

# **DETERMINATION OF THE ORGANIC MATTER, METAL CARBONATE AND MOBILE WATER IN SOILS**

## **Simultaneous TG, DTG, DTA and EGA techniques**

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### **Abstract**

It has been shown that computerized derivatographic method with EGA technique can be applied to determine contents of organic matter and carbonates in soil samples with satisfactory accuracy and reproducibility of the results. The method enables simultaneous determination of the 'mobile' and 'bound' water in the sample.

**Keywords:** soils, TG-DTG-DTA-EGA

### **Introduction**

A correlation exists between the fertility and organics and water content and mineral constitution of soils. The correlation is, however, very complicated and not completely cleared up. Hence all experimental data which contribute to the clearing up and characterization of this correlation are useful for the specialist.

In the present work three soil samples of different composition were studied by the simultaneous TG, DTG, DTA and EGA technique known for a decade [1-5]. The weight of samples (TG curve), rate of weight change (DTG curve), difference of the temperature of the sample from that of a reference material due to enthalpy changes in the sample (DTA curve) were followed as function of the temperature using the Derivatograph [1, 6, 7], and the amount of carbon dioxide evolved was measured by continuous titration [3] (TGT curve). The results enabled conclusions to be drawn concerning the organics and alkaline earth carbonate content and 'mobile' and 'bound' water in the samples.

Table 1 Results of measurements with Derivatograph C (five repetitions)

Sample	Repetition	TG curve weight loss $\Delta m / \%$				TGT curve measured CO <sub>2</sub> $\Delta m_{CO_2} / \%$			
		20-250°C	250-650°C	650-950°C	20-950°C	250-650°C	650-950°C	250-950°C	250-950°C
ED	1	2.8	4.9	4.8	12.6	5.8	3.7	9.5	
	2	2.8	4.9	4.8	12.5	4.9	4.8	9.7	
	3	2.9	5.1	4.7	12.7	5.0	4.2	9.2	
	4	3.1	5.2	4.8	13.1	5.7	4.2	9.9	
	5	2.9	5.1	4.8	12.8	5.5	4.1	9.6	
ID	Mean	2.9	5.0	4.8	12.7	5.4	4.2	9.6	
	1	2.9	5.3	2.0	10.3	6.7	1.7	8.4	
	2	3.1	5.0	2.0	10.1	6.6	1.8	8.4	
	3	3.0	5.3	2.1	10.4	6.5	2.0	8.5	
	4	3.4	5.4	2.2	10.9	6.3	1.6	7.9	
DV	5	3.3	5.5	2.2	11.1	6.0	1.5	7.5	
	Mean	3.1	5.3	2.1	10.5	6.4	1.7	8.1	
	1	3.2	5.1	2.3	10.6	6.9	2.4	9.3	
	2	2.7	4.6	2.8	10.1	6.9	3.2	10.1	
	3	3.2	5.4	2.8	11.4	6.3	2.4	8.7	
DV	4	2.8	5.0	2.7	10.5	7.1	2.8	9.9	
	5	3.3	5.5	2.8	11.6	6.6	2.5	9.1	
	Mean	3.0	5.1	2.7	10.8	6.8	2.7	9.5	

## Experimental

Parcels of land were used on the Roman Earthworks (Rimski Sancevi) near Novi Sad for scientific experiments some decades ago. The three soil samples, ED, ID and DV come from the area.

Sample ED was taken from a parcel with extensive fertilization, i.e. no fertilizer was applied but the stubble was ploughed in. In a twoyears crop rotation corn and wheat followed each other.

Sample ID was from a parcel intensively fertilized with manure and chemical fertilizer. In a two years crop rotation corn and wheat followed each other.

Sample DV was from a parcel intensively fertilized with manure and chemical fertilizer. Twelve different plants followed each other in a 12-year crop rotation.

Sampling was carried out in the usual way [8], the average sample was taken from a depth of 30 cm.

For comparison, the organic matter and metal carbonate were determined by traditional methods.

