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To cite this version:

R. Davidson. THE CONTRIBUTION OF PHOTOACOUSTIC AND PHOTOTHERMAL SPECTROSCOPY TO SURFACE CHEMISTRY : ADSORBED SPECIES, CATALYSIS AND CORROSION. Journal de Physique Colloques, 1983, 44 (C6), pp.C6-267-C6-274. <10.1051/jphyscol:1983642>. <jpa-00223201>

HAL Id: jpa-00223201
https://hal.archives-ouvertes.fr/jpa-00223201
Submitted on 1 Jan 1983

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THE CONTRIBUTION OF PHOTOACOUSTIC AND PHOTOTHERMAL SPECTROSCOPY TO SURFACE CHEMISTRY: ADSORBED SPECIES, CATALYSIS AND CORROSION

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Abstract - Photoacoustic spectra of dyes on the surface of wool and inert supports are described. The problems caused by internal reflection and the penetration of the material by the dyes are discussed. Photoacoustic spectroscopy is especially useful for the study of precious metals adsorbed on the surface of TiO₂ and WO₃. These materials are useful for harnessing solar energy. In situ examination of semiconductor electrodes is possible by the techniques of photoacoustic and photothermal spectroscopy and some results are outlined.

The availability of commercial UV/visible photoacoustic spectrometers together with the many apparent advantages of PAS over other forms of spectroscopy has led to a wide range of applications of the technique. The applications to surface chemistry fall into two main categories. Many studies have been associated with identification of species on the surface whereas others have been concerned with quantifying the relationship between signal intensity and the concentration of material adsorbed upon the surface.

A common, everyday example of species adsorbed on surfaces, is that of dyed fabrics. The assessment of colour is a highly subjective process and is usually based on measurements made by reflectance spectroscopy. Fig. 1 shows the reflectance spectra for two blue dyes (CI reactive Blue 177 and 50) applied to wool and in Fig. 2 the corresponding PA spectra are shown. There is no doubt as to the value of PAS in giving high quality spectra and consequently the technique is of value in the identification of dyes on the surface of fibres. The quality of the PA spectra is such that reasonably well-resolved spectra of some two and three-dye component mixtures have been recorded. The lack of resolution in the reflectance spectra can be overcome if corrections for reflectance are applied. However, when one embarks upon such an exercise one is not sure as to the extent to which the resultant data reflect mathematical manipulation. Figures 1 and 2 serve to emphasise the point that photoacoustic spectra are less prone to distortion due to problems associated with internal reflection. Similar results have been obtained with other dyes. Fig. 3 shows the photoacoustic spectra of Acid Blue 224 applied to wool. As can be readily seen, there is not a simple linear relationship between signal intensity and concentration of applied dye. For all the concentrations studied, well resolved spectra were obtained and consequently the lack of a linear relationship cannot be attributed to...
Fig. 1 Reflectance spectra of dyes on wool

Fig. 2. PA Spectra of dyes on wool
saturation effects. The question therefore arises as to whether the lack of a linear relationship is due to the way in which the dye is taken up by the wool (e.g. the extent of penetration of the wool by the dye) or whether it is a phenomenon associated with PAS.

Fig. 3 PA spectra of Acid Blue 224 on wool

Fig. 4 PA Spectra of Lanasol Blue on Silica
To probe this question, we studied the adsorption of dyes upon inert supports e.g. silica. Dyes adsorbed on silica gave well-resolved spectra(e.g. Fig. 4) and yet in many cases the relationship between signal amplitude and concentration of dye was non-linear (e.g. see Fig. 5).

![Fig. 5 Plots of signal amplitude versus concentration of dye for samples of dyes adsorbed on silica](image1)

To check that the non-linearity is not due to the aggregation of dyes on the surface of the support a study was made of dyes adsorbed upon ion exchange resins and the results are shown in Fig. 6.

![Fig. 6 Plots of signal intensity versus dye concentration for samples of dyes adsorbed on ion-exchange resins](image2)
We conclude, in agreement with Kirkbright and Spillane\(^5\) and Burggraf and Leyden\(^7\) that light scattering effects play an important part. There is also another possible contributory effect and that is that the dyes permeate the structures to which they are applied. The signal coming from dye molecules within the support material will have a different phase to that coming from molecules adsorbed upon the surface. A study of potassium dichromate adsorbed on various supports indicates that permeation of the support structure can have a drastic effect upon photoacoustic spectra\(^9\).

Photoacoustic spectroscopy can also be used to study the loading of various supports by precious metals\(^2\). The application of platinum to semiconductors is of particular interest in the context of the usefulness of such materials for harnessing solar energy\(^1\). Figure 7 shows some results obtained with platinised titanium dioxide. The presence of platinum is readily detected, but once again the relationship between loading and signal intensity is non-linear. This effect is particularly marked with platinised tungsten oxide (Fig. 8) where loading above a certain limit leads to a decrease in signal intensity. Loading a support with a metal is very different to loading it with dye since metals such as platinum are excellent conductors of heat. Thus the presence of a metal on the surface will affect the heat transfer properties of the material. A further complication could be due to the platinisation process producing free platinum aggregates rather than surface adsorbed platinum. Examination of the samples by microscopy (SEM) showed that at the higher metal loadings platinum aggregates were forming. To overcome this problem platinum was applied to an ion exchange resin. As can be seen from Fig. 9 the obviation of aggregation leads to a more normal response between signal intensity and extent of loading.

The photoelectrochemistry of semiconductors is of particular interest to those examining ways for harnessing solar energy\(^1\). PAS is particularly useful for measuring band gap energies of particulate semiconductors\(^2\). Fujishima and Honda\(^3\) have developed an elegant way of studying the changes in absorption spectra at electrode surfaces in situ using PAS. Their method hinges on the fact that absorption of light by a semiconductor applied to a metal electrode will lead to heat being emitted by the metal. If the emitting surface is part of a hermetically sealed cell, one side of which is a microphone diaphragm, a
Fig. 8. PAS of platinised WO₃ samples. (Modulation frequency 80Hz)

Fig. 9. PAS of platinised anion exchange resin samples. (Modulation frequency 80Hz)
photoacoustic signal will be observed (Fig. 10). This method has been used with great success. The corrosion of cadmium sulphide was studied in this way. The precipitation of cadmium was demonstrated by the loss of the characteristic band edge absorption and its replacement by a species absorbing over the monitored range (400-700nm). These spectroscopic results matched those obtained by classical electrochemical methods.

Bard et al have developed the technique of photothermal spectroscopy to measure the temperature changes attendant upon irradiation of semiconductor electrodes. In this technique a sensitive thermistor is affixed to the rear of the electrode. Upon light absorption, heat is generated and this is monitored by the thermistor. By measuring the heat evolved and the extent of electrochemical reactions taking place, the quantum efficiencies of various electrodes have been determined. This method can also be used to measure adsorption changes at electrode surfaces which result from electrochemical action, e.g. the electrochemical deposition of copper on gold.

Acknowledgement. It is a pleasure to acknowledge the support given by my colleagues (D. King, C.L. Morrison), the Wool Foundation (P.A. Duffield and D.M. Lewis) and the SERC.

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