NATIONAL BUREAU OF STANDARDS REPORT

9049

Progress Report
on
Measurement of the Surface Area and the Heats of Wetting of Dentin Powders

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U.S. DEPARTMENT OF COMMERCE

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Measurement of the Surface Area and the Heats of Wetting of Dentin Powders

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Measurement of the Surface Area and the Heats of Wetting of Dentin Powders

Abstract

The progress report describes the measurement of the "apparent heats of immersion" of powdered dentin which was characterized by surface area measurements and determination of organic matter. The specific surface area of ground dentin which is nearly independent of particle size was found to be around 10 m^2/g. The percentage of volatile matter amounted to 30.0%. The measurement of the apparent heat of wetting of dentin gave a mean value from 5 runs of 0.894 cal/m^2 with a computed standard error of 0.040 cal/m^2 (7.96 ± 0.35 cal/g) where 1 cal = 4.1840 joules. From the magnitude of this value it appears that there may be some chemical interaction between water and the surface of the dentin.

The difference in the "apparent heat of immersion" by aqueous solutions containing ionic species or organic functional groups and the heat of wetting of dentin by pure water is indicative of any reaction of the added species with components of the tooth surface and in determining those groups that will bond effectively to tooth structure in an aqueous environment.

Introduction

It has been known for a long time that a porous body such as dentin when immersed in a chemically inert liquid liberates heat. This "apparent heat of immersion" will be changed markedly if chemical reaction take place at the surface. Thus, the difference in the "apparent heat of immersion" of tooth substance by aqueous solutions and the heat of wetting by pure water indicate that the added ionic species or functional groups present in the solution react with, or dissolve the tooth surface. Measurement of these heats of reaction should assist in developing methods for modifying tooth surface and in determining those groups that will bond effectively to components of tooth structure in an aqueous environment.

This report describes some preliminary work to determine the reactivity in aqueous solutions of dentin, enamel and well-characterized inorganic substitutes.

As an initial step in this study the specific surface, the organic content and the apparent heat of wetting of powdered dentins of different particle size have been determined.

Experimental: To obtain dentin, freshly extracted teeth were cleaned by brushing and rinsing with water. The crown was removed with a carborundum disk and necrotic tissue from the pulp chamber and canal cleaned out. No. 4 and No. 8 steel burs were then used to grind out the dentin which was then sieved for 16 hours on a mechanical shaker using 100, 200 and 325 mesh sieves. The powder passing through a No. 325 mesh sieve was put on a No. 400 mesh sieve and shaken for 6 hours. The powder was stored in a deep-freeze unit and placed in a desiccator over anhydrous calcium sulfate for at least one week before use.

The specific surface of the dentin particles was determined by the Brunauer-Emmett-Teller method [1,2]. In this technique one calculates the number of nitrogen molecules which form a monolayer. The sample of dry dentin powder was degassed at 40°C for at least 18 hours. In the determination of the area, the temperature was kept constant at 77.3°K (b.p. of liquid nitrogen) and the amount of gas absorbed was measured as the pressure was altered.

In the development of the BET equation:

$$\frac{P}{V(P_o-P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \cdot P/P_o, \text{ where}$$

V = Volume of gas at 273°K, 760 mm
P_o = Vapor pressure of gas at the temperature of adsorbent.
P = Pressure
c = Constant related to the heat of adsorption
V_m = Volume of gas adsorbed in a monolayer

it is assumed that the adsorbed molecules do not interact with each other, that the net energies of adsorption of the second and subsequent layers are equal to the heat of liquefaction and that there is no limit to the number of layers that can be adsorbed on the surface.

In Figure 1 (where n = number of micromoles per g of sample (273°K, 760 mm)) $P/P_o / n(1-P/P_o) \cdot 10^5$ versus P/P_o is plotted:

It is seen that for dentin the BET equation holds over the relative pressure range from 0.05 to 0.30. The specific surface of the particles can then be obtained from the equation:

$$\text{Specific surface} = 0.0982 \left(\frac{1}{\text{Slope + Intercept}}\right) \text{m}^2/\text{g}$$

Results of the area measurements are given in Table 1.