The organic matter was determined according to Kotzmann [8–9] with potassium permanganate. The sample was oxidized of 100°C in acid solution with excess potassium permanganate. The oxidation of carbon to carbon dioxide was complete in 10 min. The excess reagent was then back-titrated with oxalic acid. However, the composition of the organic matter is never known. By convention [10], the carbon content is multiplied by a factor of 1.72 to get the organic content. Alternatively, the organic matter can be determined in soils using Tyurin's method [10], by boiling the sample in the presence of sulphuric acid and silver sulphate as catalyst with excess potassium dichromate solution. The excess is back-titrated with iron(II) ammonium sulphate standard solution in the presence of ferroin as indicator. The data in Table 2 were determined by this method.

In addition, Knop's method [8] is also known which is based on the oxidation with chromic acid and gravimetric determination of the carbon dioxide liberated, as well as the technique based on the determination of the ignition loss [8].

The calcium carbonate is traditionally determined in soils by the method of Scheibler [9, 11] or Winkler [8]. In Scheibler's method the sample and hydrochloric acid are placed separately in a two compartment vessel into the calcimeter. The calcimeter is closed, the acid is mixed with the soil sample. The amount of calcium carbonate is calculated from the volume of the liberated carbon dioxide measured in a gas burette. Winkler's method is more accurate but more complicated. It is based on the measurement of the weight of the carbon dioxide liberated after absorption on solid sodium hydroxide or in potassium hydroxide solution. The liberation of carbon dioxide from the carboxyl groups

possibly present is prevented. The soil samples were analyzed by both methods and the results are given in Table 2.

**Table 2** Average results for water content, organic matter and carbonates in dependence of the determination method

Sample	Method	Interval of TA curve	H <sub>2</sub> O		CO <sub>2</sub>	Organic	CO <sub>2</sub>	CaCO <sub>3</sub>
			Mobile	Total	material			
			20–250°C	20–950°C	250–650°C		650–950°C	
%								
ED	TG		–	–	–	–	4.8	10.9
	TGT		–	–	5.4	2.5	4.2	9.6
	H <sub>2</sub> O		2.9	6.0	–	–	–	–
	Kotzman		–	–	3.6	1.7	–	–
	Tjurin		–	–	4.9	2.3	–	–
	Scheibler		–	–	–	–	3.7	8.5
	Winkler		–	–	–	–	4.0	9.2
ID	TG		–	–	–	–	2.1	4.8
	TGT		–	–	6.4	3.0	1.7	3.9
	H <sub>2</sub> O		3.1	5.8	–	–	–	–
	Kotzman		–	–	5.1	2.4	–	–
	Tjurin		–	–	6.0	2.8	–	–
	Scheibler		–	–	–	–	1.9	4.4
	Winkler		–	–	–	–	1.8	4.1
DV	TG		–	–	–	–	2.7	6.1
	TGT		–	–	6.8	2.8	2.7	6.1
	H <sub>2</sub> O		3.0	5.1	–	–	–	–
	Kotzman		–	–	6.4	3.0	–	–
	Tjurin		–	–	6.4	3.0	–	–
	Scheibler		–	–	–	–	2.6	5.8
	Winkler		–	–	–	–	2.4	5.5

Simultaneous TG, DTG, DTA and TGT measurements [1,6, 7] were carried out using a Derivatograph C type instrument [12, 13] equipped with a computer, in oxygen (Figs 1 and 2) and nitrogen atmosphere (Fig. 3).

