

CONF- 890760--1

WHC-SA-0493-FP

Received by OSTI

AUG 24 1989

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WHC-SA--0493

DE89 016053

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Date Published
July 1989

To Be Presented at
31st Rocky Mountain Conference
on Analytical Chemistry
Denver, Colorado
July 30 - August 4, 1989

Prepared for the U.S. Department of Energy
Assistant Secretary for Defense Programs



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Hanford Operations and Engineering Contractor for the
U S Department of Energy under Contract DE AC06 87RL10930

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Printed in the United States of America

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QUANTITATIVE DIFFUSE REFLECTANCE INFRARED FOURIER
TRANSFORM SPECTROMETRIC STUDIES
OF CEMENTITIOUS BLENDS
WHC-SA-0493-FP

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INTRODUCTION

The effective immobilization of low-level radioactive liquid wastes in the form of grout depends on the quality of the dry cementitious blends used in the grout formulation. Variation in the mix ratios of the components of the blend can cause detrimental effects on the processing behavior of the grout slurry and the final properties of the cured grout. Thus the blends require thorough chemical characterization and monitoring by strict quality control protocols.

In an earlier work at our laboratories (Reference 1), Fourier transform infrared-transmission method has been successfully applied in the analysis of blends of cement, fly ash, and clays. However, this method involved time-consuming sample preparation resulting in slow turnaround for repetitive sampling. A practical approach to quality control requires a fast and simple method for the analysis of the blends. This paper describes a diffuse reflectance infrared Fourier transform (DRIFT) spectrometric procedure for the routine examination of neat blends consisting of cement, fly ash, clays and/or blast furnace slags.

METHOD

Dry blends of known compositions were prepared by mixing weighed amounts of the blend components (cement, fly ash, and blast furnace slag for 3-component blend; cement, fly ash, attapulgate clay, and indian red pottery clay for 4-component blend) in a Patterson-Kelly blender at a speed of 30 rpm for 23 hours. Test blends were obtained from the Dry Materials Facility at the Hanford Site located near Richland, Washington. This facility is dedicated to the receipt and blending of cementitious materials for the Hanford Grout Disposal Program.

To obtain reproducible particle size distributions, aliquots of the neat blend samples were ground in a Wig-L-Bug (Crescent Manufacturing Co., Chicago, Illinois) ball and mill grinder with two small steel balls added to facilitate grinding. After 60 seconds of grinding, the balls were removed and the Wig-L-Bug was shaken for another 60 seconds to produce a uniform dispersion of the mixture. Similarly, aliquots of neat samples of the blend components used as reference materials and KBr used either as background for diffuse reflectance

measurements or a non-absorbing matrix for the blend or blend component were also prepared in an analogous manner as the neat blends. The ground KBr was oven-dried at 110°C for at least eight hours and stored in a desiccator prior to use. Homogeneous diluted ground samples were obtained by shaking weighed amounts of the ground blend or blend component with the ground, dried KBr (100 parts KBr to one part of ground blend/blend component) in the Wig-L-Bug for five minutes without the addition of the two steel balls.

Loading of the sample into the small sampling cup (3 mm dia. by 2 mm high) of the diffuse reflectance accessory to produce repetitive particle packing was performed as follows: (1) a small plastic funnel with a stem diameter slightly greater than the diameter of the sampling cup and 5 mm high was seated on a clean plastic film; (2) using a small spatula, the funnel was filled with the ground sample to slight overflow; (3) excess sample was removed by leveling off the rim of the funnel with a glass slide; (4) the sampling cup was fitted to the funnel and by careful inversion of the funnel, the sample was transferred to the sampling cup with uniform sample packing; (5) the funnel was then removed and excess sample was leveled off the rim of the sampling cup with a glass slide. Insertion of the sampling cup into the front slider of the diffuse reflectance accessory and pushing the slider inside the accessory placed the sample directly under the large off-axis ellipsoids of the accessory.

Diffuse reflectance spectra were recorded at room temperature using an FT-IR spectrometer equipped with a triglycine sulfate detector with a resolution of 4 cm^{-1} over the mid-infrared region. One hundred scans were co-added and ratioed to a KBr background spectrum. Spectral data were displayed in diffuse absorbance units ($-\log R$ where R is the ratio of the reflectance of the sample to the reflectance of the background). This expression was used instead of the Kubelka-Munk (K-M) function (Figure 1) because the relative intensities of strong and weak bands may be distorted by the K-M function. Use of this function results in the exaggeration of strong bands while weak bands are slighted/depressed.

A sequential spectral subtraction program using the spectra of neat components of the blends as reference was used to measure the concentration of each component of the blend. By nulling bands unique to each blend component, the amount of that component can then be calculated from the relation

$$\% \text{Component} = \text{FCR} \times \frac{W_R}{W_S} \times 100$$

where FCR is the subtraction factor for the reference, W_R is the weight of the reference, and W_S is the weight of the sample. Figures 2 and 3 are illustrations of the application of the sequential spectral subtraction technique on typical blend spectra obtained by diffuse reflectance and transmission-KBr pellet methods.

The sample preparation reproducibility was evaluated using ten milled samples from the same batch of the blend. The effect of the sample area exposed to the infrared radiation was also assessed by changing the micro sampling cup (3 mm dia. by 2 mm high) to a macro sampling cup (13 mm dia. by 2 mm high). All diffuse reflectance spectra were analyzed by the sequential spectral subtraction method.

RESULTS

The K-M relationship shown in Figure 1 is the equation most commonly used to describe the reflectance from a scattering medium. However, this equation breaks down in several important situations in the mid-infrared region. Most notably, this relationship does not account for specular reflection (reflection from the front surface of a sample). A display of the K-M function treatment of the diffuse reflectance data of neat cement is presented in Figure 4. As can be seen, the K-M function accentuates the strong bands and slights the weaker bands. The results have been presented in the form of diffuse absorbance ($-\log R/R_0$; R is sample reflectance and R_0 is background reflectance) analogous to absorbance ($-\log T/T_0$; T is sample transmittance and R_0 is background transmittance). This expression allows spectral intensities to be compared according to classical concentration relations.

When a sample reflects diffusely and specularly as do all real-world samples, the specular reflection is superimposed on the diffuse reflection creating an artifact which could easily be misinterpreted as a real spectral feature. The specular reflectance component cannot be separated from the diffuse reflectance component.

