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DIELECTRIC-DIFFERENTIAL THERMAL ANALYSIS PART I: METHOD

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A thermal analyzer design is described. The instrument is capable of performing simultaneously differential thermal analysis and dielectric thermal analysis under the same experimental conditions. The theoretical basis of dielectric thermal analysis is superficially analyzed, and results obtained on different kinds of substances are presented.

At the present time, several methods are used to identify rocks and minerals. Many of these methods are based on changes produced by temperature.

One such method is thermoelectrometry, where the specific property that varies with temperature is the ohmic resistance, the conductivity, or any other electric property of the material [1].

The changes brought about in the dielectric parameters of substances by dynamic conditions of temperature for the analysis of mineral substances, polymers, etc., have been studied for the past 20 years [2–9].

The dielectric constant depends on the effects of electronic, atomic, dipolar and interfacial polarization [10], and it therefore provides wide information about rocks. On the other hand, this constant varies as a result of chemical processes and qualitative and structural modifications of the material [11], and mainly the crystalline structure.

The dielectric constant variations produced by temperature are therefore determined by the properties of the material itself, so that, if the relation existing between the dielectric parameters and the temperature is determined, an unknown mineral can be identified.

This is the principle of dielectric thermal analysis formulated by Roque-Malherbe et al. in 1979 [12].

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In spite of the possible information provided by this method, it has not been widely used for the study and identification of minerals. There are very few reports about this subject, among them the most relevant being those by Roque-Malherbe et al. and Egerer [13–16]; these show the validity of this method, but also that the complexity of preparation of the samples and the low instrumental sensitivity detract from the practical value of the method.

The aim of this paper is to report a thermal analyzer capable of yielding DTA and dielectric thermal analysis curves simultaneously in a practicable and quick way.

Method

A thermal analyzer was designed and constructed; its diagram is shown in Fig. 1. The temperature programmer was designed according to established methods [17, 18], as was furnace [19, 20] and the temperature controller.

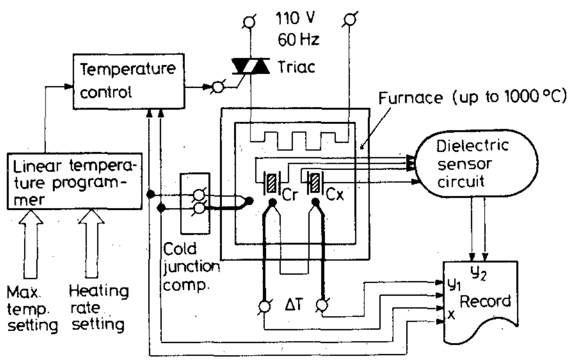


Fig. 1 Block diagram of dielectric-differential thermal analyzer

The dielectric thermal analyzer is composed of three parts:

1–The specimen holders (C_r and C_x Fig. 1).

2–The dielectric sensor circuit.

3–The recorder.

The specimen holders are two cylindrical capacitors, C_r (reference) and C_x (specimen), supported on a porcelain DTA specimen holder (Fig. 2a), constructed from 0.15 mm thickness nickel sheets, and the output conductors are made from platinum-rhodium.

The dielectric sensor circuit is shown in Fig. 2b.

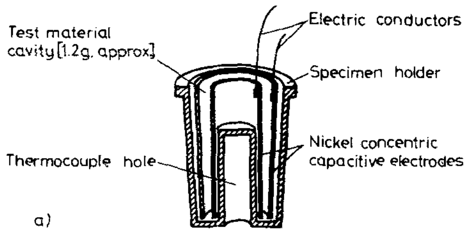
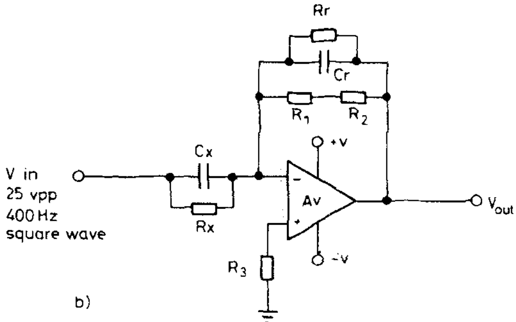


