

## THE USES OF DIELECTRIC SPECTRA AND IMMERSIONAL CALORIMETRY IN THE CHARACTERIZATION OF LOW-RANK COALS

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### Introduction

Moisture in low-rank coals is believed to involve at least two fundamentally different mechanisms for binding water to the coal matrix (1). The first type of moisture behaves as if were "free"; the vapor pressure versus temperature behavior is that of pure water. The second type occurs at sites where it is bound more tightly, resulting in a lowering of the vapor pressure relative to that of pure water at the same temperature. Such moisture may be hydrogen bonded to oxygen-containing functional groups or it may be incorporated as water of hydration of ion-exchangeable cations. There might also be tightly entrained moisture, in the pore structure, between the thermodynamically "free" moisture and the chemically bonded moisture. The objective of our work was to investigate the application of two experimental techniques, dielectric relaxation spectroscopy and immersional calorimetry, to the characterization of moisture content and pore structure of low-rank coals.

Dielectric techniques can sometimes prove valuable in studying bulk matter containing specific polar molecules (2, 3). From a theoretical standpoint, a parallel plate capacitor with a vacuum between its electrodes ceases to behave as a pure capacitance (at all frequencies) when a condensed matter dielectric is inserted. If an alternating voltage is applied to the capacitor containing a dielectric, the current and voltage will no longer be precisely  $\pi/2$  radians out of phase,  $\pi/2$  being the value for a vacuum-filled capacitor. The degree of departure from  $\pi/2$  radians as expressed by the angle  $\delta$ , depends on the "lossyness" of the dielectric.

The process of absorption (defined as the concentration of a substance on a surface where the substance, the absorbate, is in a gas or liquid form and the absorbent a solid) is spontaneous and is characterized by a fall in the entropy of the system and a decrease in surface free energy. This necessitates the absorption process to be exothermic, the resultant energy being referred to as the heat of immersion or heat of wetting. Therefore the exothermic heat liberated when a porous solid is immersed in a liquid is related to the surface energy of the solid and the measurement of it can be used to determine the surface area of various solid samples.

### Apparatus and Materials

#### (a) Dielectric Cell.

The dielectric cell was constructed from two stainless steel electrodes attached to corresponding outer stainless steel supports by means of a screw sandwiching a disk of insulating Teflon (see Figures 1 and 2). One electrode was 63 mm in diameter. The other, 50 mm in diameter, was surrounded by a 6 mm wide stainless steel annulus from which it was insulated by Teflon tape. This outer guard ring was kept at ground potential to eliminate fringing fields, edge effects and surface conduction across the dielectric being studied. The impedance measuring instrument used was a General Radio 1621 precision capacitance measuring system. This experimental setup enables the measurement of the equivalent parallel capacitance and resistance of the cell to be made at a given temperature and

frequency. For the subambient temperature measurements, the cell was placed in a styrofoam box and cooled with liquid nitrogen to the starting temperature.

(b) Differential Calorimeter.

The differential calorimeter consists, in essence, of two discrete units, each a calorimeter in its own right (see Figures 3 and 4). Each would have its own (identical to the other) paddle stirrer mechanism, heater circuit, temperature sensing circuit and Dewar flask. This twin calorimeter unit would then be operated in differential mode; i.e., a similar amount of wetting liquid would be put into each calorimeter Dewar, the calorimeters being imbedded in a metal heat sink for the thermal stability required, and the coal or carbon sample would be added to one Dewar. The temperature measuring circuit consists of a pair of matched thermistors, inserted into opposing arms of a Wheatstone bridge. Thus the heat liberated when the solid sample was added to the working Dewar would upset the balance conditions of the Wheatstone bridge due to the resistance change of the working Dewar's thermistor, with respect to the reference Dewar's thermistor resistance, and would produce an out-of-balance current that can be directly measured on a potentiometric chart recorder. This method of temperature measurement has the advantage that it is referenced to ambient conditions and not, for example, to the temperature of melting ice. The heat sink was fabricated from a 38 x 30 x 23 cm aluminum block. Two holes were bored in the heat sink of diameter slightly larger than the diameter of the Dewars, to enable them to be easily lowered inside. The stirring mechanism was designed to rapidly mix the material to be tested with the wetting liquid, producing a maximum dispersion of the material in the liquid with a minimum production of heat from the work of stirring. The work of stirring should ideally be constant. The rotating paddle type of stirrer was used, the glass paddle being mounted inside a guide tube which was in turn supported in a ground glass cone.