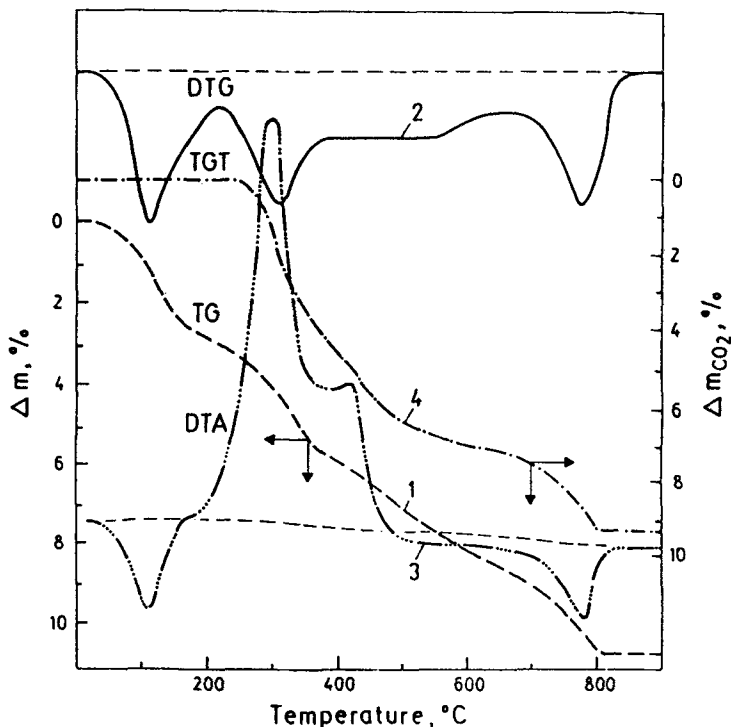


Fig. 1 Thermoanalytical curves of DV soil sample in oxygen atmosphere

As the curves were very similar for all the three samples studied, only the curves obtained for sample DV are presented. Thermo-gas titrimetric (TGT) measurements were carried out as described earlier [3]. The sample weight was about 200 mg, rate of heating 5 deg·min<sup>-1</sup>. Five parallel measurements were made in each case. The results are presented in Table 1.

## Discussion

The thermal decomposition of the soil samples studied proceeded in three steps.

Between 20 and 250°C the mobile water was released in a reversible process. The amount of this water was determined by projecting the minimum of the DTG curve (at 250°C) onto the TG curve and reading the weight loss from the TG curve (Table 1). As shown by the TG and DTG curves, this 'mobile' water cannot be determined by drying at 110°C, as believed earlier, since only part of this water is released up to 110°C. On drying at a higher temperature for a long time there is a danger of further water loss (curve 3 in Fig. 2), or decomposi-

tion of the organic matter (curves 2 and 3 of Fig. 1 and curves 3 and 4 of Fig. 2).

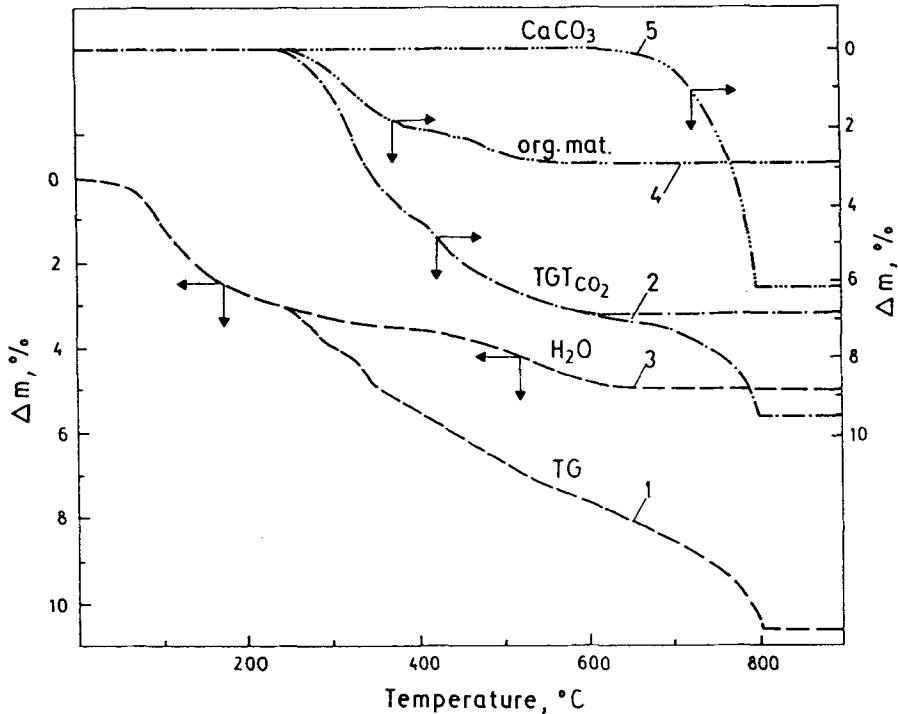


Fig. 2 Computer-resolved decomposition curve of DV soil sample in oxygen atmosphere

The fact that water release takes place in a wide temperature range indicates that the mobile water is bound in the soil by different forces, in different ways.

