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DYNAMIC DIELECTRIC ANALYSIS. A NEW THERMAL ANALYSIS TECHNIQUE

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ABSTRACT

Applications of dynamic dielectric analysis (DDA) in studies on the thermal decomposition and phase transformations of solid materials are discussed. Three illustrative examples are presented for (a) a system undergoing a chemical reaction or thermal alteration on application of heat, (b) a system undergoing a crystallographic transformation and (c) detection of moisture in naturally occurring materials. The advantages derived by applying a combination of DDA and a conventional thermal analysis technique such as DTA to studies on thermal processes are demonstrated. It is shown that the information obtained from techniques such as DTA or TG is limited in scope unless used in conjunction with a method which sheds light on the mechanistic aspects of the physical or chemical process of interest.

INTRODUCTION

The inclusion of new techniques such as thermomechanometry, thermosonimetry, thermoacoustimetry, and thermomagnetometry [1], in the general realm of thermoanalytical methods of investigation adds a new dimension and scope to the characterization and property determination of various types of materials. The type of information obtainable from techniques such as DTA, DSC and TG reflects only the gross macroscopic thermal behavior of the experimental sample. Additional techniques which would throw light on the changes taking place in the sample on a molecular level as a result of the application of heat, are therefore desirable. In addition, such techniques, when used in conjunction with conventional thermal analysis techniques such as DTA, DSC and TG, could conceivably yield useful complementary information which could greatly facilitate interpretation of the obtained thermal data.

Apart from the techniques mentioned above, methods for characterizing the a.c. thermoelectrical behavior of materials have received increasing attention in recent years [2—5]. The electrical behavior of materials in alternating current fields yields a variety of information related to the mechanisms of conduction and polarization operative in them. For example, changes in

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the dielectric constant, ϵ' of a material with temperature can arise from corresponding changes in the orientational freedom of its component molecules (or group(s) of molecules) brought about by a chemical reaction or phase transformation. The variation of ϵ' with frequency can also be studied to provide information on the magnitude of dispersion brought about by polarization by various mechanisms. Peaks in the dielectric loss factor, ϵ'' or loss tangent tan $\delta(=\epsilon''/\epsilon')$ as a function of temperature or frequency, can be traced to dielectric relaxation mechanisms; which in turn can be correlated with a defect model assumed for the test material. Trends in the changes of a.c. conductivity (which is related to the loss factor) with temperature can yield information on the activation energies for carrier mobilities, formation energies of point defects and the type of point defect predominant in the material [6]. Similar measurements at low temperatures, in addition throw light on the extent of defect aggregation, impurity precipitation and formation of impurity-defect complexes. The examples quoted above demonstrate the versatility and powerfulness of a.c. electrical techniques in studies on solid materials. Measurement techniques in d.c. fields on the other hand, are considerably limited in scope; polarization effects inherent in conduction mechanisms of most ionic solids preclude a straightforward interpretation of the data obtained therein.

Although several examples of the application of a.c. electrical techniques to the study of ionic solids and polymers exist in the current literature [5—7], three factors have stood in the way of their use in conjunction with thermal analysis techniques: (a) the majority of techniques for monitoring a.c. electrical properties rely on the use of various types of bridges and are manually operated; (b) manual measurements based on the use of bridge circuits, are not readily amenable to situations where the temperature is continually changing (e.g. linear ramp, which is usually the case with most thermal analysis techniques such as DTA, TG or DSC); (c) the frequency range for bridge circuits is usually restricted; this results in the use of different types of bridge circuits for various frequency domains.

The above factors therefore preclude a direct coupling of conventional a.c. electrical measurement techniques with DTA, TG or DSC. An alternative technique which can work for linear temperature ramps and which can be readily automated is therefore necessary. Such a technique was first developed in our laboratory; the application of this technique to studies on naturally occurring materials was communicated in previous papers [8,9]. The use of this technique simultaneously with DTA in studies on solid materials was also demonstrated [9]. We call the above technique Dynamic Dielectric Analysis or DDA *, the term dynamic refers to the continuous sampling of a large range of frequencies (typically 50—10^6 Hz) and temperatures (room temperature—~500°C) and is a major feature of this technique. A refinement of the electrical circuitry employed in this technique which

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* The Nomenclature Committee of ICTA has adopted the name "Thermoelectrometry" to the class of thermal analysis techniques dealing with an electrical characteristic (e.g. resistance, capacitance and conductance) of material [11]. On this basis, the present technique could also be called "Dynamic Thermoelectrometry."

would further minimize measurement errors and a technique for the concurrent applications of DDA and DTA to studies on solid materials will be reported elsewhere [10]. The aim of this paper is to highlight some of the applications of DDA in studies on the thermal decomposition, and phase transformation of solid materials. Three illustrative examples are presented for (a) a system undergoing a chemical reaction or thermal alteration on application of heat, (b) a system undergoing a crystallographic transformation and (c) detection of moisture in naturally occurring materials.

