COMPARATIVE STUDY OF DIFFUSE REFLECTANCE AND PHOTOACOUSTIC SPECTROSCOPY FOR POWDER SAMPLES
D. Meichenin, F. Auzel

To cite this version:
D. Meichenin, F. Auzel. COMPARETIVE STUDY OF DIFFUSE REFLECTANCE AND PHOTOACOUSTIC SPECTROSCOPY FOR POWDER SAMPLES. Journal de Physique Colloques, 1983, 44 (C6), pp.C6-151-C6-158. <10.1051/jphyscol:1983623>. <jpa-00223182>

HAL Id: jpa-00223182
https://hal.archives-ouvertes.fr/jpa-00223182
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
COMPARATIVE STUDY OF DIFFUSE REFLECTANCE AND PHOTOACOUSTIC SPECTROSCOPY FOR POWDER SAMPLES

D. Meichenin and F. Auzel
CNET, 196, rue de Paris, 92220 Bagneux, France

Abstract: A comparative study of diffuse reflectance and photoacoustic spectroscopy on powder is presented: quantitative determination of bulk absorption and sensitivity versus wavelength domain and grain diameter are discussed.

I - INTRODUCTION

Photoacoustic spectroscopy (PAS) has often been put forward as a good method to deal with powder samples. However one of the questions sometime asked about this relatively new method is: how does it compare with the older diffuse reflectance spectroscopy (DRS)? In this paper we intend to present for the first time quantitative studies and comparison between both methods applied to identical samples.

Starting from Melamed's theory [1] on diffuse absorbance of powders as a common approach to both technics, quantitative values of bulk absorption coefficient are shown to be obtained on powders by both methods, provided a number of conditions on absorption coefficient, grains diameter and index of refraction be fullfilled.

A comparative study between PAS and DRS has already been performed by Freeman et al [2] using Kubelka-Munk's theory (K.M.) to deal with diffusion both in photoacoustics and diffuse reflectance. However, this theory, as shown by the Kubelka-Munk's formula given in Kortüm [3]:

...
\[ R_\infty = 1 + \frac{K}{S} - \left[ \frac{K}{S} + 2\frac{K}{S} \right]^{1/2} \]

involves phenomenological parameters proper for relatives studies and not for absolute bulk characterization:

\[ R_\infty \] is the diffuse reflectance of a sample of infinite thickness; \( K \) is a phenomenological absorption parameter for the powder; \( S \) is a phenomenological scattering coefficient.

Though the relative spectral behaviour has been shown to be correctly described \([2]\) by PAS and DRS, of course no absolute value can be obtained for the bulk.

In another comparison between PAS and DRS in the case of opaque samples, Tilgner \([4]\) has stressed the role played by diffusion when the condition for saturation is met \((\mu_s > \mu_k; \mu_s \text{ thermal diffusion length of sample}; \mu_k \text{ optical absorption length of sample})\). Then effective absorption is reduced by scattering as shown by the occurrence of the ratio \( K/S \) in KM's formula.

In our study, in order to recover quantitative bulk values from powder sample of grain diameter \( d \) we shall use Melamed's diffusion theory which involves bulk absorption parameter. However, as we shall see, it practically requires that \( kd \leq 1 \) where \( k \) is bulk absorption and \( d \) average grain diameter.

II - MELAMED's DIFFUSION THEORY

The main difference of Melamed's theory with previous ones such as K.M. is that absolute diffuse reflectance \( R \) is obtained from properties of individual particles and not from layers of particles.

Then \( R \) can be related to bulk optical absorption for considered particles. It assumes, as for K.M., Lambertian scattering on particle surface however with a combination of Fresnel specular reflection which was neglected in K.M.
Formulation is the following:

\[ R = 2 \times \bar{m}_e + \frac{X(1-2\bar{m}_i) \times T (1-\bar{m}_e) \times R}{(1-\bar{m}_e) \times R - (1-X)(1-\bar{m}_e) \times T} \]

with \( X = 0.285/0.57 \times T \)

\[ T = (1-\bar{m}_i) \times N (1-\bar{m}_i) \times N \]

\[ N = \frac{2}{(kd)^2} \left[ 1 - (kd+1) \times e^{-kd} \right] \]

where \( \bar{m}_e \) and \( \bar{m}_i \) are respectively average value for reflection coefficient at external and internal surfaces of individual particles;

\( X \) is the probability that light emerging from a particle is scattered towards a particle one particle closer to the surface; \( T \) is transmission of each particle and average transmission of a collection of particles; \( N \) is total radiation reaching surface after one pass.

Plot of \( R \) versus \( kd \) with refraction index \( n \) as parameter is presented on Fig. 1 according to Melamed's theoretical formula \( n \) enters \( R \) through \( \bar{m}_e \) and \( \bar{m}_i \) which are given by Fresnel's law integrated on all possible angles. From these curves, it can be noted that diffuse reflectance \( R \) becomes less sensitive to \( kd \) for \( kd > 1 \) and relatively more sensitive to \( n \).

III - BULK ABSORPTION MEASUREMENT FROM POWDER SAMPLES BY DRS

Measurements are performed with a CARY 17 spectrophotometer with the double integrating sphere attachment. The two beams are first equilibrated with Magnesium Carbonate samples.

The studied samples are Schott neutral, BG 18 and RG 780 filters reduced to powder; their transmission having been previously verified on the bulk.

The powder is passed through sieves of mesh dimensions: 20, 40, 60, 75, 100, 150, 200, 500 \( \mu m \). In each class of grain the average diameter is used to compute \( kd \). The Schott glass filter used have an average refraction index of 1.5.
Diffuse reflections coefficients \((R)\) obtained at various wavelength \((\lambda)\) on the three types of filters have been measured. Results are plotted on Fig. 1 versus \(kd\) where \(k\) is the bulk measure at given \(\lambda\).

