results presented above show that this combined method is suitable for the determination of the sulphate, sulphide, carbonate, illite and chlorite contents of rocks. Nevertheless, there are limits in the accuracy and the results may be treated only as semiquantitative ones.

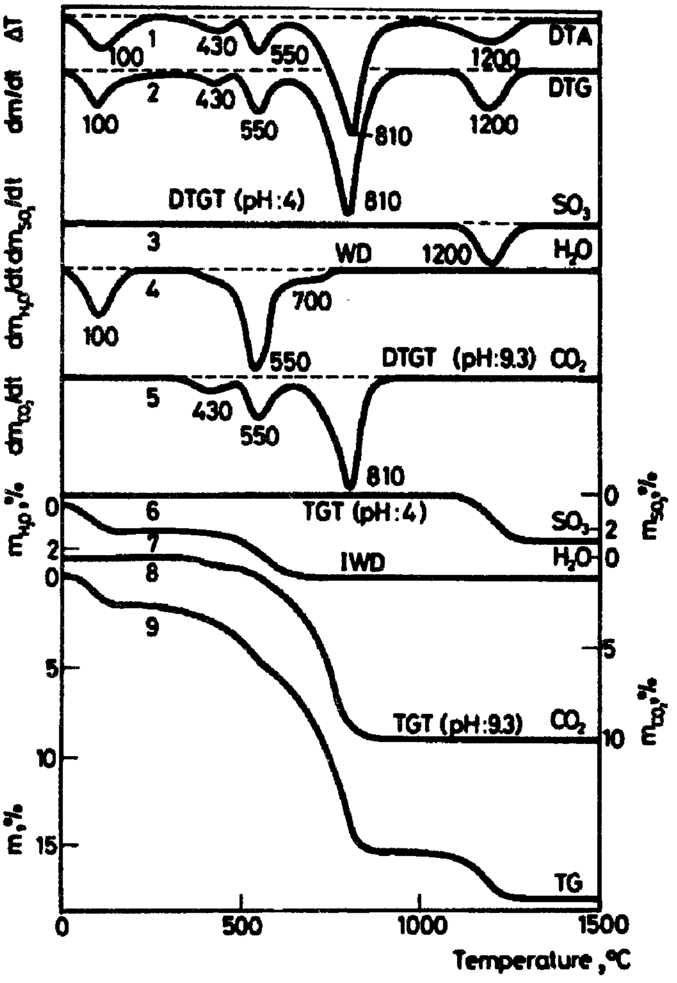

Fig. 10 Thermoanalytical curves of sample K 37 in N_2 atmosphere

Table 5b Amounts of gaseous decomposition products, determined by conventional and thermoanalytical methods

Sample	Determined by thermoanalytical methods						
	H_2O (-)	H_2O (+) (org. mat.)	CO_2 (CO_3^{2-})	SO_3 (S^{2-})	SO_3 (SO_4^{2-})	SO_3 total	Δm 20-1000 °C
	8	9	10	11	12	13	14
				%			
Lebork L11	0.8	2.3	5.3	2.0	2.2	4.2	9.1
Lebork L 150	0.9	2.2	7.7	1.3	2.0	3.3	11.5
Mielnik M 40	1.3	1.7	6.7	1.2	1.6	2.8	10.5
Mielnik M 82	0.7	1.9	10.0	0.2	1.4	1.6	13.8
Kaplonosy K37	1.2	2.6	9.8	1.2	2.4	3.6	14.8

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4 J.Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 25 (1982) 327.

Zusammenfassung - Mittels der in Teil I beschriebenen Methoden wurden fünf Silurschiefer untersucht und deren Sulfat-, Sulfid-, Karbonat-, Illit- und Chloritgehalt halbquantitativ ermittelt.