RESULTS AND DISCUSSION

(a) Study of chemical reactions and thermal alterations

Oil shales of the western United States are potential sources of vast reserves of energy and have therefore been the subject of intensive study in recent years [12]. An examination of the changes taking place in the material on application of heat is crucial for efficient process control and design. A DTA run on these materials typically shows a single endothermic peak around ~500°C corresponding to the decomposition of the organic matter in the shale *. (The presence of air or small amount of oxygen give rise to intense exothermic peaks arising from the oxidation of the shale hydrocarbons. All experiments with such materials are therefore carried out under an atmosphere of rapidly flowing inert gas around the samples.) Without other supporting data, one would therefore conclude the presence of only one chemical reaction at 500°C in the material. An examination of the data obtained from DDA carried out on these materials, however, reveals interesting effects.

A plot of the a.c. electrical resistivity (ρ) of a Green River oil shale sample is shown in Fig. 1 as a function of temperature and frequency. A smooth decrease in the ρ values from room temperature to ~200°C followed by a sharp increase to ~400°C and then an abrupt fall at temperatures <450°C is evident. These changes in the resistivity are indications of alterations in the chemical or physical properties of the material. Postponing an interpretation of the observed effects for the moment, let us examine a similar plot for the same material, this time cooled back to room temperature after the above experiment and reheated to ~500°C (Fig. 2). The change in the ρ values with temperature is now quite monotonic and shows the expected exponential decrease in the magnitude of ρ with temperature. Comparison of the results shown in Figs. 1 and 2 immediately confirms the fact that the material has undergone an irreversible change at temperatures significantly below the range where the DTA traces show a noticeable effect.

Figures 3 and 4 depict the changes in the dielectric constant (ϵ') of the material is a function of temperature and frequency. The ϵ' values initially

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* The presence of minerals which decompose at temperatures below this point e.g., nahcolite, dawsonite, analcime, in the oil shale samples would give rise to additional endotherms.

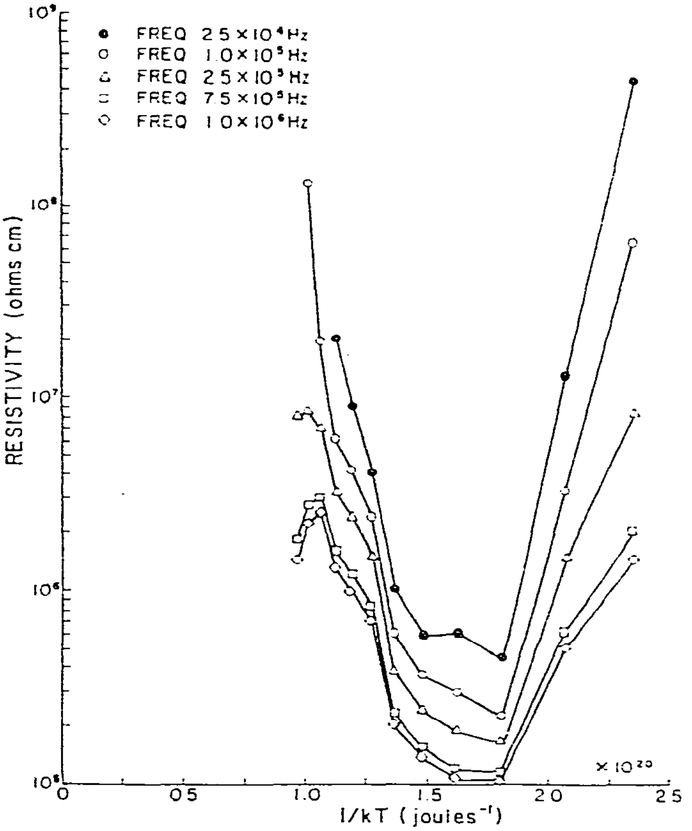

Fig. 1. Semi-log plot of resistivity (ρ) vs. reciprocal temperature ($1/kT$) for a 27.5 gallons per ton oil shale from the Green River formation.