Table 1

Specific Surface of Dentin Powders

Particle Diameter Range	Specific Surface (m^2/g) Run 1	Run 2	Run 3	Average
mm				
.044-.074	10.5	10.4	10.7	10.6
.037-.044	11.1	9.8	-	10.5
<.037	8.67	9.25	8.67	8.9

Variations between different runs of dentin of the same particle size are not significant since the values of the specific surface measured by the BET method are considered accurate only within 10%. For the two large particle sizes the specific surface is practically the same but unexpectedly the smallest particle size dentin has a somewhat smaller specific surface. The small change of surface area with particle size is an indication of the porous nature of the dentin powders.

The percentages of organic matter in the dentin powders were determined to ascertain whether or not the organic bonds are broken more rapidly on pulverizing powders to different particle size leading to differences in the composition of the pulverized dentin. The samples were dried over anhydrous calcium sulfate and the loss of organic matter and volatiles after heating to 600°C for 3 days was determined gravimetrically (Table 2).

Table 2

Determination of Volatiles and Organic Matter in Dentin

Particle Diameter Range	Method of Drying Specimen	Method of Heating		Weight Loss, Percent			Procedure Used
		Temperature	Time	Run 1	Run 2	Avg.	
mm		°C					
.044-0.74	anhyd. $CaSO_4$	102	45 min.	2.8		2.8	TGA[c]
.044-0.74	anhyd. $CaSO_4$	1000	[b]	31.3		31.3	TGA
.044-0.74	anhyd. $CaSO_4$	600	3 days	30.3	29.9	30.1	grav.
.037-.044	anhyd. $CaSO_4$	600	3 days	30.5	29.6	30.1	grav.
<.037	anhyd. $CaSO_4$	102	45 min.	2.7		2.7	TGA
<.037	anhyd. $CaSO_4$	1000	[b]	30.1		30.1	grav.
<.037	vacuum[a]	102	45 min.	0.11	0.13	0.12	TGA
<.037	vacuum[a]	1000	[b]	28.0	26.9	27.4	TGA

[a] Approximately 3 mm/Hg for 5 days

[b] Heating rate 20°C/min.

[c] Thermogravimetric

[d] Gravimetric

The amount of volatiles and organic matter was also measured using a thermogravimetric balance. Ten to twenty milligram samples were dried over anhydrous calcium sulfate for five days or kept in a vacuum at about 3 mm/Hg pressure for five days. The samples were then heated to 102°C and maintained at this temperature for approximately 45 min. to obtain constant weight. They were then heated to 1000°C at a rate of 20°C/min. Again constant weight was obtained. Results of the percentage volatiles and organic content as obtained from the thermogravimetric analysis are also given in Table 2.

Inspection of Table 2 shows that total weight loss is independent of particle size diameter provided the specimens are dried in the same manner prior to the determination of the weight loss.

The results of the thermogravimetric weight losses with the smallest particle size powders which were used in later studies indicate that drying for five days over anhydrous calcium sulfate is insufficient to remove all sorbed water. Hence, the powders were dried in a vacuum in the determinations of the apparent heats of wetting. By such treatment the amount of water and products volatile at 100°C is reduced to about 0.1%.

Since it was assumed that the heat of immersion of dentin would be less than 10 cal/g a calorimeter of the constant temperature environment (isothermal) type was built which allowed measurement of changes in temperature of the order of 10^{-4} °C (Figure 2).

The calorimeter assembly consisted of a copper canister (A) with a screw-type lid similar to the calorimeter described by Sunner and Wadsö (3). A seal between the two units is provided by an "O" ring gasket. The can was immersed in a bath the temperature of which was kept constant within 0.002°C. The 100 cm^3 capacity glass calorimeter (B) hung from the lid of the surrounding copper can. The calorimeter contained wells for a 1500 ohm thermistor (C) serving as one arm of a Wheatstone bridge and a manganin heating wire (D). The combined glass ampoule holder and stirrer (E) was mounted in two Teflon bearings (F) and the stirrer was connected by a belt and pulley to a synchronous motor rated at 300 rpm. The ampoule holder contained two openings through which a sealed bulb (G) containing the sample could be inserted. At the desired time the bulb was broken by the solid center rod (H) which was connected to a spring. The heat evolved in breaking the bulb was less than 0.2 cal.

The electrical circuit employed in calibrating and using the calorimeter is shown in Figure 3. A ballast resistor of approximately the same resistance as the calorimeter heater was used for at least one hour or more before an experiment until the batteries reached a constant voltage. The energy dissipated = $VV_st/4.184R_s$ where

R_s = Resistance of standard resistor
V_s = Potential drop across standard resistor
V = Potential drop across heater
t = Time in seconds.