One of the undesirable characteristics of diffuse reflectance when examining neat samples is oftentimes the severe distortion of strong bands due to a large opposing contribution from specular reflectance. This effect is vividly demonstrated in the spectra of neat samples of cement (Figure 5), attapulgite clay (Figure 6), indian red pottery clay (Figure 7) blast furnace slag (Figure 8), fly ash (Figure 9) and a sample of a 4-component blend (Figure 10). It is interesting to note the large number of overlapped peaks and band saturation in the 1200 cm^{-1} to 400 cm^{-1} region. The result is a broad relatively featureless region invalid for spectral interpretation.

Three distinct regions appear in the mid-infrared absorption spectra of neat samples. They are: (1) region I, 3700 cm^{-1} to 3200 cm^{-1} ; (2) region II, 2000 cm^{-1} to 1400 cm^{-1} ; and (3) region III, 1400 cm^{-1} to 400 cm^{-1} . Region I shows the various O-H band stretches from the clays and gypsum present in cement and blast furnace slag. Region II consists principally of the bending modes of water from various environments such as those of the clays and gypsum. This region also contains ripples that may be attributed to the enhancement of

weak features including overtones and combination bands. However, these enhanced bands are just as useful as the strong fundamentals for spectral analysis. For example, the three small peaks occurring in the region from 2100 cm^{-1} to 1850 cm^{-1} can serve as monitors in the determination of the concentration of indian red pottery clay. Region III (1400 cm^{-1} to 400 cm^{-1}) is very complicated. It is characterized by broad overlapping saturated bands giving a wavy absorption profile. The stretching and bending modes of the Si-O band appear in this region. The Si-O-Si species is very strongly absorbing, allowing very little penetration of the incident radiation into the sample. Because of this phenomenon, front surface reflections are much stronger causing severe distortion of the band shapes. This is clearly depicted in the absorption spectra of neat fly ash and blast furnace slag. For this reason, this region is not suitable for quantitative spectral analysis.

The effect of front-surface reflection on the quantitative measurements of cement, attapulgite clay, indian red pottery clay, and fly ash in 4-component blends was assessed by using two sizes of sampling cups for presenting samples to incident radiation. The results obtained for the macro and micro sampling cups are summarized in Tables 1 and 2. The data show that the size of the sampling cup does not affect the measurement of the concentration of cement, attapulgite clay, or indian red pottery clay in the blends. This is expected since a cursory look at Figure 10a, the diffuse reflectance spectrum of the blend, indicates no severe band distortion in Region II where the bands for monitoring cement and the clays appear. Except for enhancement of the small bands in this region, the diffuse reflectance spectrum of the neat blend resembles the transmission-KBr pellet spectrum of a 1% blend in KBr shown in Figure 10b.

Sampling cup size affects the determination of fly ash contents in blends. Values of fly ash obtained using the macro sampling cup are significantly lower than those obtained by the micro sampling cup and its known value in the blend. As noted earlier, all absorbance bands of fly ash appear in Region III, the region severely distorted by specular reflections as depicted in Figure 9a. Since the particle size distributions used for both cases (macro and micro sampling) are similar, the difference may be attributed to the morphology of fly ash. Fly ash consists of smooth, spherical particles. The smooth surfaces of the fly ash particles contribute to the poor diffuse reflectance of this material. By reducing the surface area exposed to the incident radiation, the intensity of the specular reflectance is proportionally reduced.

The effect of grinding on particle size distribution of a 3-component blend was evaluated using 10 replicate aliquots of the blend ground 30 seconds per aliquot. For comparison, another 10 replicate aliquots of the same batch of the blend were ground for 60 seconds per aliquot. The results are listed in Table 3. From the data, it is apparent that the particle size distribution of aliquots ground for 30 seconds are similar to those ground for 60 seconds.

Similarity in sample particle size distributions strongly suggest no significant change in the scattering coefficient of the blend with grinding. This also indicates that the particles are relatively hard and resistant to grinding. The good agreement of the 30-second and 60-second grinding values for each component of the blend shows high reproducibility of the sampling procedure.

Figures 5b, 5c, and 5d represent the spectra of 50% cement in KBr, 1% cement in KBr (Diffuse reflectance), and 1% cement in KBr (transmission-pellet method), respectively. Spectra of attapulgite clay, indian red pottery clay, blast furnace slag, and fly ash obtained under similar conditions as those of cement are presented in Figures 6 to 9. The spectrum of 1% blend in KBr examined by transmission-pellet method is depicted in Figure 10b.

It is evident from these figures that dilution of neat samples with a non-absorbing material such as KBr reduces specular reflections. The spectra of diluted samples recorded using diffuse reflectance have features very similar to their transmission spectra. It is important to note that as long as particle size is controlled and band absorb is weak, the diffuse reflectance spectrum matches very nearly its transmission spectrum and the K-M law is obeyed.

The agreement of the values of blend components from diluted blends obtained by diffuse reflectance and those obtained by the transmission-KBr pellet method is very good as shown in Table 4. Table 4 also compares values obtained by diffuse reflectance using both neat and diluted blends, and again the values are very similar. It is apparent that the use of a micro sampling cup for the examination of blends gives acceptable fly ash values that are within the +/-5 wt% accuracy required by quality control.

CONCLUSION

The diffuse reflectance spectra of inorganic compounds can vary dramatically when neat samples are analyzed separately rather than as dilute dispersions in a non-absorbing medium. Sample preparation is an important factor in the generation of high quality data. It is also strongly influenced by the finish of the sample surface. For multicomponent analyses, precision is improved by grinding the sample for at least 30 seconds. In spite of specular reflectance interferences, neat blend samples can be reliably analyzed by the diffuse reflectance method, provided the developed sampling preparation protocol is followed.

REFERENCE

1. T. V. Rebagay, D. A. Dodd, and R. H. Guymon; "Quantitative Analysis of Cement, Clays, and Fly Ash by Infrared Spectrometry," 28th Rocky Mountain Conference on Analytical Chemistry and Applied Spectroscopy, August, 1986.