show a smooth decrease for temperatures up to 250°C (Fig. 3) whereafter they increase again (Fig. 4) attaining values comparable to those observed initially at temperatures below 85°C (Fig. 4). These results now permit us to provide a consistent explanation for the observed trends in ϵ' and ρ as a function of temperature. The initial decrease in ϵ' with temperature is probably caused by the gradual release of moisture and pore water from the oil shale matrix. On this basis, the smooth decrease in the ρ values (Fig. 1) can be correlated with the increased defect concentration and disorder in the oil shale matrix resulting from the release of water molecules. The subsequent sharp peaks in the ρ vs. $1/kT$ plots (Fig. 1) arise from a phase change in the material with accompanying changes in its mechanical properties [13]. This phase change is probably related to a loosening of the kerogen bonding structure in the oil shale matrix prior to its thermal decomposition. Evidence for this postulate is provided by the increase of ϵ' values with temperature above 250°C (Fig. 4). The increase of ϵ' could also arise, however, from the presence of a space charge layer in the material at elevated temperatures arising from blocking of current carriers at the electrodes [14]. The occurrence of a low frequency spike or cut-off in the plots of dielectric loss factor, ϵ'' vs. temperature and frequency (Fig. 5) (which is typical of blocking electrode effects) also supports the above hypothesis. Thus the exact origin of

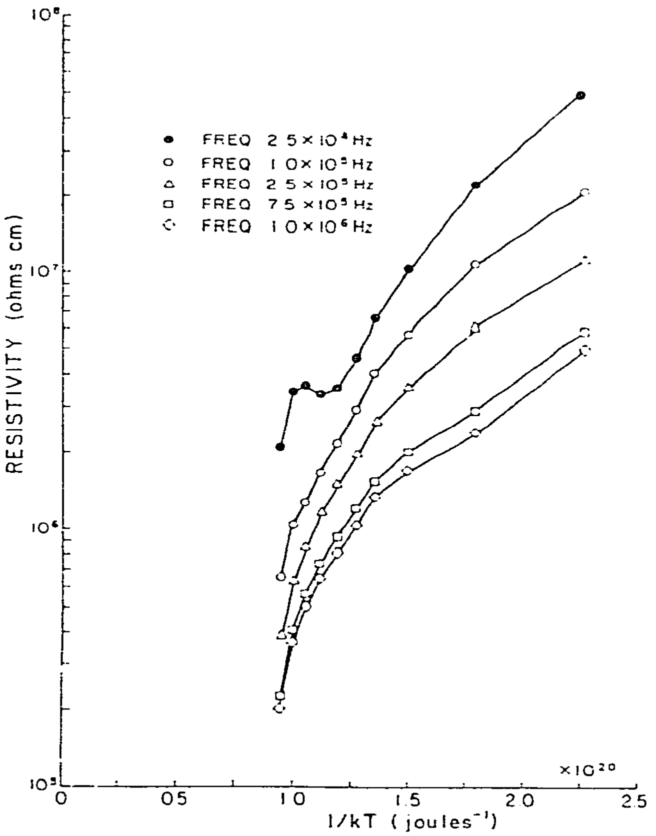

Fig. 2. Same plot as in Fig. 1 for the sample after complete decomposition of the organic matter.

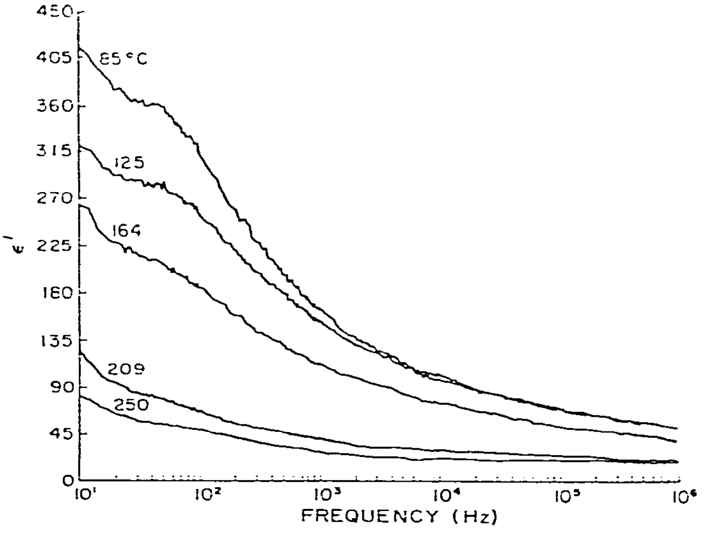

Fig. 3. Frequency and temperature dependence of the relative dielectric constant (ϵ') for Green River oil shales at temperatures below ~250°C.