![Figure 1](image1)

Fig. 1 shows that Melamed's theory is rather well verified at small \(kd\) and that the discrepancies increased for \(kd \geq 1\). So absolute measurement of bulk absorption property can be obtained on powder by DRS.

IV - ABSOLUTE ABSORPTION MEASUREMENTS BY PAS.

In the case of Photoacoustic spectroscopy Melamed's theory gives relative values \([5]\) with \(\text{PAS} \propto (1-R_s)\) which can be transformed as we shall see to absolute ones by Melamed's theory and a calibration of the photoacoustic cell already described elsewhere \([6]\).
The calibration curve (Fig. 2) is obtained with the same powder samples as above. All measurements were performed at 20 Hz. For all \( k \), the optical length \( \mu_k \) is larger or equal to the grain diameter \( d \) and the thermal diffusion length \( \mu_s \) is estimated for a glass in bulk to be \( \approx 110 \) \( \mu \). Then, measurements correspond to the thermally and optically thin case of Rosencwaig-Gersho's theory where there is no saturation. As seen from the curve a linear relationship is found on a Log-Log plot; the slope being 0.55.

**V - DISCUSSION**

**V.1. Spectral domain for DRS**

The true reflectance value \( R_s \) of the powder layer is given by integrating sphere theory by [7]:

\[
R_s = \frac{\left[ S(1-R) + A_1 + A_2 + A_3 \right] T}{S(1-R) + A_1 T + A_2 + A_3}
\]

\( R \) is reflectivity of sphere walls.
\( A_1, A_2, A_3 \) are areas of sample, entrance, and exit ports.
\( S \) is net sphere wall area less ports.
\( T \) is reading of instrument

Knowledge of coefficient \( R \) is needed to obtain \( R_s \) and \( R \) has to be as near unity as possible in order to have a good signal and to avoid fastidious corrections.

- FIGURE 3

![Graph](image-url)
In fact as seen from Fig. 3 R is far from being even constant with wavelength. Practically MgO, BaSO₄ coatings uses are limited to visible and near infra-red domain. On the other hand, detectors have to be changed: a photomultiplier and a PbS cell are respectively used.

V.2. Spectral domain for PAS.

In the case of PAS spectral domain is restricted by source emissivity, and absorption of the wall and window of PAS cell. Practically these restrictions can be alleviated by a careful choice of the cell materials. Also saturation of PAS signal for high k allows to find more easily a black reference for PAS than a white reference for DRS. Consequences are that useful spectral domain of PAS is much larger and not limited at all by detectors than the DRS one.

V.3. Sensitivity comparison between PAS and DRS in two spectral ranges

PAS and DRS spectra have been obtained around 0.65 μm and 1.5 μm for two types of glass materials: a germanate glass doped with Er₂O₃ and an aluminoborate glass doped with 1.6% of Er₂O₃. Both were ground to powder of average grain diameter \( \bar{d} = 20 \) μm.

Figures 4, 5 and 6, 7 give spectra for different Er₂O₃ concentration...
for both glasses which differ essentially by their quantum yield: For example they are for the 1.5 μ transition 2.8 % and 76.5 % for respectively the aluminoborate and germanate glass [9] at a doping level of 1.6 10⁻²⁰ cm⁻³.

The sensitivity limit for PAS and DRS as well is taken as a point where signal/noise (S/N) ratio is unity when concentration of Er³⁺ is reduced. Measured values are given in Table I:

**SENSITIVITY COMPARISON FOR Er³⁺ DOPED GERMANATE GLASS**

<table>
<thead>
<tr>
<th>Spectral Domain</th>
<th>PAS</th>
<th>DRS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pin</td>
<td>C_{Er³⁺}(S/N=1)</td>
</tr>
<tr>
<td>1.5 μm</td>
<td>9 mW</td>
<td>2.6 % (n=0.5)</td>
</tr>
<tr>
<td>0.65 μm</td>
<td>6 mW</td>
<td>2.6 % (n=0)</td>
</tr>
</tbody>
</table>

Experimental conditions for sensitivity limits measurements were the following:

- sensitivity of PAS cell with carbon black sample = 0.5 mV/mW
- Minimum detected power with this sample is < 16.5 μW that is 3.5 μV_r.m.s. at the output of the microphone (type EM35 BF from L.E.M. France) [8].
- Quantum efficiency variations with Er³⁺ concentration is taken into account [9].
VI - CONCLUSION

This study has shown that both PAS and DRS can provide absolute $k$ values of bulk from powder sample provided Melamed's theory can be applied. Advantages of PAS over DRS can be summerized as follow:
- useful spectral domain of PAS is larger
- sensitivity limits is of same order as for DRS in the near I.R. with our experimental conditions. However, it should be noted that sensitivity of our cell was not at its best with 0.5 mV/mW: values quoted in the literature are around 2 mV/mW [10] and reach 6 mV/mW [11].

Then, with PAS a better sensitivity than with DRS can be expected in the near I.R. provided a slightly better cell as well as a larger input power be used, conditions which could be readily obtained.
- quantity of sample material required is much smaller for PAS than for DRS.

REFERENCES

1 N.T. Melamed, J. Appl. Phys. (1963) 34, 560
7 Instruction Manual for cell-space total diffuse reflectance Accessory, Varian Instrument division, n° 01-017 R170
8 for microphone EM35BF, sensitivity is 7.5 mV/Pa and NEP = 31dB/S (LEM-France, 127 Av République - 92320 Chatillon - France).
9 F. Auzel, Ann. Telecom (1969), 24, 199
10 P. Poulet, thèse Strasbourg 1980
11 D.M. Munroe, M.S. Reichard, Application note 147 PAR Corporation.