FIGURE 1

Kubelka-Munk Equation

$$F(R) = \frac{(1-R)^2}{2R} = k / s = 2.303 ac/s$$

where $R = \frac{\text{Reflectance of Sample}}{\text{Reflectance of Background}}$

a = absorptivity

c = concentration

s = scattering coefficient

FT-IR Analysis of a Cementitious Blend: DRIFT Technique

FIGURE 2

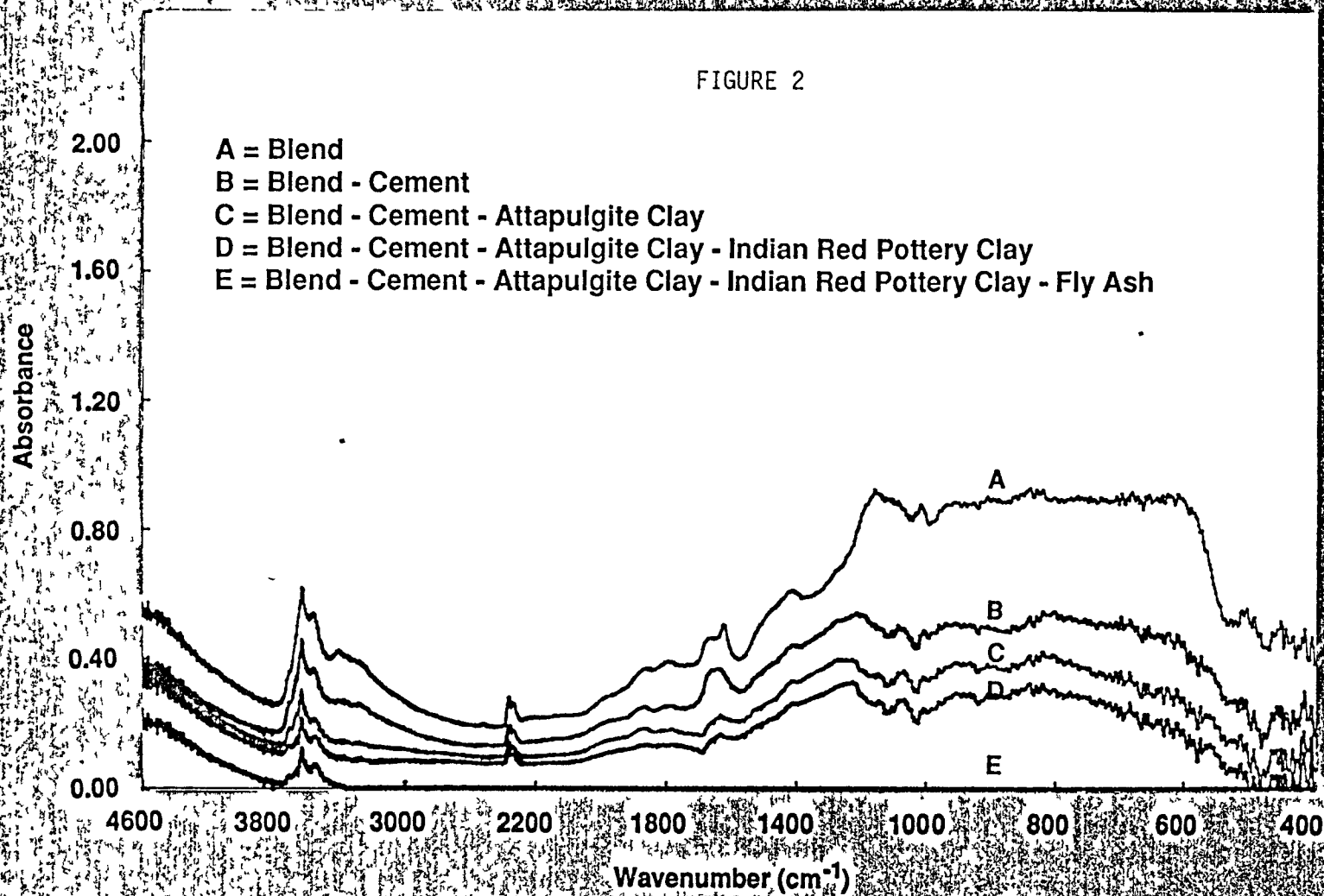


FIGURE 3

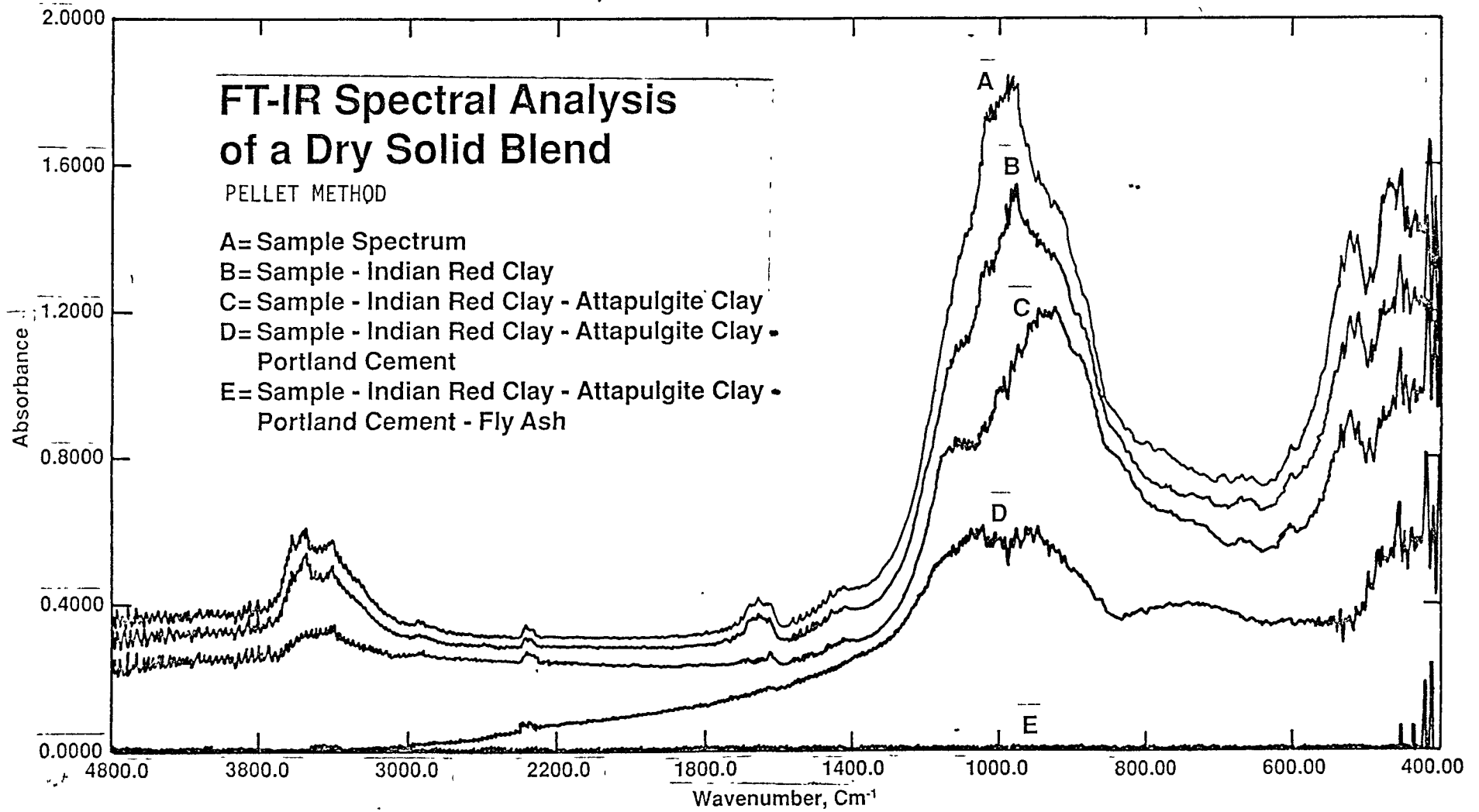
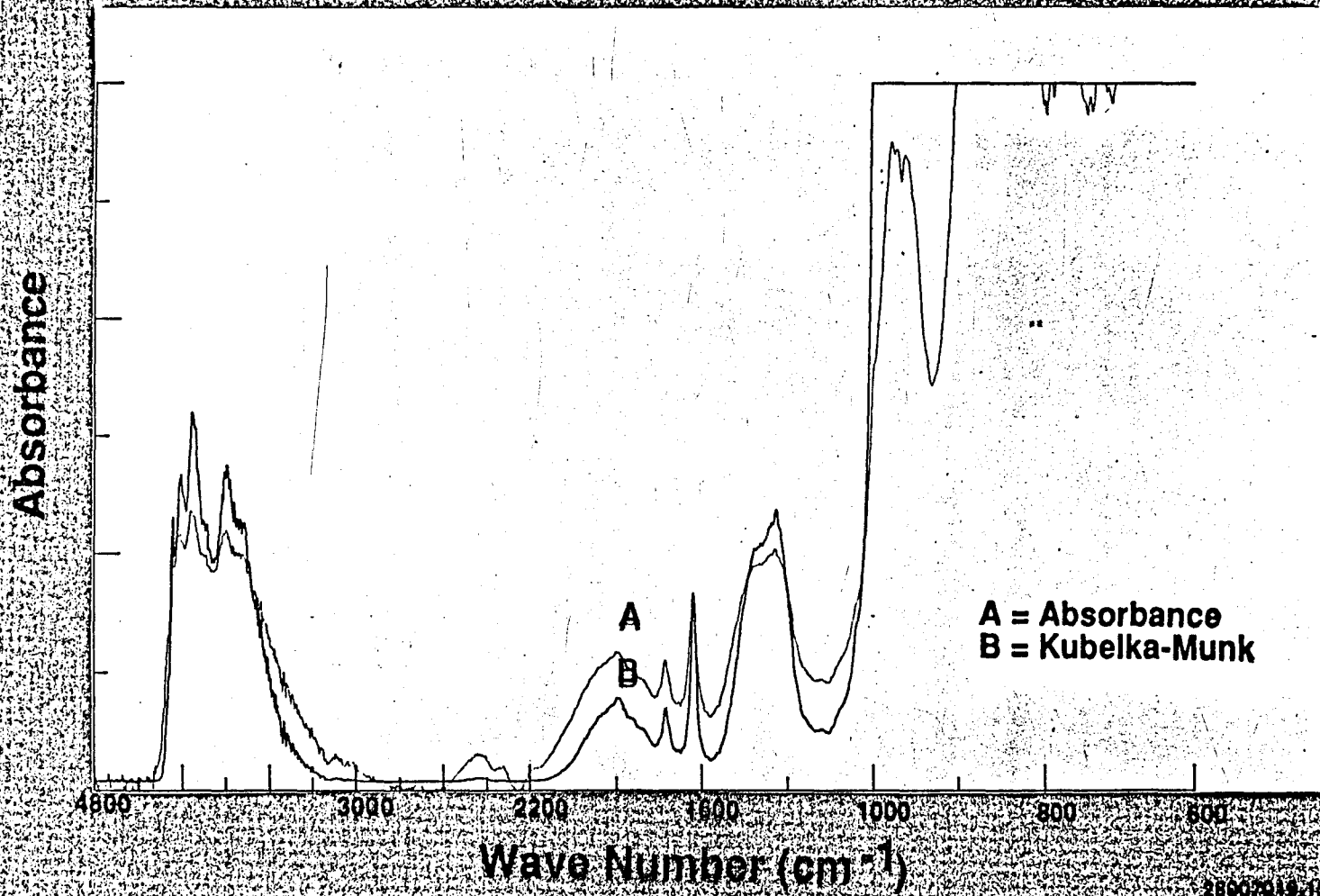
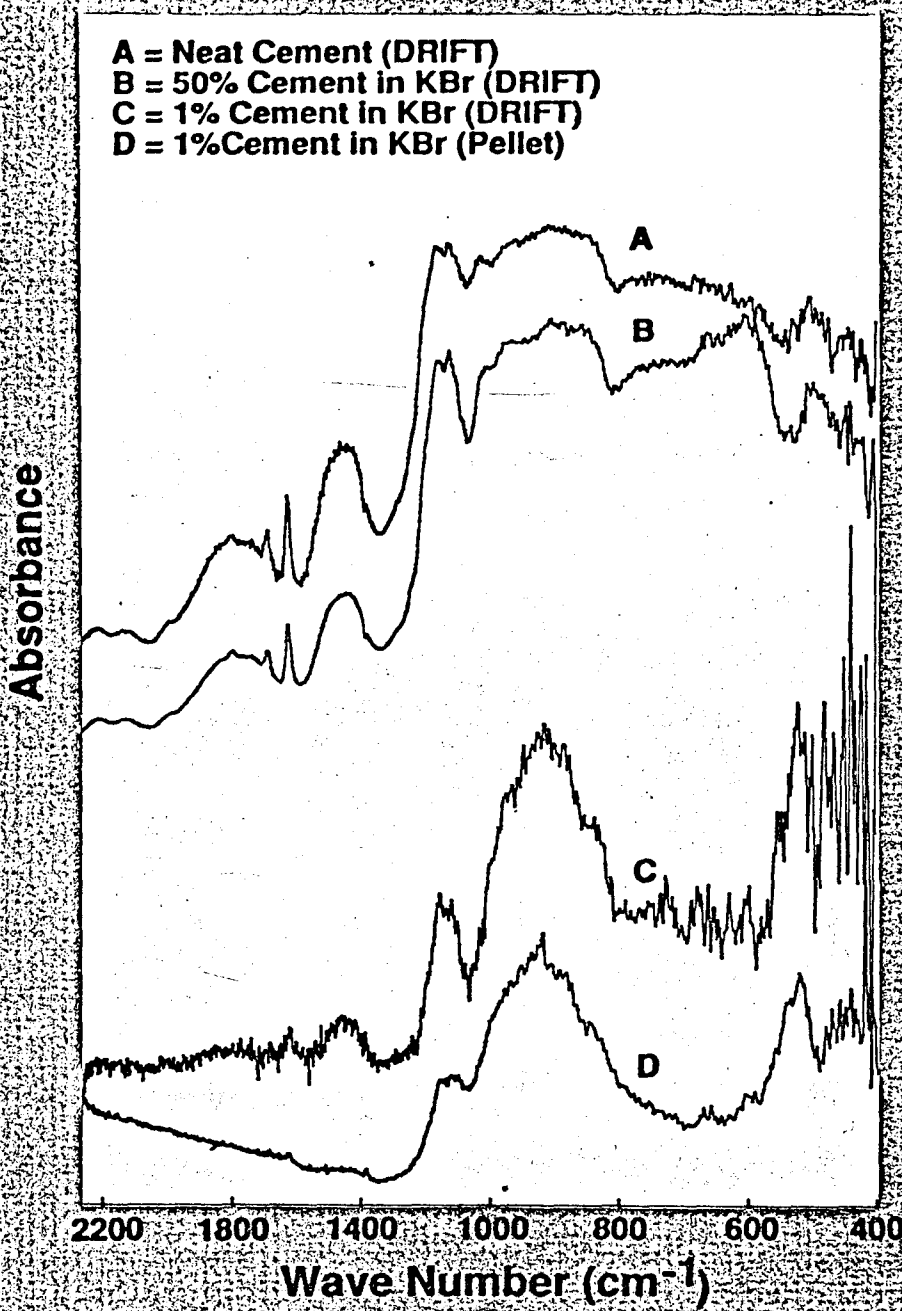