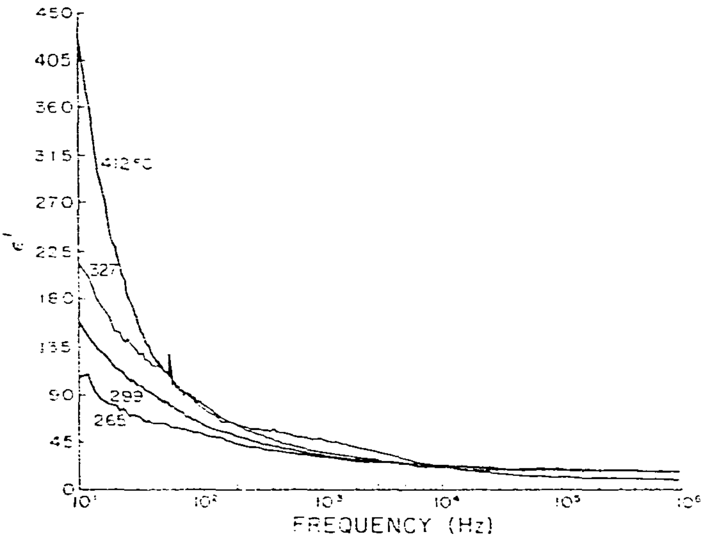

Fig. 4. Frequency dependence of ϵ' for Green River oil shales at elevated temperatures.

the peaks in ρ and the increase of ϵ' at higher temperatures is somewhat uncertain at present.

The absence of noticeable peaks in the DTA corresponding to the release of absorbed moisture and pore water is probably explained by the wide temperature range (~200°C) over which these processes take place and their extremely small heat effects. A pronounced drift in the baseline was observed in most cases. An examination of the TG traces for these shales again shows a gradual weight loss starting from around ~80°C right up to the kerogen decomposition temperature viz ~500°C. The processes of release of adsorbed moisture, dehydration and decomposition are so intimately related that it is impossible to separate their individual effects by either TG or DTG.

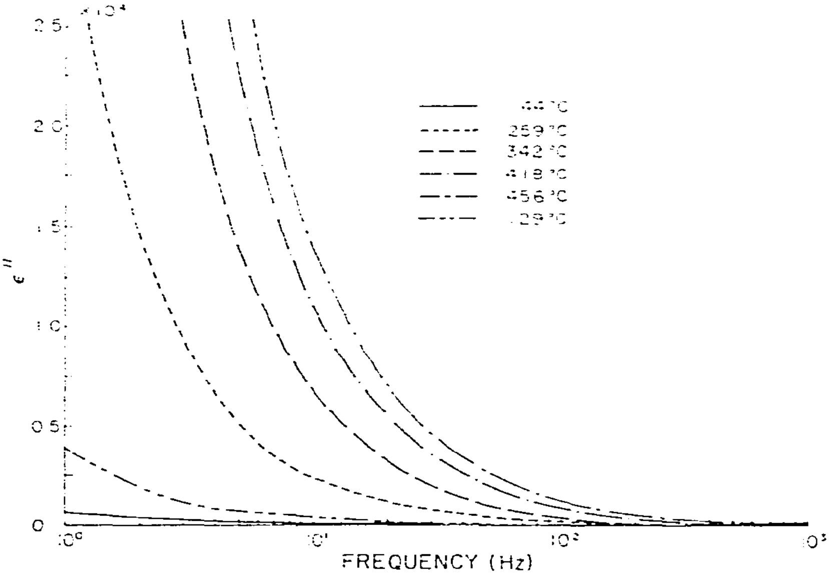

Fig. 5. Representative plot for the variation of the dielectric loss factor, ϵ'' with frequency at different temperatures.