(c) Coal Samples.

Two coals were chosen for study: Gascoyne (North Dakota) lignite and Yampa (Colorado) subbituminous. The samples were obtained from the University of North Dakota Energy Research Center coal sample library. Composition data is given in Table I.

### Testing Procedures

(a) Dielectric Measurement.

Samples of several forms were used in the dielectric cell. Initial tests were performed with 63 mm diameter, 3 mm thick disks of coal sawn from solid blocks. Subsequent work involved 16, 30, 60, and -60 mesh powders. The connected and loaded cell was lowered into the styrofoam box and liquid nitrogen added to cool the cell and contents to around -190°C. The capacitance bridge was balanced and then the cell was allowed to warm up, during which time the measurements of T, temperature; F, frequency; C, capacitance, and G, conductance were performed. These variables would then subsequently be inserted into Equation 1 to determine the phase shift  $\tan \delta$  at a given frequency. The phase shift, expressed as the phase angle between voltage and current, is a function of the specific resistance of the coal, which in turn is dominated by the presence of its conductive phase, water.

$$\tan \delta = \frac{G}{2\pi FC} \quad 1)$$

A typical experiment involved taking data over a temperature range of -170° to 0°C at 0.1, 1.0 and 10.0 kHz. The temperature was measured by means of a chromel-alumel thermocouple attached to the guard ring. Plots of  $\tan \delta$  against temperature yielded the required dielectric spectra for that frequency.

Table I. Characteristics of Coal Samples.

Sample	Gascoyne	Yampa
	Rank Mine Location Heating Value (maf), Btu/lb	Lignite Bowman Co., North Dakota 11677
<u>Proximate Analysis, (As Rec'd); wt%:</u>		
Moisture	37.60	10.30
Volatile Matter	29.06	32.20
Fixed Carbon	0.00	44.00
Ash (ASTM)	9.70	13.50
<u>Ultimate Analysis (maf); wt%:</u>		
Carbon	69.05	80.81
Hydrogen	4.73	4.50
Nitrogen	1.04	2.53
Oxygen	23.15	11.30
Sulfur	2.03	0.79

(b) Differential Calorimetry.

The technique used with the differential calorimeter was to add 75 ml of wetting fluid (methanol or tetralin) to each of the clean, dry Dewar vessels. The top sections, complete with sensing and stirring apparatus were then lowered into the Dewars. Two grams of sample in a stoppered bottle was placed on top of the heat sink so that it could attain the same temperature as the rest of the system. The chart recorder was started after the bridge had been adjusted to its optimum operating conditions (250 mV). When the temperature remained constant, shown by a straight horizontal line on the trace, the calibration heater was switched on for 60 seconds (A to B, Figure 5). During this time, the voltage across the heater and the current passing through it were determined. After a reasonable portion of the cooling curve had been recorded for extrapolation purposes (B to C, Figure 5), the weighed sample was introduced to the working Dewar by means of the funnel mounted in the cone (C to D, Figure 5). A reasonable portion of the cooling curve was again recorded (D to E, Figure 5) and later another application of the heater for a known time period was applied to the working Dewar with the resulting temperature rise (E to F, Figure 5).

The heat of wetting in calories per gram is given by:

$$H = \frac{VIT}{J\sigma_h} \times \frac{\sigma_w}{W} \quad 2)$$

where V is the heater voltage in volts.

I is the heater current in amps.

T is the time the heater was switched on for (in seconds)

which produced the corrected temperature deflection of  $\sigma_h$ .

$\sigma_w$  is the corrected temperature deflection when the sample was wetted with the wetting liquid.

J = A constant = 4.18 joules per calorie.

W = weight of sample in grams.

Note that the second application of the heater (after the addition of the sample) will always produce a lower deflection, due the contribution of the sample to the total specific heat capacity of the Dewar and contents. The expression for describing the thermal capacity of the system is:

$$C = C_F + M_L S_L + M_C S_C \quad 3)$$

where  $C$  = thermal capacity of system,  
 $C_F$  = thermal capacity of fixed apparatus in the Dewar  
(heat supports, stirrer, Dewar, etc.),  
 $M_L$  = mass of liquid,  
 $S_L$  = specific heat capacity of wetting liquid,  
 $M_C$  = mass of sample,  
 $S_C$  = specific heat capacity of sample.