FIGURE 4

Portland Cement Kubelka-Munk vs. Absorbance

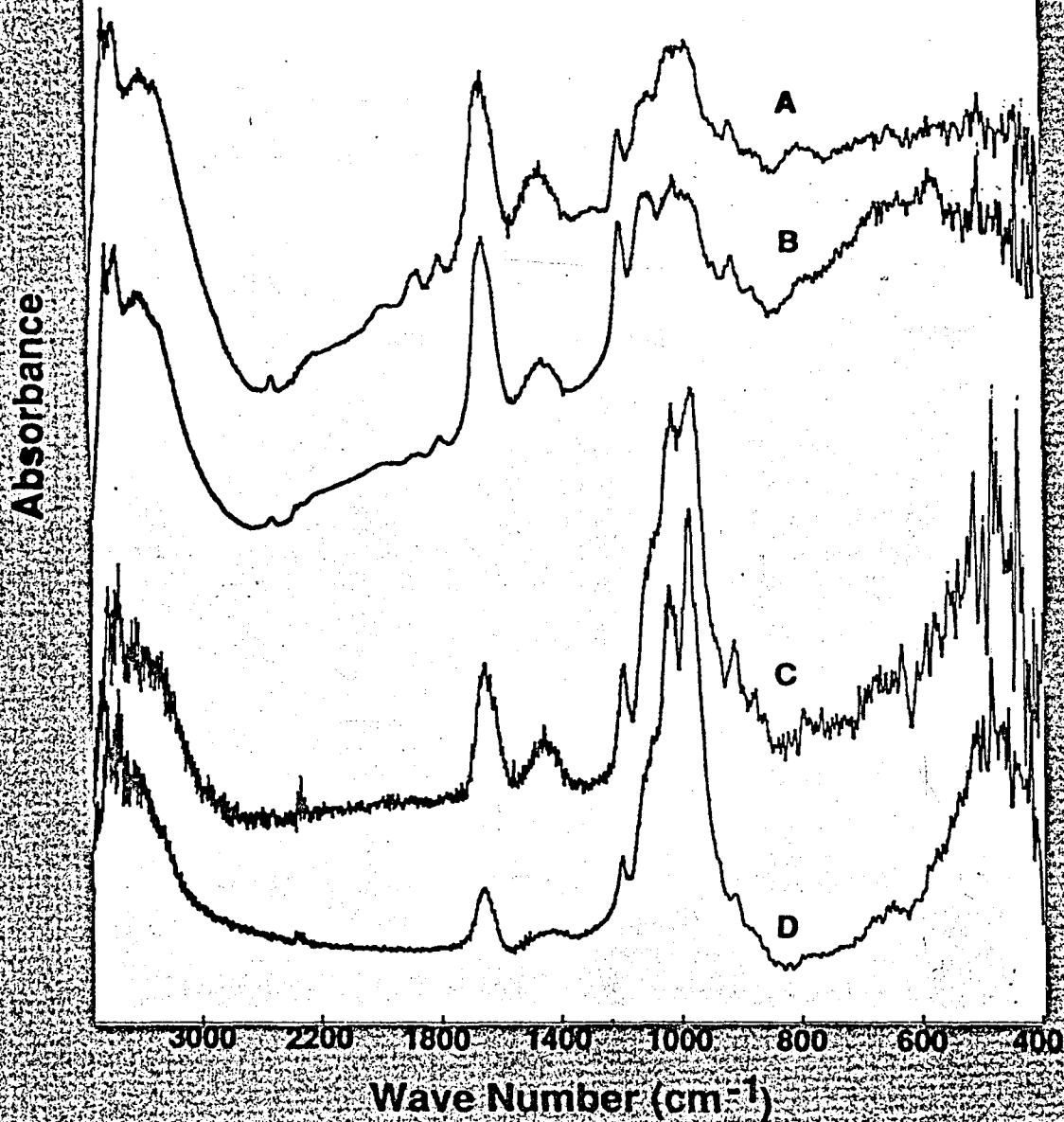


Portland Cement



Attapulgite Clay

- A = Neat Clay (DRIFT)
- B = 50% Clay in KBr (DRIFT)
- C = 1% Clay in KBr (DRIFT)
- D = 1% Clay in KBr (Pellet)