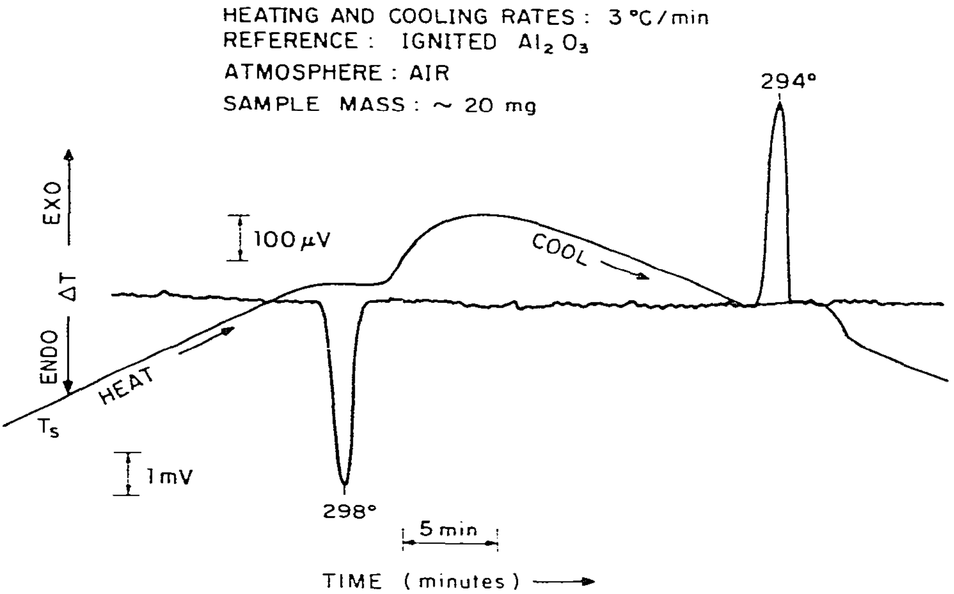

Fig. 6. Representative DTA curves (heating rate, 3°C min^{-1}) for the crystal structure transformation in potassium perchlorate.

(b) *Study of crystal structure transformations*

Potassium perchlorate is commonly used as an oxidizer in composite rocket-propellant formulations. The crystal structure of potassium perchlorate is bipyramidal orthorhombic at room temperature. The material undergoes an orthorhombic $\rightleftharpoons$ cubic transformation around 300°C. The DTA peak temperatures reported for this crystal structure transformation by various investigators are, however, somewhat at variance owing to differences in the method of DTA measurement (type of sample cell, heating rate, particle size, position of detector, etc.) [15].

The results of a DTA study on this transformation at a heating rate of $\sim$3°C min^{-1} are shown in Fig. 6. The presence of a small hysteresis in the transformation in the forward and reverse directions is to be noted and is consistent with previous DTA studies on this transformation [14]. Apart from the temperature of the transformation and the endothermic nature of the transformation (in the forward direction), very little additional information can be gained from the DTA results *.

Let us now examine the results obtained by DDA carried out concurrently on the same sample. Figure 7 shows the sample capacitance, C_s, vs. temperature for various frequencies in the range 500—10^5 Hz. The sharp increase in C_s values at the transition in the forward direction and a corresponding decrease in capacitance for the reverse transition (Fig. 8) are to be noted. Figure 9 shows the sample conductance, G, plotted as a function of frequ-

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* A quantitative measure of the magnitude of the heat effect, ΔH_{tr}, for the transformation can also be obtained from DSC studies; such measurements by DTA, on the other hand, are at best semi-quantitative.

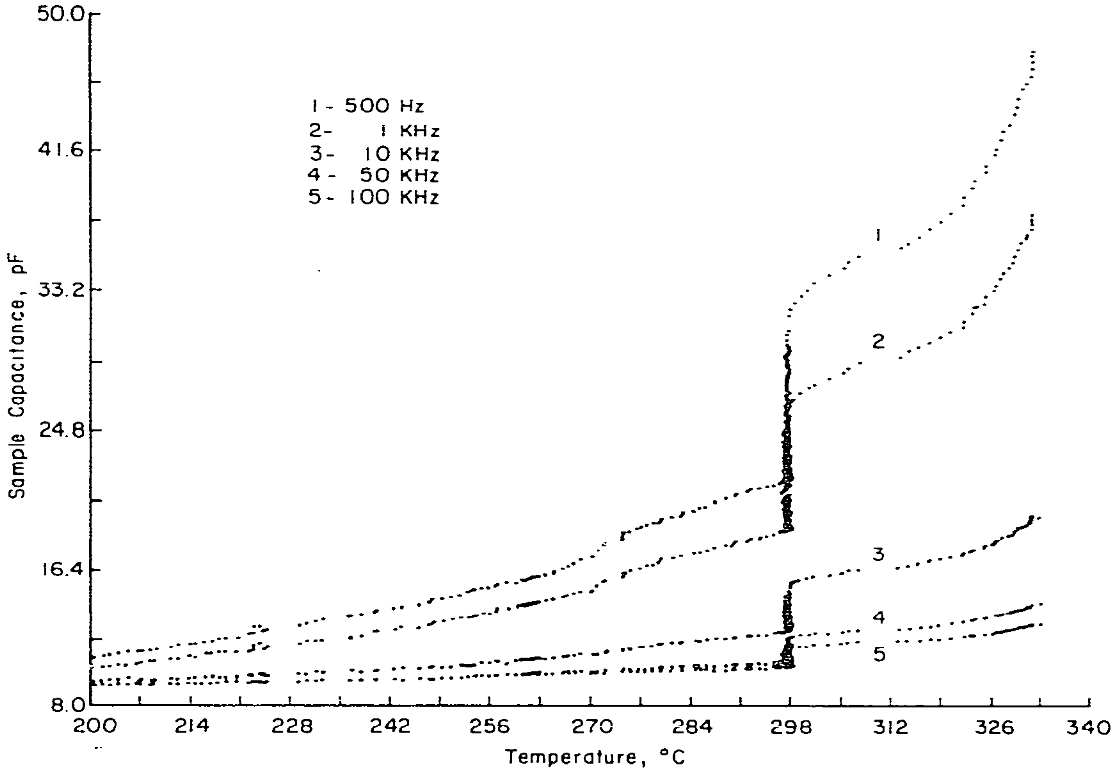

Fig. 7. Variation of sample capacitance, C_s, with temperature and frequency in the forward (heating) direction.