Fig. 2a Inside view of specimen holder for dielectric-differential thermal analysis



b Electronic circuit of dielectric sensor

The relationship between the output voltage (V_{out}) and the input voltage (V_{in}) is given by:

$$A_v \text{ closed loop} = \frac{-V_{out}}{V_{in}} \quad V_{out} = \frac{(Z_r)}{(Z_x)} V_{in} \tag{1}$$

$$\frac{1}{(Z_x)} = \sqrt{(WC_x)^2 + \left(\frac{1}{R_x}\right)^2} \tag{2}$$

$$\frac{1}{(Z_r)} = \sqrt{(WC_r)^2 + \left(\frac{1}{R'_r}\right)^2}\,; \tag{3}$$

where

$$\frac{1}{R'_r} = \frac{1}{R_r} + \frac{1}{R_1 + R_2}$$

Substitution of (2) and (3) into (1) gives:

$$V_{out} = \frac{\sqrt{(WC_r)^2 + \left(\frac{1}{R_x}\right)^2}}{(WC_r)^2 + \left(\frac{1}{R'_r}\right)^2} \tag{4}$$

if

$$\frac{1}{R} = \lambda(\sigma_p + \sigma_\Omega) \tag{5}$$

(λ = form factor; σ_Ω = ohmic conductivity; σ_p = loss conductivity), substitution of (5) into (4) gives:

$$V_{out} = \frac{\sqrt{(WC_x)^2 + \lambda^2(\sigma_{\Omega x} + \sigma_{px})^2}}{\sqrt{(WC_r)^2 + \lambda^2(\sigma'_{\Omega R} + \sigma'_{pR})^2}} V_{in} \tag{6}$$

From (6) we concluded that, with V_{in} = 25 V_{pp}, 400 Hz, the output voltage depends upon C_x, C_{ref}, λ, $\sigma_{\Omega x}$, σ_{px}, $\sigma_{\Omega R}$ and σ_{pR}. We used Al_2O_3 as reference substance, which displays no appreciable change in its dielectric properties with temperature up to 1000° [14–16]. The voltage V_{out} will therefore depend mainly upon the dielectric changes in the substance tested.

The recorder used is a Philips model PM–8120 XY recorder. It was necessary to rectify the A–C voltage of V_{out} to obtain records of variation curves of dielectric parameters (V_{out}) vs. temperature.

The substances used were analytically pure or were analyzed and characterized previously by other methods of analysis. In all cases the heating rate was 16 deg/min.; the quantity of substance was 1.1 g (0.1 < d < 0.2 mm); T_{max} = 1000°.

Results

The method and equipment were with the following pairs in C_x and C_r: air—air (Fig. 3); zeolite 13 X—Al_2O_3 (Fig. 4); mordenite—Al_2O_3 (Fig. 4a); quartz—