In all runs the voltages across the heater and across the standard resistor were kept within a narrow range so that the total energy dissipated varied between 3 and 4 cal (1 cal = 4.1840 joules = 4.1840 x 10^7 ergs). The time in seconds and the resistance of the standard resistor were accurately known. The observed temperature rise (as measured by the change in resistance of the thermistor) corresponding to the electrical input yielded an energy equivalent of 1.875 cal/ohm with a calculated standard error of the mean of 0.016 cal/ohm (with a 95% confidence interval of 0.041 cal/ohm for 6 runs) for this calorimeter. Since 0.005 ohms could be estimated, it was possible to detect 10^{-4} °C or 0.01 cal if the volume of water in the calorimeter was 100 ml.

The calorimeter was also calibrated by determining the endothermic heat of solution using 0.1 samples of KCl. Results of these measurements are given in Table 3.

Table 3

Heat of Solution of KCl

T = 30.2 ± 0.1C

Wt. of Sample g	ΔΩ ohm	ΔΩ/g	Heat of Solution cal/g
.1002	2.895	28.89	54.17
.1040	3.017	29.01	54.39
.1054	3.016	28.61	53.64
.1156	3.318	28.70	53.81
.1016	2.923	28.77	53.94
.1044	2.980	28.54	53.51

Avg. value: 53.91 cal/g
95% confidence limit = 0.35 cal/g;
Standard error = 0.14 cal/g.

The "best" value for the heat of dilution at infinite dilution at 25.0°C is 4115 ± 10 cal/mole [4]. Correcting for the average KCl concentration employed (1.41×10^{-2}M) by using Table XV of reference 4 gives a value of 4160 cal/mole. Since $\Delta H_{30.2°C} = \Delta H_{25.0°C} + dT\ (c_{p(solution)} - c_{p(solid)})$ where T is the temperature and c_p are the apparent molal heat capacities of the solute (-26.7 cal/deg/mole) and the crystalline solid (12.3 cal/deg/mole) a "best" value for $\Delta H_{30.2}$ of 53.1 cal/g is obtained. The 1.5% difference between the accepted and the observed value (53.9 ± 0.3 cal/g) is quite satisfactory considering that our results were obtained using much lower concentrations of KCl which will decrease the accuracy of the measurement. Since calibration with KCl requires considerably less equipment and can be handled by one person, recalibration of the equipment, which is necessary from time to time, was conducted by this method.

Figure 4 shows a typical apparent heat-of-wetting curve of dentin (dried previously in a vacuum) of 400 mesh (less than 0.037mm) particle size in 100 ml of water. The resistance of the thermistor decreases with increase in temperature. Therefore, at the time of wetting the resistance shows a sharp decrease. To obtain the corrected total change in resistance the shaded area above the curve should be equal to the area below the curve. Table 4 shows the results of the apparent heat-of-wetting determinations.

Table 4

Particle Diameter <.037 mm

Wt. of Sample	Change in Resistance ΔΩ	ΔΩ/g	Apparent Heat of Wetting	
g	ohm	ohm/g	cal/m²	erg/cm²
0.986	3.55	3.60	0.758	3173
0.988	4.23	4.28	0.902	3776
1.003	4.14	4.13	0.870	3642
1.012	4.60	4.55	0.958	4010
1.018	4.91	4.82	0.983	4115
Average:			0.894 (7.96 cal/g)	3743

Since preparation of dentin is very time-consuming about 1 g samples of particle diameter <.037 mm were employed for each run. The average value of the 5 runs is 7.96 cal/g with a standard error of 0.35 cal/g or 0.894 ± 0.040 cal/m^2 (95% confidence limit: 0.894 ± 0.110 cal/m^2) for this particle size. This is considerably higher than the heats of wetting given in the literature for inert solids which range from 7×10^{-3} to 0.15 cal/m^2 [5]. Thus, it is likely that, to some degree, the water either reacts chemically with dentin or some dissolution takes place.

The apparent heat of wetting of dentin is dependent on the method of preparation. In the present study the powders were conditioned in a vacuum desiccator. Although studies of the weight loss of such particles at 100°C indicate that the adsorbed water may not have been completely removed from the surface some dehydration of the dentin and denaturation of the collagen may have taken place in subjecting the powders to the vacuum. However, since in the subsequent studies the same empirical methods of sample preparation will be used the results of the measurement should give an indication of the reactivity of dentin under an environment approximating the oral cavity.