ency and temperature in the form of conventional log (GT) vs. $1/T$ plots. The results are shown only for the forward (heating) direction although similar results are obtained on cooling. The presence of a sharp change in the sample conductivity at the transition point is apparent.

There have been prior speculations [16], which are unsupported by experimental data, on the mechanistic aspects of this transformation. According to these authors, the transformation in potassium perchlorate (as well as in isomorphous Na, Rb, Cs, analogues) is believed to be brought about by the onset of rotation of ClO_4^- ions. The abrupt change in C_s (or ϵ') values at the transition point observed in the present study is in essential agreement with the above postulate. The increase in the volume available for the perchlorate ion as a result of the transformation (104.19 Å^3 for the cubic phase compared with 80.49 Å^3 for the low-temperature orthorhombic phase, ref. 14) probably facilitates increased rotational freedom of the ClO_4^- groups with accompanying increase in the capacitance or dielectric constant values. The abrupt change in conductivity of the material at the transition point can also be accounted for, on the basis of the volume effect.

Although it is possible to extract activation energies from the slopes of plots such as Fig. 9, the use of polycrystalline samples in the present study and the presence of grain boundary conduction, precludes a straightforward interpretation of the values obtained in terms of defect mobilities and formation.

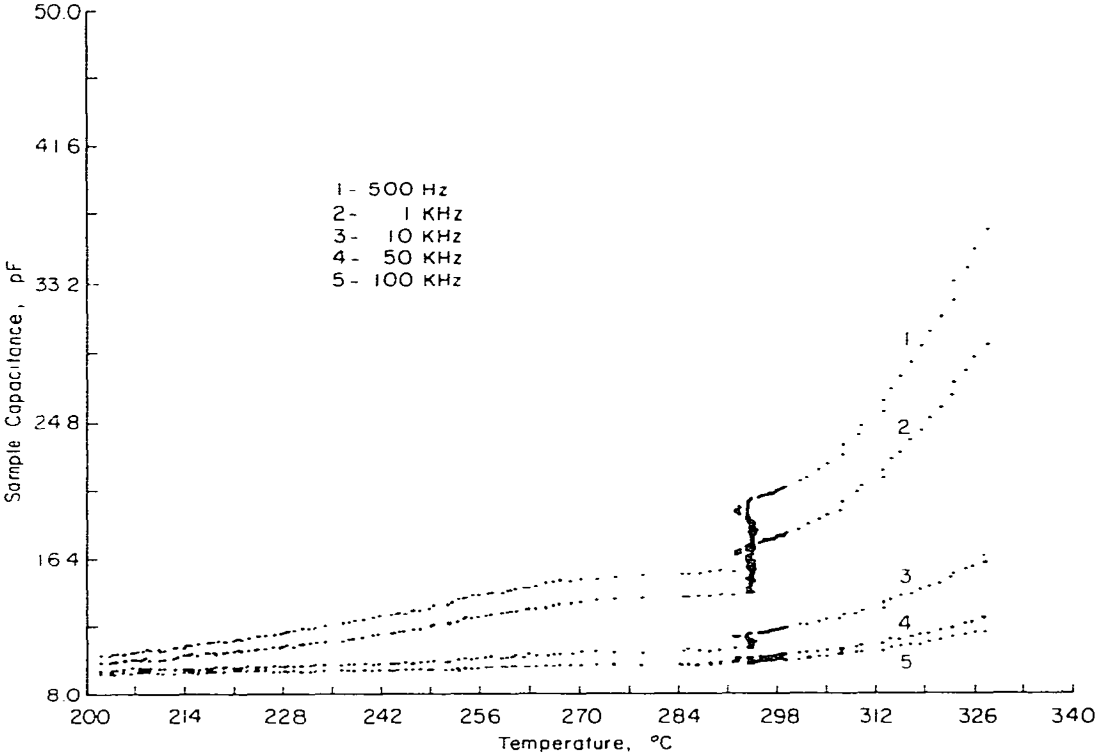

Fig. 8. Variation of C_s with frequency and temperature for the reverse, cooling cycle.

