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SOME OBSERVATIONS REGARDING QUANTITATIVE ANALYSIS USING PHOTOACOUSTIC SPECTROSCOPY

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1. Introduction

Recent developments [1 - 4] have indicated that Photoacoustic Spectroscopy (P.A.S.) can be employed to perform quantitative analysis on a variety of solid samples. It is clear, however, that analyses utilising P.A.S. must be treated with some caution since the processes involved in signal production are not completely understood. This point is particularly relevant for powder samples since theoretical treatments of P.A.S. use a film as model for the sample. Solid samples, however, are generally most readily available in particulate form and it is most often desirable that analysis be performed without any physical or chemical changes in the analyte.

This paper presents the results of an investigation into the variation of P.A. signal with the concentration of absorbing material and also with the particle size of the sample over a wide spectral range (Visible - Mid Infra Red).

2. Experimental

A. Instrumental

The spectrometers employed in this work have been described elsewhere [4 - 6].

The spectrometer utilised for measurements in the Visible region [5] was modified by the addition of a digital data collection system as has been described elsewhere [2]. That for the Near Infra Red [4] was also similarly modified. Quantitative data was obtained by time averaged single wavelength measurements.

The Mid Infra Red data was collected utilising a commercially available cell (EDT Research, Park Royal, London, UK) with a Potassium Bromide window fitted, interfaced to an interferometric system (Nicolet Type 7199, Nicolet Instrument Corp., USA) [6]. All quantitative data was obtained from measurements of the peak heights in the spectra obtained from this system.

In all regions the spectra obtained were normalised by division with the spectrum of a sample of powdered carbon black to correct for spectral variations in the output intensity of the source.

B. Practical

In the Visible region the samples employed were a set of sieved sodium metaborate glass powders doped with cobalt chloride. Measurements of the absorptivity were taken at 605 nm.

The Near Infra Red measurements were performed on samples of a synthetic animal foodstuff containing varying amounts of adsorbed moisture. The P.A. signal due to the adsorbate was monitored at 1.93 μ.

For the Mid Infra Red region a set of samples of polyvinyl chloride containing varying amounts of vinyl acetate as co-polymer were employed. The change in signal due to the variation in the concentration of the vinyl acetate could be studied by monitoring the intensity of the carbonyl band at 1745 cm^{-1}.

3. Results and Discussion

The results obtained in the Visible region for the variation in P.A. signal with concentration of absorber is shown in Figure 1 for two different particle size ranges. It is immediately obvious that the P.A. signal increases with decreasing particle size as has been widely reported. Further, it can be seen that the pattern of behaviour changes, both curves rise steeply but, although the smaller particle size levels off into saturation, the P.A. signal from larger sized sample becomes linear in response with respect to the concentration of the absorber.

The initial steep rise in the P.A. signal is probably due to an increase in the photon flux in the upper layers of the sample caused by scattering [8]. The scattering effect will, however, diminish with increasing absorption coefficient and also with increasing particle size. Thus the effect is observed most strongly for small particles of low absorptivity where response obtained will be severely non-linear. However, for strongly absorbing, large particles the effect is negligible and a linear calibration is obtained.

Corroborative evidence for this supposition may be obtained from the results in the Near Infra Red and Mid Infra Red. As scattering power is related to wavelength (increasing as the wavelength decreases) [8] we would expect the effects of scattering to be far less severe in these regions.

Figure 2 shows a calibration for the water content of a synthetic animal feedstuff. A similar result has been reported elsewhere [4] for a ratioed measurement, however, in the present study the calibration was obtained from a single wavelength measurement (at 1.93 μm). The calibration is linear and passes through the origin, i.e. the non-linearity observed at low concentration in the Visible is not exhibited by this sample. Similar results were obtained in the Mid Infra Red for a calibration of the quantity of vinyl acetate present as co-polymer in a polyvinyl chloride powder sample. Further, the signal magnitude for the two particle sizes varies by a factor of between 200 - 300% in the Visible results, whereas in the Near Infra Red the change is only ca. 50% and in the Mid Infra Red ca. 30% over similar ranges of particle size.

4. Conclusion

From the results presented above indication that quantitative data may be obtained with relative ease for a wide variety of particulate systems despite the effects of radiation scattering. In the Infra Red region of the spectrum it would appear that scattering is not severe enough to affect quantitative measurement whilst in the near Ultra-Violet and Visible regions, suitable care with regard to selection of concentration range and particle size will permit quantitative measurements to a reasonable degree of accuracy.

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Figure 1. P.A. Signal vs. % Cobalt Chloride (w/w) for varying particle size.

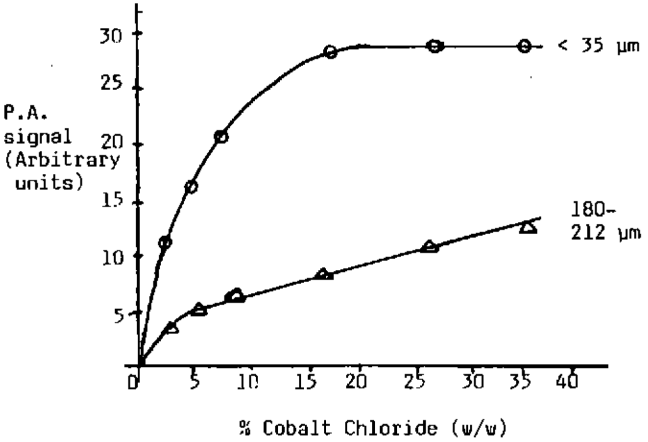

Figure 2. P.A. Signal vs. Moisture Content