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FIGURE 7

Indian Red Pottery Clay

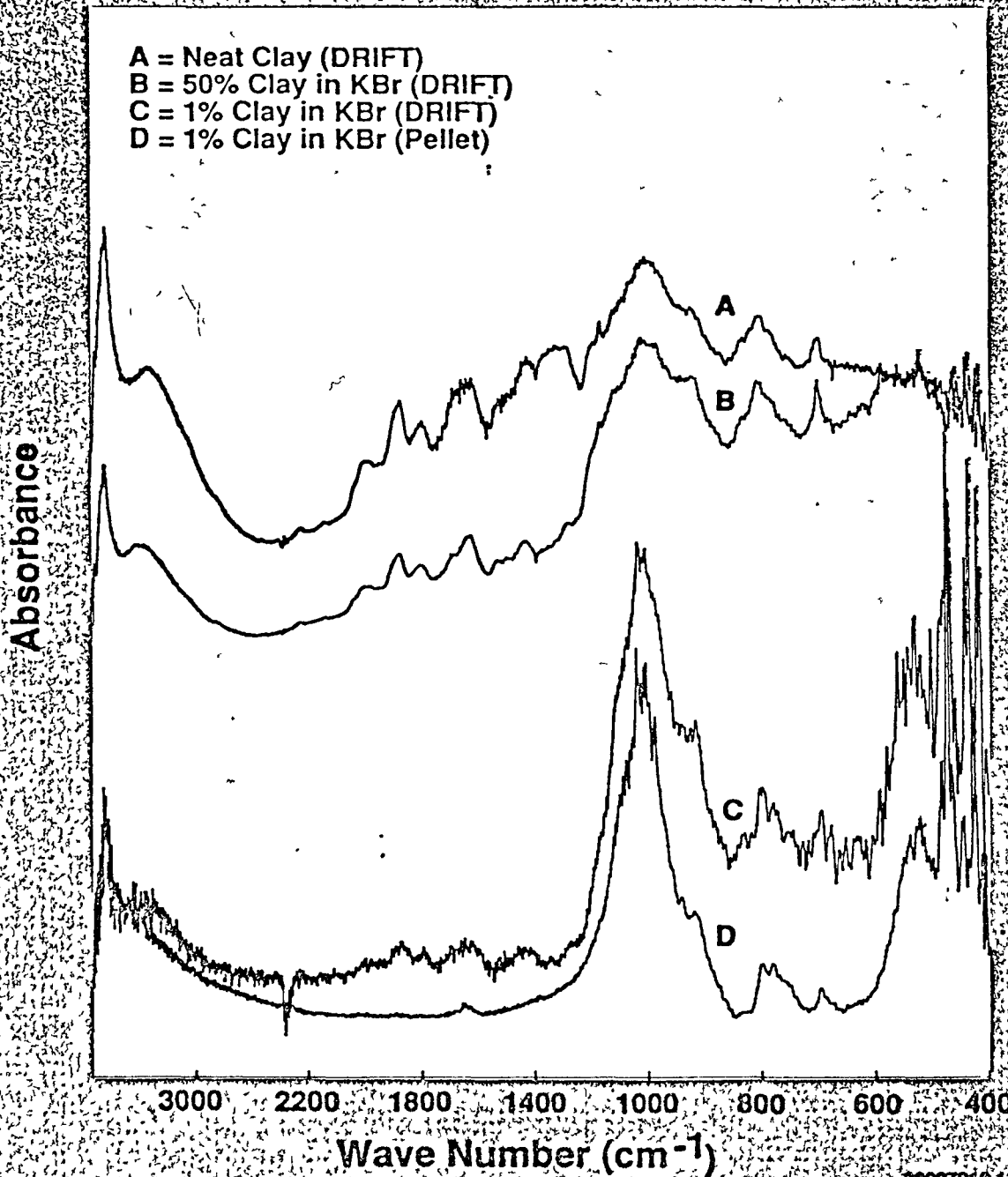
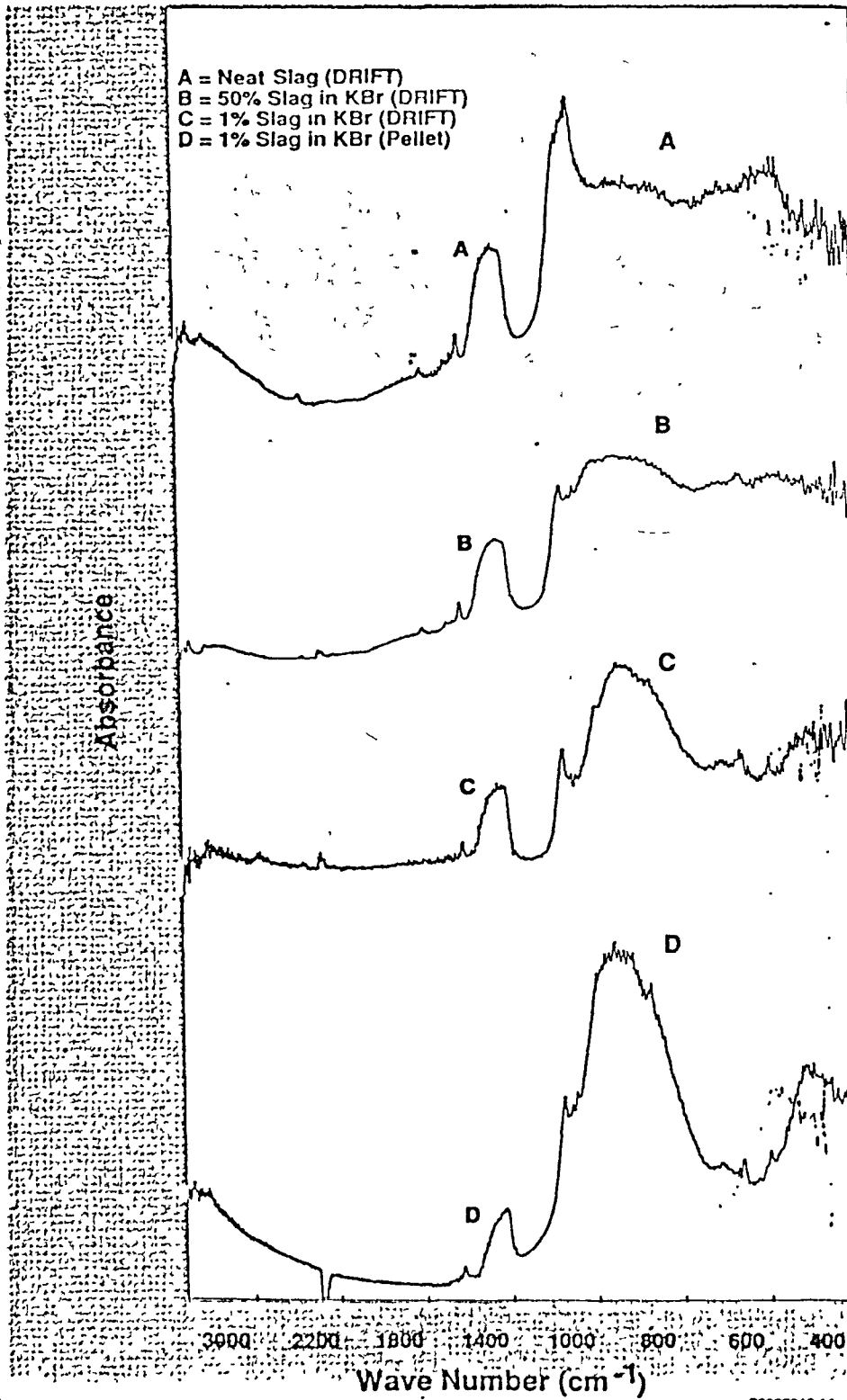