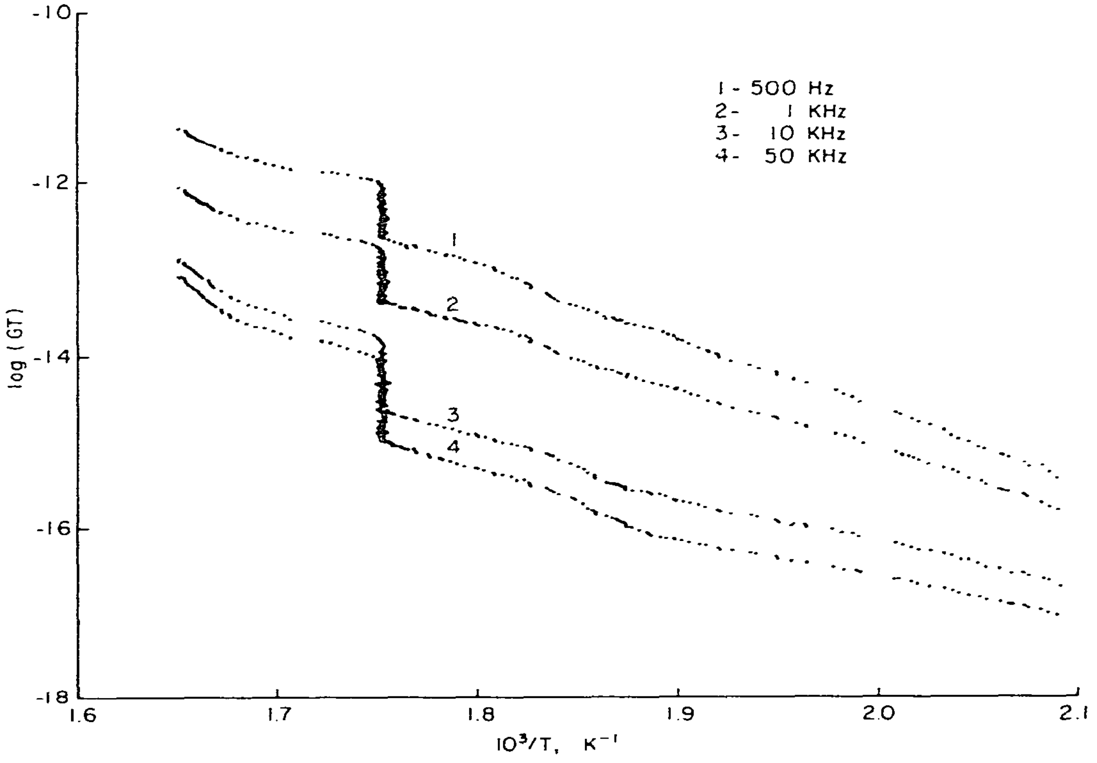

Fig. 9. Plot of log (GT) vs. $1/T$ for various frequencies.

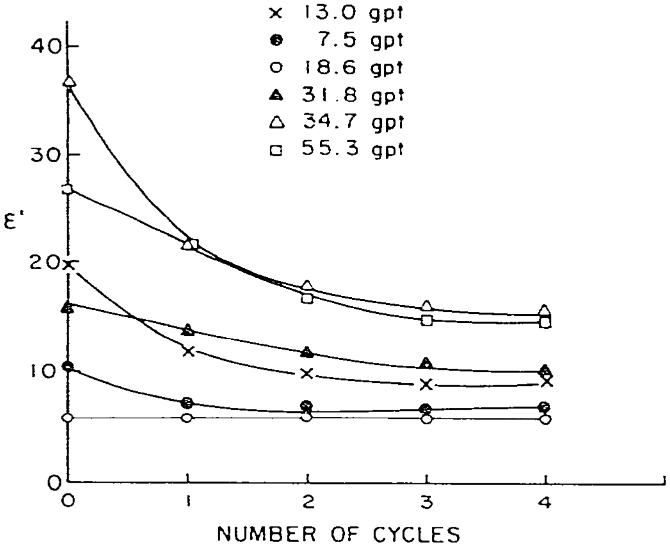

Fig. 10. Variation of ϵ' with number of heating cycles for several grades of Green River oil shales.

(c) Detection of moisture in naturally-occurring materials

Moisture can be readily detected in a material by a.c. electrical methods * because (a) water has a characteristically high dielectric constant and will therefore tend to increase the capacitance of the test material, and (b) the presence of moisture in the material gives rise to significant interfacial (Maxwell—Wagner) polarization with accompanying dispersion in capacitance (or ϵ') vs. frequency plots. Both these effects are clearly seen in the results obtained on Green River oil shales shown in Figs. 10 and 11, respectively. Similar results are obtained for corresponding variation in the dielectric loss factors of these materials.