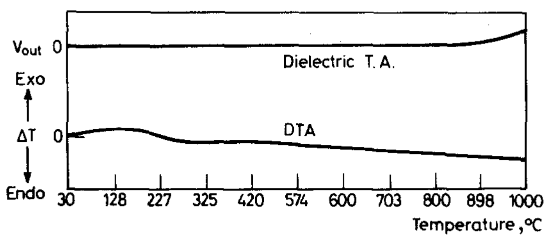


Fig. 3 Dielectric-differential thermal analysis curves of C_x: air and C_r: air

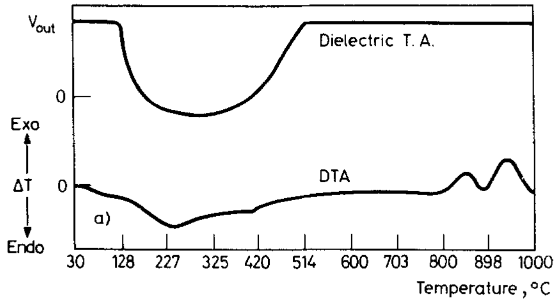
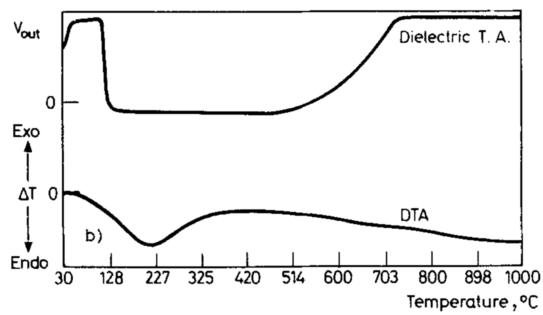


Fig. 4a Dielectric-differential thermal analysis curves of C_x: zeolite 13 X and C_r: Al_2O_3



b C_x: Mordenite and C_r: Al_2O_3

Al_2O_3 (Fig. 5) and $CaCO_3$—Al_2O_3 (Fig. 6). The air—air curves showed an admissible baseline, which is essential for a thermal analysis method. The analyzed zeolites (13 X; mordenite) gave curves similar in appearance: only one peak, whose width depends on the kind of zeolite and is strongly related to the loss of water. The

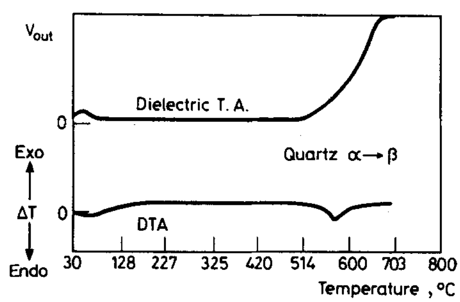


Fig. 5 Dielectric-differential thermal analysis curves of C_x: Quartz and C_r: Al_2O_3

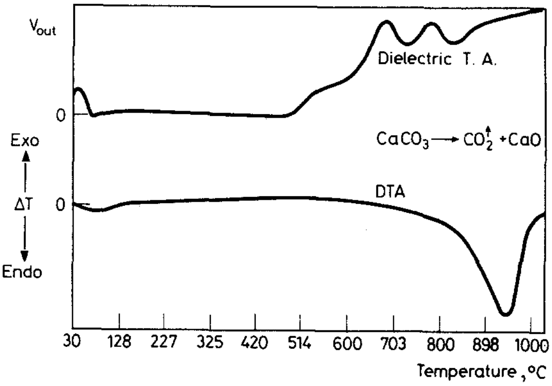


Fig. 6 Dielectric-differential thermal analysis curves of C_x: $CaCO_3$ and C_r: Al_2O_3

curve for quartz shows the transformation (578°) in a convincing way, while in the case of $CaCO_3$, the decomposition $CaCO_3 \rightarrow CaO + CO_2$ is evident.

Conclusions

A dielectric thermal analyzer was designed. Its practical utilization and its coupling to a differential thermal analyzer permit a combined thermal analysis method. Dielectric-differential thermal analysis allows two curves to be obtained in parallel, one of them reflecting the changes in dielectric properties (resistance, capacity and dielectric losses), and the other relating to classical differential thermal analysis.

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Zusammenfassung — Es wird eine Thermoanalyzer-Konstruktion beschrieben. Mit dem Gerät können differentialthermoanalytische und unter den Bedingungen der thermischen Analyse vorgenommene dielektrische Messungen simultan unter gleichen Bedingungen ausgeführt werden. Die theoretische Grundlage der dielektrischen Thermoanalyse wird kurz behandelt. Für Substanzen verschiedener Art erhaltene Ergebnisse sind angegeben.

Резюме — Описано конструкционное решение термического анализатора. Аппаратура дает возможность при тех же самых экспериментальных условиях проводить совмещенный дифференциальный термический анализ и диэлектрический термический анализ. Кратко представлены теоретические основы диэлектрического термического анализа, а также результаты, полученные с различными типами веществ.