It should therefore be possible to get an idea of the heat capacity of the sample by the difference in deflections between the first and second applications of the calibration heater.

The heat of wetting per unit area for any given liquid on a particular surface is a constant for that liquid provided the liquid wets the surface of the solid perfectly. The value of this constant is given by Bond and Spencer (4) as 10.7 for methanol. In order to convert the heat of wetting results into surface areas, Bond and Spencer measured the heat of wetting of a non-porous carbon black having a surface area of 230 m<sup>2</sup>/gm. Thus, the heat of wetting per m<sup>2</sup> = 10.7/230 calories. Alternatively, 1 calorie of heat is liberated when 21.5 m<sup>2</sup> of carbon surface is wetted by methanol.

The corrected temperature rises were obtained (6) by extrapolating the cooling curve until it crossed the vertical line drawn from the point when the heater was initially switched on, or the point when the coal was added. In this way the effect of the cooling of the Dewar, which would occur during the time the heater was on, would be nullified. Therefore, each time the heater was turned on or the coal was added, enough time had to elapse afterwards for a representative amount of the cooling curve to be recorded for an accurate extrapolation to be made. This vertical distance would be measured and treated as the corrected temperature rise.

In most cases, the slope of the temperature against time curve before and after heat input was the same, making the actual time at which the corrected temperature rise was determined not critical.

## Results and Discussion

Figure 6 shows the  $\tan \delta$  versus temperature behavior for a Yampa (Colorado) subbituminous coal of 10% to 12% moisture; the coal had been stored under water and air-dried before insertion into the cell. No appreciable weight loss occurred during air drying. Between -60° and 0°C (not shown) the  $\tan \delta$  increases without bound; this is most likely caused by an ionic double layer formed by mobile ions present in the coal. The peaks show a simple Debye-like behavior in that they are relatively narrow and the temperature maxima shift to higher temperatures with increasing frequency. The solitary curve at the bottom of the figure is a 0.1 kHz  $\tan \delta$  plot for the same sample after it had been freeze-dried for two days at 10 microns pressure. The total loss of moisture was approximately 10% of the original weight of the coal. The complete loss of the large dispersion upon water removal is taken to be evidence that the dispersion is indeed caused by the relaxation of water molecules. When the coal sample was reconstituted with water after freeze-drying, there was no significant difference in dielectric spectra with the original spectra from the mine fresh sample. Figure 7 shows the dielectric characteristics of this Yampa coal on removing and replacing the moisture for one frequency.

Figure 8 is the resultant dielectric spectra of the Gascoyne lignite sample. Here there are two distinct sets of peaks; one set at  $-102^\circ$ ,  $-92^\circ$ , and  $-80^\circ\text{C}$ , the other set at  $-60^\circ$ ,  $-50^\circ$ , and  $-36^\circ\text{C}$ . The latter set is likely attributable to the presence of macroscopic crystals of ice. Accurate dielectric measurements on pure bulk ice have placed the spectrum in this vicinity (5). Figure 9 presents the spectrum of the same lignite after air drying for several days until a constant weight had been achieved. The upper set of peaks is missing and the lower set appears at  $-108^\circ$ ,  $-100^\circ$ , and  $-90^\circ\text{C}$ . The peak locations are virtually identical to those in the Colorado subbituminous coal. Finally, freeze-drying resulted in the loss of more water and produced the 1 kHz spectrum shown at the bottom of the Figure. Note again the evidence for associating the large relative maxima with the presence of water.

When the Gascoyne sample was reconstituted with water after freeze-drying, two distinct set of peaks were again apparent; the spectrum was not significantly different from that of Figure 8. These experiments indicate that this lignite incorporates 80% of its moisture in a loosely-bound form which freezes to ice below  $0^\circ\text{C}$  and that the remaining 20% is present in the coal possibly as water of hydration, which does not crystallize into ice. The Colorado subbituminous coal contains only the latter type of bound moisture. These results are consistent with the conclusion about two types of bound water, based on vapor pressure studies (3).

Samples of -60 mesh Yampa subbituminous and Gascoyne lignite were tested to see what effect powdering had on the dielectric spectral quality. The spectra displayed in Figures 10 and 11, respectively, show resolved  $\tan \delta$  peaks at approximately the same temperature locations observed for the solid disk experiments. This proves that the powdered coal samples show  $\tan \delta$  peaks of sufficient quality to alleviate the need for preparing solid disk samples.