Detection of moisture in materials such as oil shales is important because the performance of many of the electromagnetic methods that are currently being investigated for the processing of these materials is critically dependent on the presence or absence of moisture in the shale deposits. The coupling of the input electromagnetic energy with moisture is a complicating effect that has to be considered in any energy balance analysis of the particular process.

Although in certain favorable cases, quantification of the contained moisture by a.c. electrical techniques is possible (by repeated drying and measurement, for example), the presence of both adsorbed moisture and pore water in materials such as shales and rocks and the overlapping temperature regimes for their evolution, complicate matters somewhat. This problem has been pointed out before in studies on the role of water in the electrical resistivity of rocks [17].

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* The detectability and sensitivity of electrical methods far surpass that obtainable by other methods because even the smallest amount of moisture can cause a relatively large electrical effect.

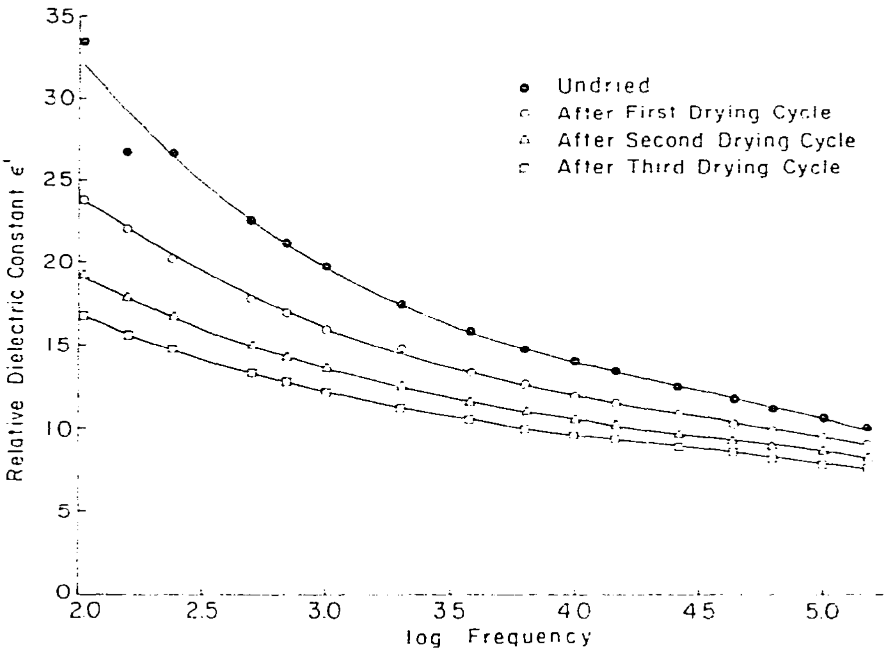

Fig. 11. Variation of ε' with frequency and heat treatment for Green River oil shales.

CONCLUSIONS

The advantages derived from the application of the DDA technique developed in this laboratory to studies on solid materials have been highlighted. It is demonstrated that the information obtained from a technique such as DTA is limited in scope unless used in conjunction with another method which throws light on the mechanistic aspect of the physical or chemical process of interest. In this respect, it is useful to note that combination of techniques such as the widely employed DTA (or DSC)—TG—DTG will be handicapped by the same drawback (see examples (a) and (b) above). Some of the currently available thermal analysis techniques are classified separately in Table 1; in this scheme "primary" thermal analysis techniques fall under Group A and complementary methods which yield mechanistic information comprise Group B. An ideal combination of techniques would then be those coupling Group A techniques with the methods listed under Group B. It must be noted that the term "combination" is used in the present context to mean a

TABLE 1

Some currently available thermal analysis techniques: primary thermal analysis techniques (Group A); complementary methods yielding mechanistic information (Group B)

Group A	Group B
Differential scanning calorimetry, Differential thermal analysis, Thermogravimetry, Derivative thermogravimetry, Evolved gas analysis	Thermoacoustimetry, Thermosonimetry, Thermoelectrometry, Thermomicroscopy, X-ray diffractometry, Thermomagnetometry, Thermomechanical analysis

concurrent or simultaneous application of two or more techniques and does not include supportive data obtained from separate measurements (viz., chemical analysis, spectroscopy, etc.). It should also be emphasized that the concurrent mode is superior to a simultaneous determination in view of the fact that the requirements for the optimum performance of each individual technique in the combination are not sacrificed in any manner in the concurrent mode unlike in simultaneous measurements. The main arguments in favor of either concurrent or simultaneous measurements are of course, substantial savings in time, and exposure of the test sample to identical experimental conditions.

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