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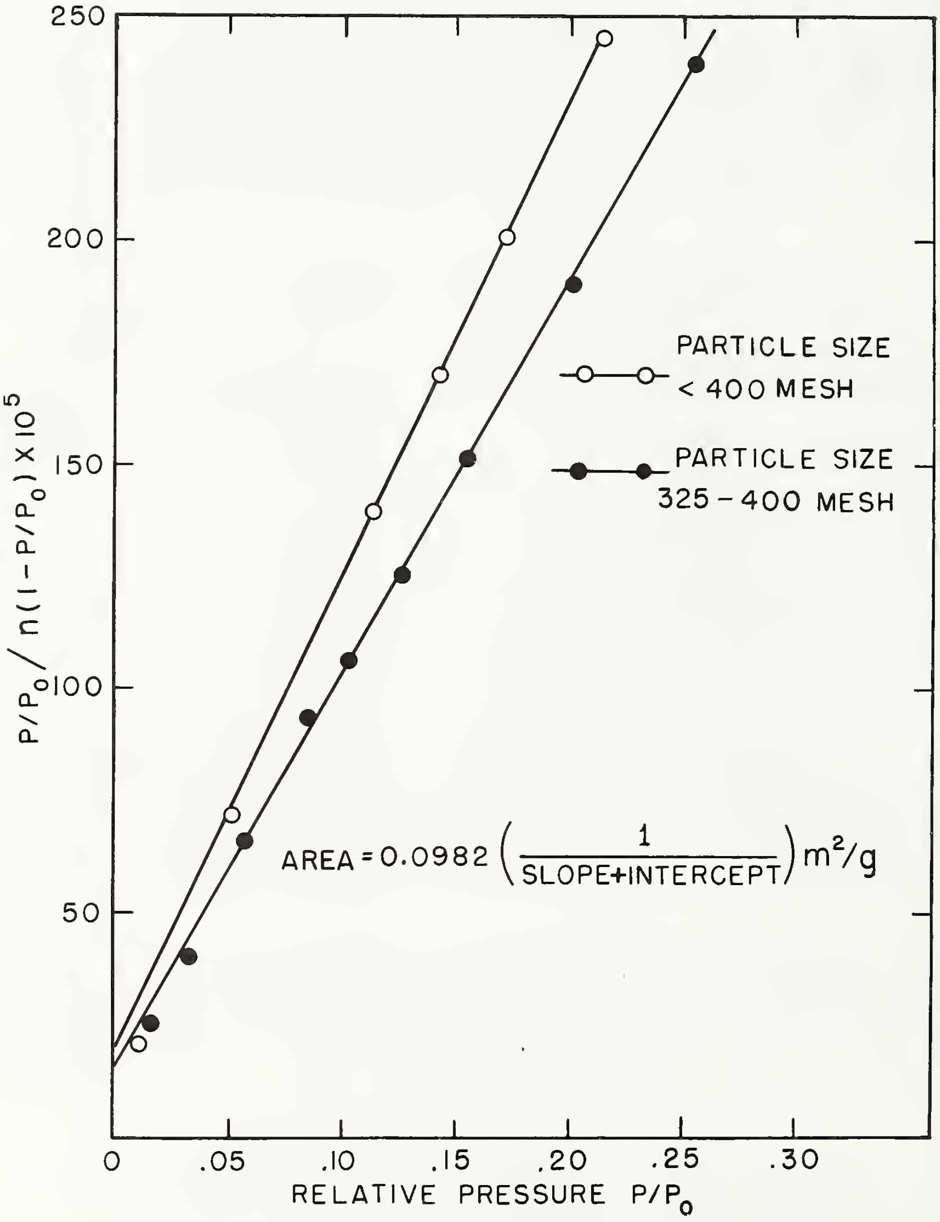