FIGURE 8

Blast Furnace Slag

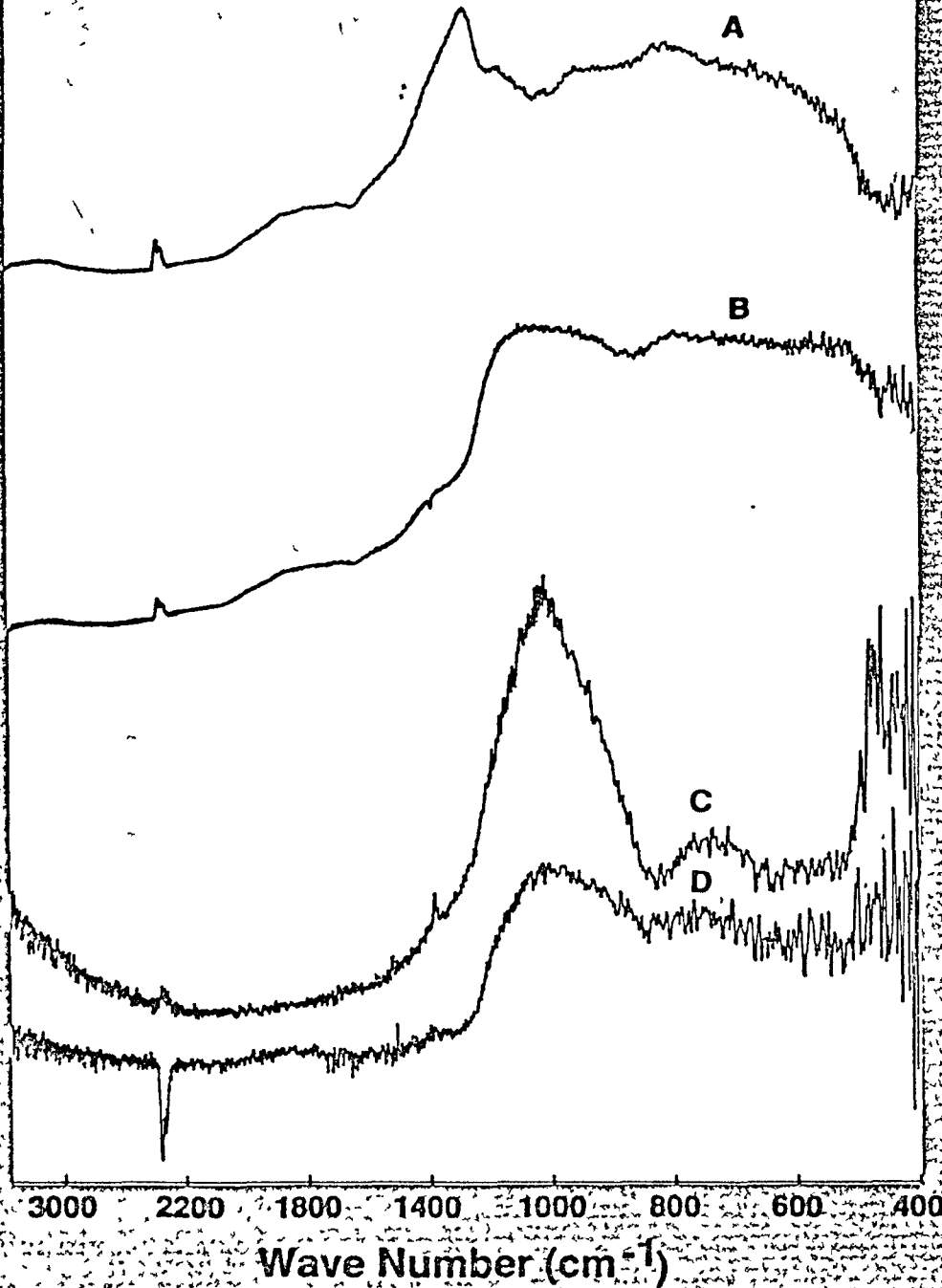


Fly Ash

FIGURE 9

Neat Fly Ash (DRIFT)
50% Fly Ash in KBr (DRIFT)
1% Fly ash in KBr (Pellet)
1% Fly in KBr (DRIFT)