A series of experiments were conducted to test the effect of different mesh sizes of coal granules on spectral peaks and spectral quality, to determine if particle size had an effect on the type or amount of water content of the coal. Yampa (Colorado) subbituminous was sieved into mesh sizes 16, 30, 60, and fines less than -60. The spectral quality for the first set of peaks (presumably corresponding to the tightly-bound water of hydration) improves as the size of the specimen particle decreases. The spectral peaks are much more clearly defined for the -60 mesh size than for those at 16 mesh.

The interpretation of the dielectric spectra and correlations of dielectric results with other measurable coal characteristics is still in progress. However, the size, location, and number of peaks in dielectric spectra provide a significant quantity of information on the state and behavior of the coal's intrinsic moisture. There are many ways in which water may be attached to the coal, either loosely as water in the pore structure or chemically bonded to the coal matrix as, for example, water of hydration. Measurement of dielectric properties of this water present in the coal has indicated the distinction between at least two of the mechanisms of the water bonding.

A sample of the Gascoyne lignite was tested in the immersion calorimeter with methanol. Its heat output (determined from Figure 12) was found to be 65.74 joules per gram (15.49 calories, per gram). Using a 10.7 conversion factor (4) gives a surface area of  $165.72 \text{ m}^2\text{gm}^{-1}$ . A similar sample of Yampa subbituminous coal was tested and gave rise to the output shown in Figure 13. It is interesting to note the key difference between these two figures, that of the nearly instantaneous heat output of the lignite (the exothermic heat of wetting was liberated in a few seconds) in comparison with that of the subbituminous coal. In the latter case, the heat output occurred over several hours, presumably as the methanol wetting liquid explored the system of micropores which were approaching molecular dimensions. The specific and corresponding surface area were not calculated due to the difficulty in obtaining a corrected temperature deflection  $\sigma_w$  from Figure 13.

Further testing was carried out on various mesh sizes of Gascoyne lignite to determine if the external or apparent surface area was a significant factor in the total (including internal pores) surface area value. Mesh sizes of 16, 30, 60, and

powder less than -60 were used without significant variation in the heat output. The total surface area of a coal is therefore very tolerant of sample powder size, the internal pore surface area term being dominant when compared to the external or apparent surface area term. This is the expected result if the pores are very small.

A probe liquid of larger molecular volume than methanol should not be so able to penetrate the porous structure, especially the micropore region which can account for up to 95% of the total surface area. Tetrahydronaphthalene (tetralin) was thus used because of its relatively large sized molecules and because of its interest as a hydrogen donor in liquefaction. Yampa subbituminous and Gascoyne lignite were then tested in the calorimeter using tetralin. The results of the surface area determinations are tabulated in Table II along with the corresponding results for the two coals in methanol.

Table II. Surface Area of Coals Using Different Wetting Liquids.

Coal Sample	Surface Area ( $m^2/gm$ )	
	Methanol	Tetralin
Colorado Subbituminous	>200	9.05
Gascoyne Red lignite	165.72	5.15

Since the tetrahydronaphthalene is a larger molecule than methanol, it is unable to penetrate the smallest pores in the coal. Heat is only liberated from the very large pores and the external or apparent surface as if the porous coal had transformed into a non-porous carbon black. In future experiments the use of probe liquids of intermediate molecular sizes between those of methanol and tetrahydronaphthalene will yield information on the relative amounts (distributions) of micro, transitional and macropores.

#### Acknowledgment

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#### Literature Cited

1. Schobert, H.H. "Characterization of Low-Rank Coals Important in Their Utilization." Oral presentation at Penn State; short course on coal. November 1-5, 1982.
2. McCrum, N.G.; Read, B.E.; and Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids." Wiley, New York, 1967.
3. Daniel, V.V. "Dielectric Relaxation", Academic Press, New York, 1967.
4. Bond, R.L. and Spencer, W.D. Proceedings of the 1957 conference on carbon (University of Buffalo), 1958, p. 357.
5. Mahajan, O.P. "Coal Structure." Meyers, R.A., Ed., Academic Press, New York, p. 65, 1982.
6. Tye, C. "Design, Building and Operation of a Differential Calorimeter." Final year project, University of Salford, U.K., April 1983.