Certainly part of the water is bound to the surface of the particles by adsorption. This water was found to be released between 20 and 100°C, at maximum rate at 80°C. Hence, it can be assumed that the components of the sample which have a gel structure (e.g. organic compounds) bind a significant amount of water by colloid chemical forces.

It seems to be probable that lamellar clay minerals are responsible for the dragging out of the water release, as they can bind water between their layers. These clay minerals (illite, montmorillonite, nontronite, vermiculite) lose most of the interlayer water up to 250°C, a small portion up to 350°C (Fig. 4). Hence, the water binding capacity of soils can be characterized by the amount of water released up to 250°C.

Between 250 and 650°C a number of different processes take place. In oxygen atmosphere the organic water is oxidized. This process is indicated by a large exothermal peak at 400°C on the DTA curve (curve 3) in Fig. 1.

For comparison, the curve taken in nitrogen atmosphere is also shown (Fig. 3).

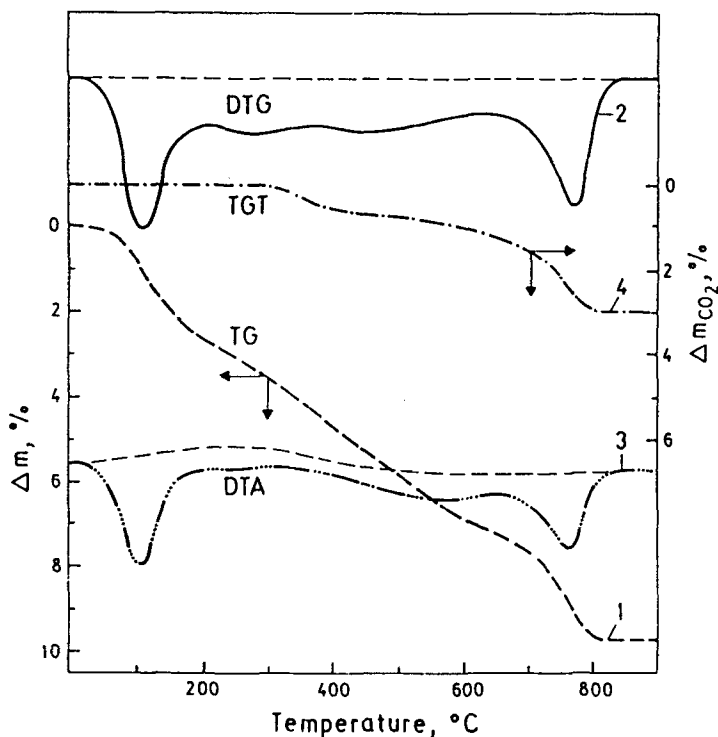


Fig. 3 Thermoanalytical curves of DV soil sample in nitrogen atmosphere

In the presence of oxygen the organic matter is burnt practically completely, the carbon content yielding carbon dioxide, the hydrogen content water. Carbon, gaseous hydrocarbons ( $\text{CH}_4$ ,  $\text{CH}_2=\text{CH}_2$ , etc.) and tar are produced only in trace amounts. This allows the organic content to be determined from the amount of carbon dioxide taken from the TGT curve between 250 and 650°C (Fig. 2, Table 2). It has been observed earlier that the organic compounds in the soil have a composition which enables the organic matter to be represented by the carbon content multiplied by a factor of 1.72. The organic matter in the soils studied was determined this way (see curve 4 in Fig. 2 and column 'org. mat' in Table 2).

Clay minerals are decomposed between 250 and 650°C. Kukin [14] investigated chernozem type soils from the region of Backa by X-ray diffraction tech-

nique and found illite to occur most often (30–70%), montmorillonite being the second (30–50%). Calcite occurs in amounts between 5 and 10%, vermiculite, chlorite and kaolinite between 5 and 20%. Quartz and feldspat play only a minor role. The decomposition of these minerals is represented by the DTG curves in Fig. 4.