Figure 1. BET free surface plots for dentin

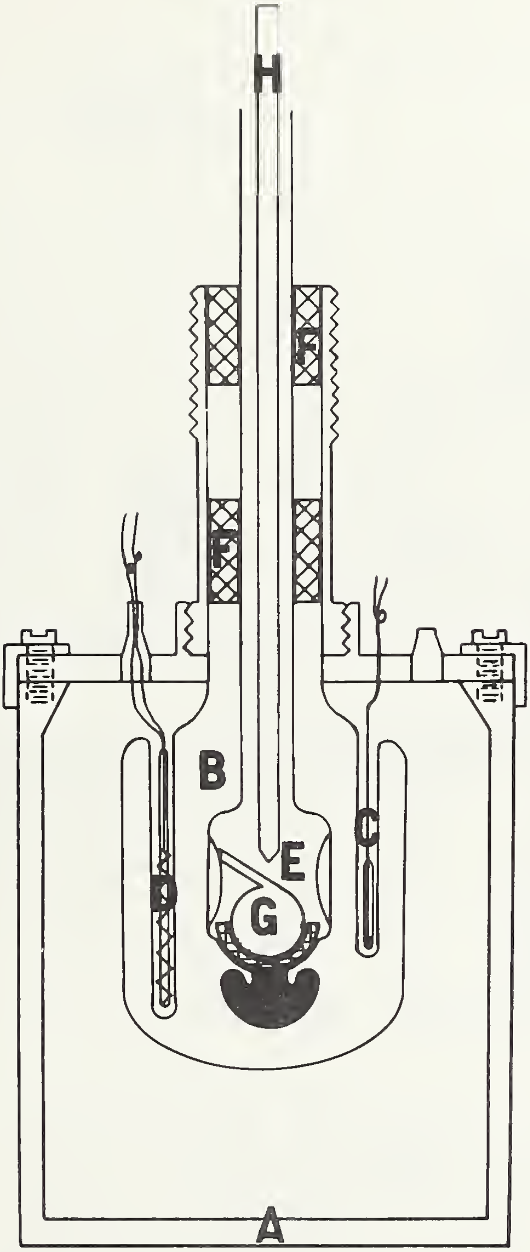

Figure 2. Calorimeter used for measuring the heat of wetting

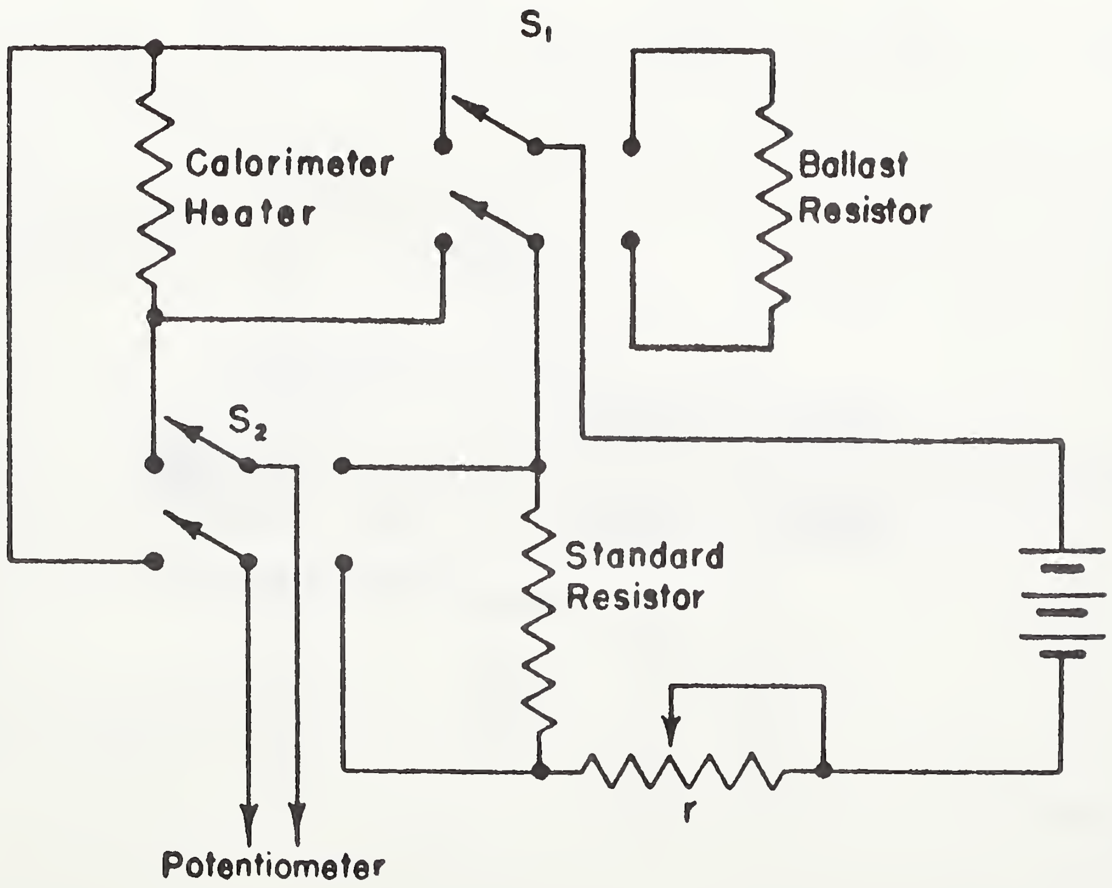