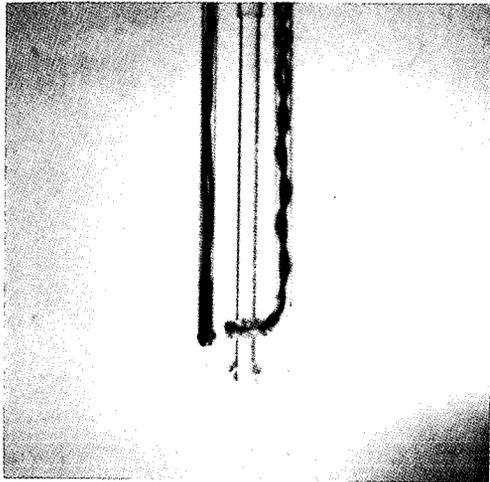


Figure 3. Shows details of one calorimeter.

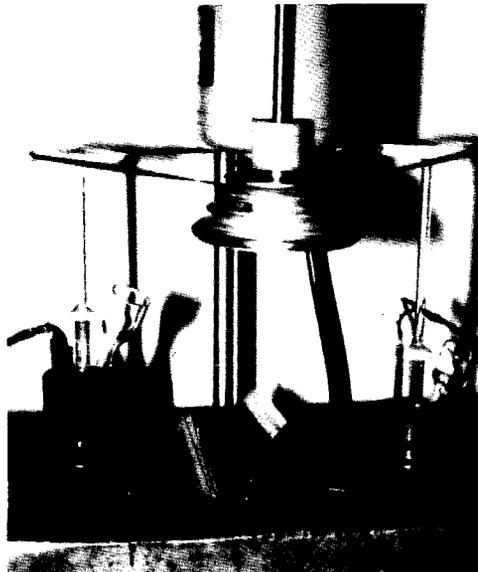


Figure 4. Shows overall differential calorimetry system.



Figure 1. The disassembled cell and a water-saturated solid sample of Gascoyne Red lignite.

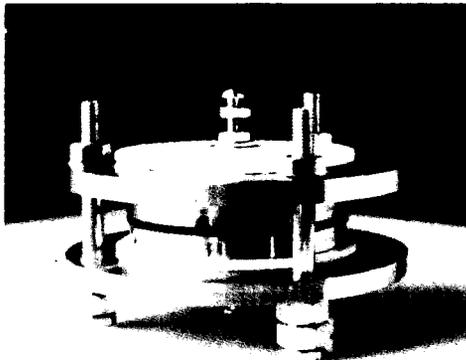


Figure 2. The assembled dielectric cell.

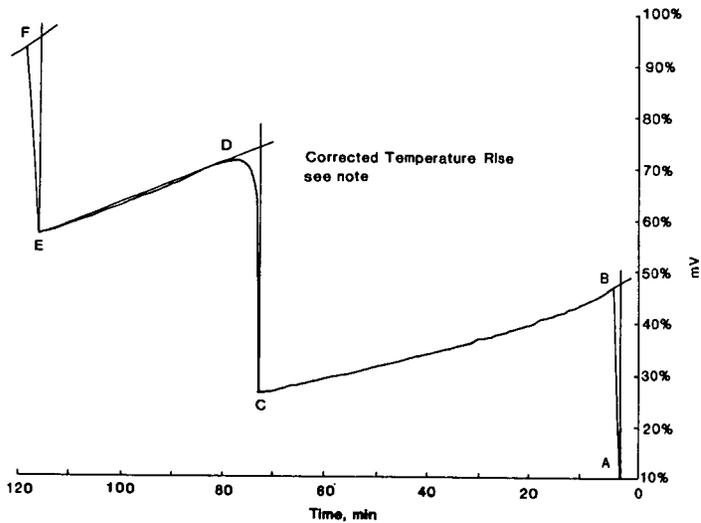


Figure 5. Trace for activated coconut shell carbon (2 mV full scale deflection 120 mm per hour).