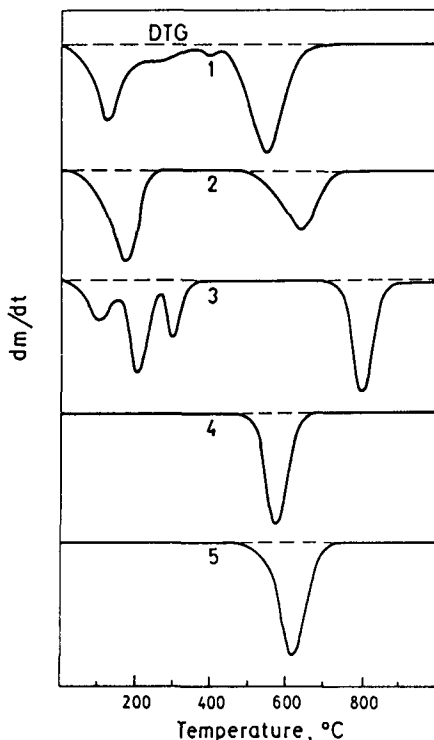


Fig. 4 DTG curves of some clay minerals present in the soil samples. 1. illite, 2. montmorillonite, 3. vermiculite, 4. kaolinite, 5. chlorite

The presence of these minerals is not indicated by the TG, DTG or DTA curves in Figs 1 and 2, since all processes are covered up by the oxidation of organic matter, accompanied by a remarkable heat release, thus the endothermal process of the water release from clay minerals between 250 and 650°C is not shown up on the DTA curve (3) in Fig. 1. This is also clear from a comparison of curves 3 in Figs 1 and 3. The water release from clay minerals between 250 and 650°C is not shown by the TG and DTG curves, either. The structural water in clay minerals is little.

With a Derivatograph C the curve designated by H<sub>2</sub>O in Fig. 2 was constructed to visualize the release of the 'mobile' and 'bound' water from the sample. The curve was constructed on the basis of the following considerations:



The organic matter was oxidized completely between 250 and 650°C. From the amount of CO<sub>2</sub> released (curve 2) the change in weight of the organic matter was calculated as function of the temperature (curve 4), and the latter was subtracted from the TG curve (curve 1). Between 20 and 250°C the TG and H<sub>2</sub>O curve coincide since the only gaseous decomposition product was 'mobile' water. Between 650 and 950°C only the CO<sub>2</sub> due to the decomposition of CaCO<sub>3</sub> left (curve 2) the sample. Hence, this was subtracted from the corresponding section of the TG curve (curve 1). As a result of the calculations a curve was obtained which represented the process of water release alone (curve 3). Although the curve does not allow the identification of the clay minerals, it enables the 'mobile' interlamellar water released up to 250°C and the total amount of 'bound' water released in a dehydroxylation process from the minerals around 500°C to be determined.

Between 650° and 950°C only CaCO<sub>3</sub> is decomposed; the corresponding weight change (curve 5 in Fig. 2) was calculated from the TGT curve. The CaCO<sub>3</sub> content was also determined from the TG curve as well, since no other thermal decomposition occurred in this temperature range. The two values obtained for the amount of CaCO<sub>3</sub> show an acceptable agreement (Table 2).

Of the TG, DTG and DTA curves taken simultaneously in nitrogen atmosphere (Fig. 3) only the section between 20 and 250°C can be interpreted which corresponds to the release of 'mobile' water. Above 250°C the decomposition of the organic matter starts. The decomposition proceeds in a different way than in the presence of oxygen. The amount of CO<sub>2</sub> released is less, as the CO<sub>2</sub> comes only from the decomposition of the carboxyl groups present (curve 4). The oxygen is released in the form of H<sub>2</sub>O and CO. The decomposition products include coke, tar and gaseous products. Due to the complicated nature of the decomposition process, it is nearly impossible to interpret the TG, DTG and DTA curves. The DTA curve, however reflects the absence of exothermal oxidation processes, the CO<sub>2</sub> curve shows that the amount of CO<sub>2</sub> produced between 250 and 650°C is small. The curve for H<sub>2</sub>O cannot be constructed in this case.

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**Zusammenfassung** — Es wurde gezeigt, daß computerderivatografische Methoden mit EGA Technik in Bodenproben mit zufriedenstellender Genauigkeit und Reproduzierbarkeit zur Bestimmung des Gehaltes an organischer Substanz und an Karbonaten verwendet werden können. Diese Methode ermöglicht die parallele Bestimmung des Probengehaltes an "mobilem" und "gebundenem" Wasser.