Figure 3. Calorimeter heater circuit

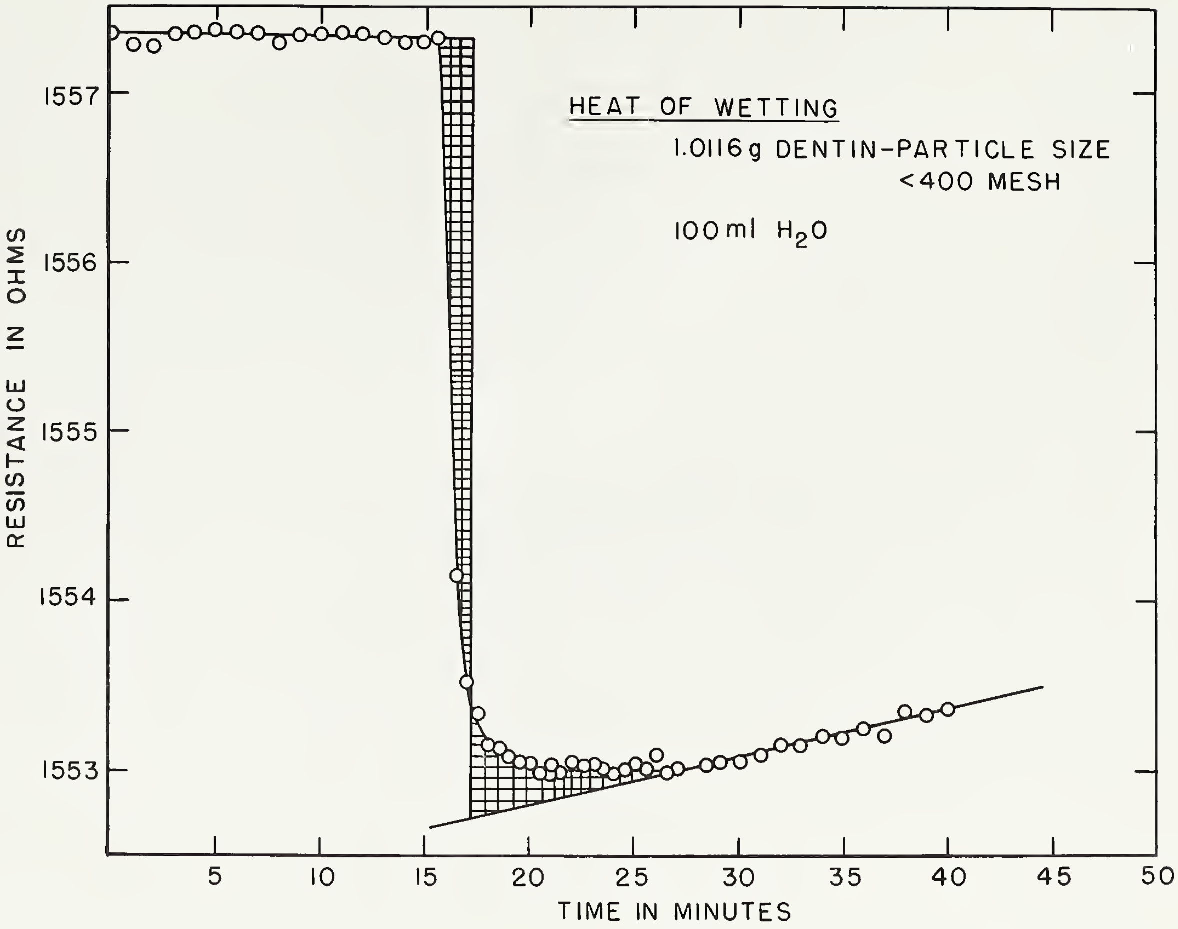

Figure 4. Typical run for the determination of the heat of wetting


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