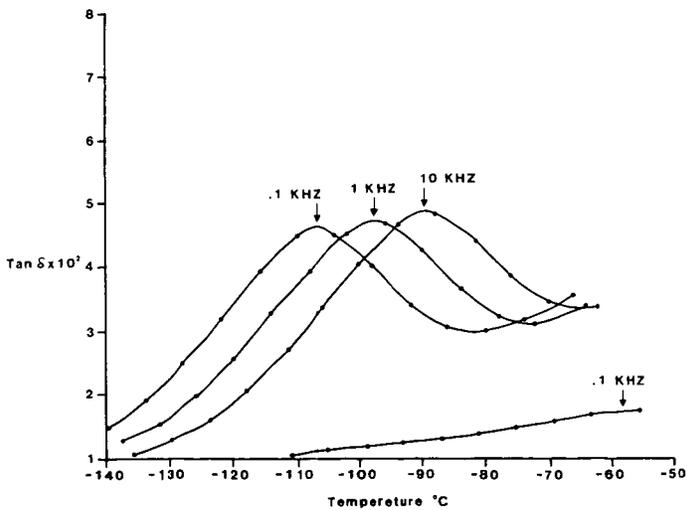


Figure 6. Phase shift vs. temperature for air-dried Yampa (Colorado) subbituminous coal.

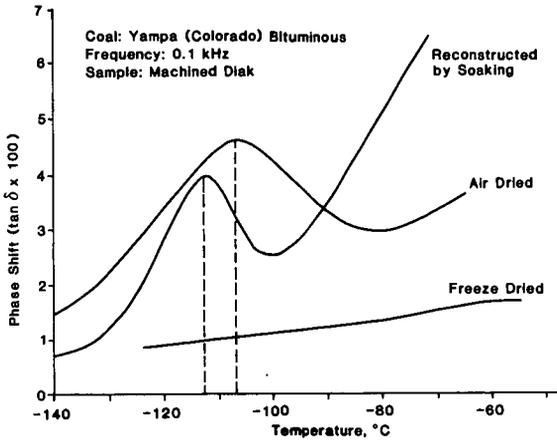


Figure 7. Dielectric characteristics of a subbituminous coal, showing effect of removal and replacement of tightly bound moisture.

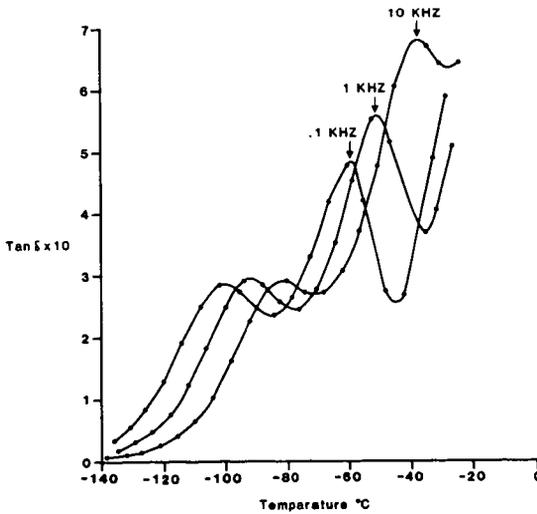


Figure 8. The temperature dependence of  $\tan \delta$  is depicted for the water-saturated Gascoyne Red lignite.

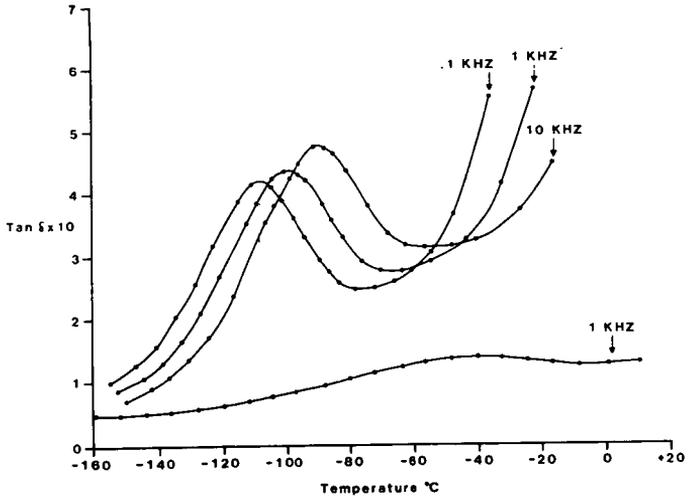


Figure 9. The temperature dependence of  $\tan \delta$  is depicted for the air-dried Gascoyne lignite. The lower (kHz) dispersion is for the freeze-dried coal.