Absorbance



28007019.17

FIGURE 10

4 - Component Blend

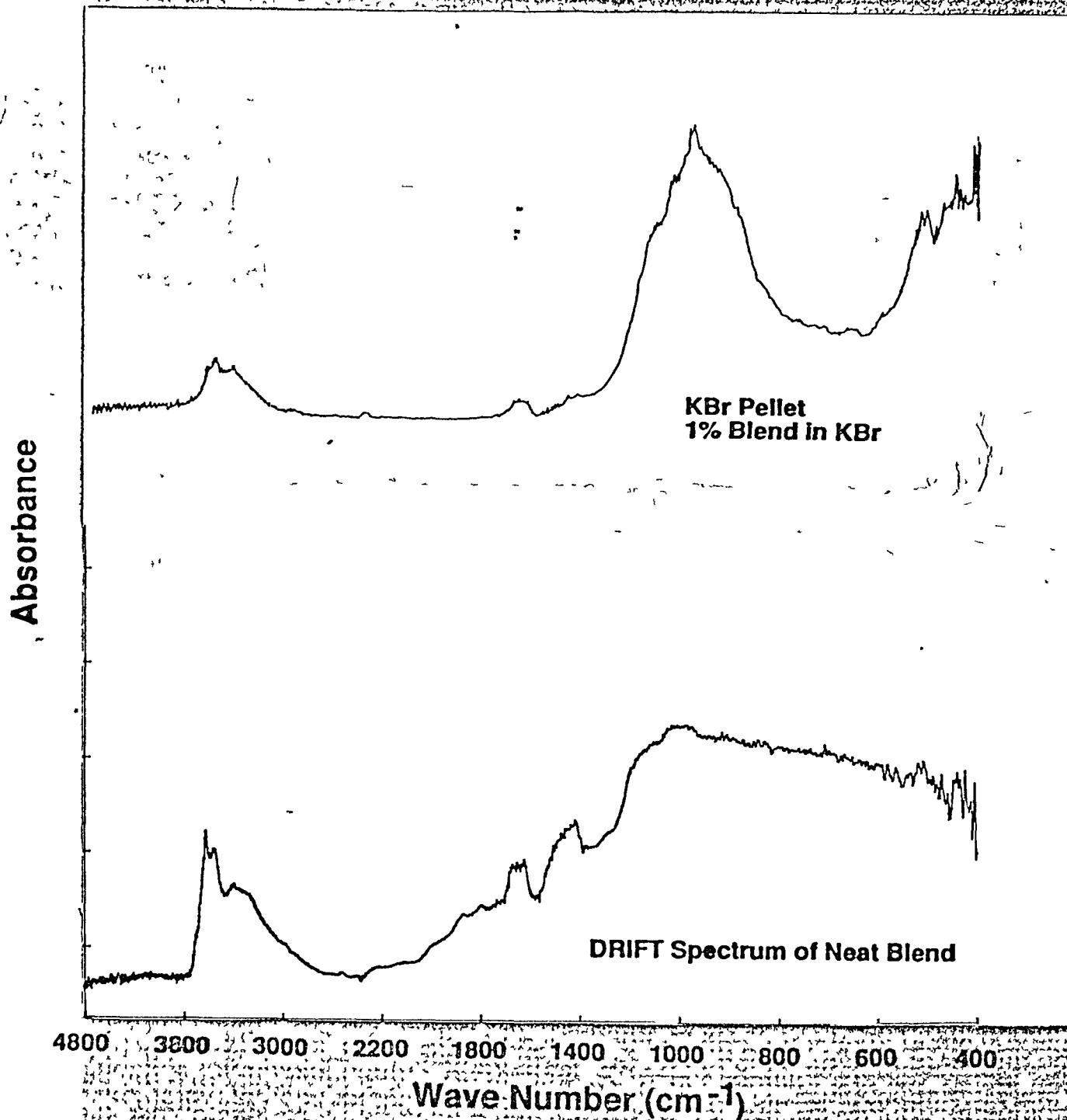


TABLE 1

Effect of Size of Sampling Cup on DRIFT Analysis of Neat 4-Component Blend*

Sampling Cup A: 13 mm dia. x 2 mm high
Sampling Cup B: 3 mm dia. x 2 mm high

<u>Trial No.</u>	<u>Indian Red Pottery Clay, wt%</u>		<u>Attapulгите Clay, wt%</u>	
	A	B	A	B
1	7.86	8.17	11.13	11.15
2	8.27	8.11	11.09	11.11
3	7.95	7.96	10.95	11.06
Average (Dev)	8.03 (0.22)	8.08 (0.11)	11.06 (0.09)	11.11 (0.05)

* Blend Composition:

8.00 wt% Indian Red Pottery Clay
11.0 wt% Attapulгите Clay

41.00 wt% Portland Cement
40.00 wt% Fly Ash

TABLE 2

Effect of Size of Sampling Cup on DRIFT Analysis of Neat 4-Component Blend*

Sampling Cup A: 13 mm dia. x 2 mm high
 Sampling Cup B: 3 mm dia. x 2 mm high

<u>Trial No.</u>	<u>Portland Cement, wt%</u>		<u>Fly Ash, wt%</u>	
	A	B	A	B
1	41.45	40.93	37.00	40.05
2	41.06	41.51	37.43	39.64
3	41.57	40.48	37.60	40.01
Average (Dev)	41.36 (0.27)	40.97 (0.52)	37.34 (0.31)	39.90 (0.23)

* Blend Composition:

41.00 wt% Portland Cement
 40.00 wt% Fly Ash

8.00 wt% Indian Red Pottery Clay
 11.0 wt% Attapulgitic Clay

TABLE 3

Effect of Grinding on Particle Size Distribution of a 3-Component Blend

Grinding Time

<u>Component</u>	<u>Number of Determinations</u>	<u>30 Seconds Average (Dev) (wt%)</u>	<u>60 Seconds Average (Dev) (wt%)</u>	<u>True Value (wt%)</u>
Cement	10	6.09 (0.08)	6.08 (0.11)	6.00
Slag	10	47.15 (0.22)	47.13 (0.23)	47.00
Fly Ash	10	47.85 (0.54)	47.17 (0.53)	47.00

FIGURE 4a

Comparison Between KBr Pellet and Diffuse Reflectance Methods in the Analysis of 4-Component Blends

Concentration, wt%

<u>Sample/Trial No.</u>	<u>KBr Pellet Method</u>	<u>Diffuse Reflectance Method</u>	
	1% Blend in KBr	1% Blend in KBr	<u>Neat</u>
Component: Indian Red Pottery Clay			
1	8.02	8.20	8.17
2	7.97	8.03	8.14
3	8.27	8.23	8.29
Average	8.09 (0.16)	8.15 (0.11)	8.20 (0.08)

FIGURE 4b

Comparison Between KBr Pellet and Diffuse Reflectance Methods in the Analysis of 4-Component Blends (Cont.)

Concentration, wt%

<u>Sample/Trial No.</u>	<u>KBr Pellet Method</u>	<u>Diffuse Reflectance Method</u>	
	1% Blend in KBr	1% Blend in KBr	<u>Neat</u>
Component: Attapulgite Clay			
1	11.14	11.08	11.22
2	10.84	11.21	10.97
3	11.01	10.84	11.07
Average	11.00 (0.15)	11.04 (0.19)	11.09 (0.13)

FIGURE 4c

Comparison Between KBr Pellet and Diffuse Reflectance Methods in the Analysis of 4-Component Blends (Cont.)

Concentration, wt%

<u>Sample/Trial No.</u>	<u>KBr Pellet Method</u>	<u>Diffuse Reflectance Method</u>	
	1% Blend in KBr	1% Blend in KBr	<u>Neat</u>
Component: Portland Cement			
1	40.62	40.63	41.15
2	41.06	41.09	41.26
3	40.27	41.35	41.32
Average	40.65 (0.40)	41.02 (0.36)	41.24 (0.09)

FIGURE 4d

Comparison Between KBr Pellet and Diffuse Reflectance Methods in the Analysis of 4-Component Blends (Cont.)

Concentration, wt%

<u>Sample/Trial No.</u>	<u>KBr Pellet Method</u> 1% Blend in KBr	<u>Diffuse Reflectance Method</u>	
		1% Blend in KBr	<u>Neat</u>
Component: Fly Ash			
1	40.35	40.14	39.56
2	40.29	40.61	40.03
3	39.90	40.00	39.54
Average	40.18 (0.24)	40.25 (0.32)	39.57 (0.28)