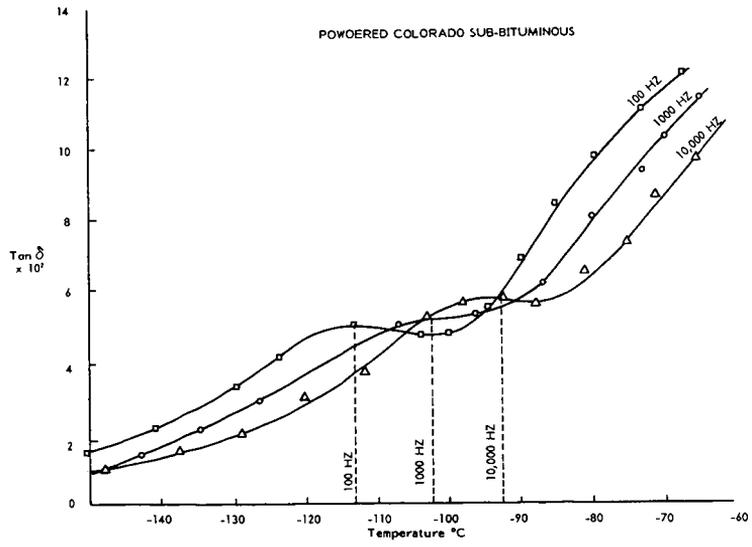


Figure 10. Spectra for powdered Yampa subbituminous.

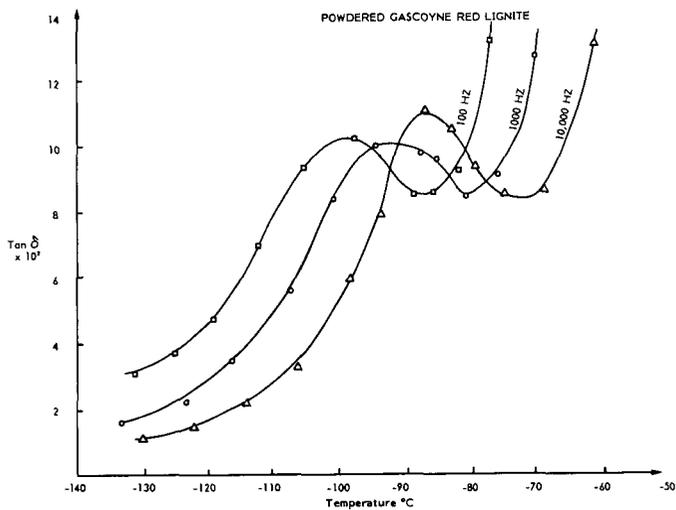


Figure 11. Spectra for powdered Gascoyne Red lignite.

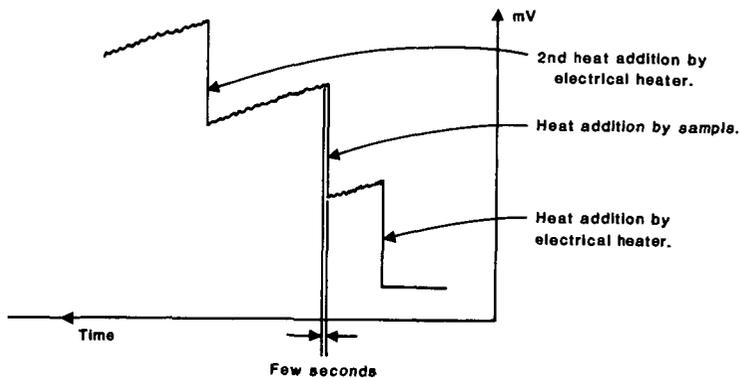


Figure 12. Characteristic of lignite type coals.

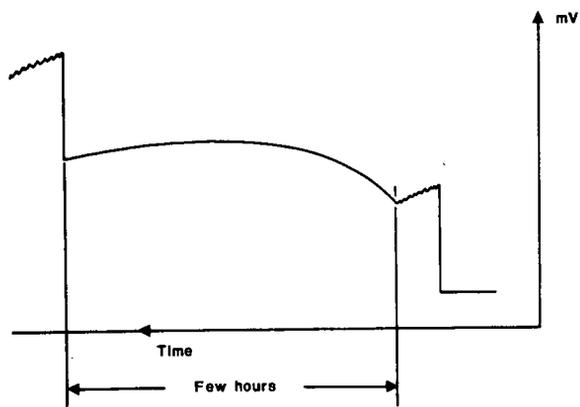


Figure 13. Characteristic of subbituminous type coals.