

## APPLICATIONS OF PHOTOACOUSTIC AND DIFFUSE REFLECTANCE SPECTROSCOPY IN MINERALS FLOTATION

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**Résumé** - La spectroscopie photoacoustique (PAS) et la spectroscopie par réflexion diffuse (DRS) nous ont servi à mesurer la concentration superficielle du cuivre à la surface de poudres de sulfure de zinc ou de blende. Les appareillages ont été préalablement testés sur un système modèle (colorants adsorbés sur de la silice).

**Abstract** - Photoacoustic spectroscopy (PAS) and diffuse reflectance spectroscopy (DRS) have been used to get the surface concentration of copper on powders of zinc sulfide or sphalerites. Spectrometers were first tested on a model system (dyes adsorbed on silica).

Industrial flotation of ZnS by xanthates usually requires activation by copper ions, that is presence of copper at the surface of the zinc sulfide. Copper can come from Cu(II) ions added to the solution for that purpose (industrial activation by copper sulfate), or from copper minerals present in the ore (natural activation generally unwanted in selective flotation process). This presence improves the natural flotability of the ore in water by a mechanism which will not be discussed here. The important point for us is that the surface concentration of the copper must be carefully controlled because an excess can be damaging for the following steps in selective flotation processes.

Direct and quantitative measurements of adsorption isotherms are difficult. Some techniques such as IR or ESCA require dry samples or high vacuum conditions which disturb adsorption equilibrium and quantitative performances are not yet so good. Among the few possible means of investigation, visible spectroscopy by diffuse reflectance measurements (DRS), photoacoustic measurements (PAS) or photothermal deflection measurements (mirage spectroscopy) seem the best. PAS and DRS are now routine techniques and measurements can be performed on undried powders. However, samples are still in contact with air. Mirage spectroscopy used in a subsequent paper of this issue by V. PLICHON and N. ROLLAT, is still a laboratory technique. But it presents the advantage to work directly at the powder-water interface, that is in conditions much more similar to flotation conditions.

It must be pointed out that only relative measurements are obtained with all three techniques and before we experimented them on sphalerite, we tested them on a model system of dyes adsorbed on silica with known surface concentrations(1).

I - SPECTRA OF METHYLENE BLUE AND MALACHITE GREEN ADSORBED ON SILICA

Spectra of methylene blue and malachite green adsorbed on silica at various surface concentrations are represented on Fig. 1 for PAS and Fig. 2 for DRS. Following results were obtained, detailed for PAS in ref(1) :

- from the wavelength of the absorption maximum (Fig. 1), one can conclude from PAS that malachite green is adsorbed in the monomeric form, whereas the methylene blue prevails in the dimeric one : the wavelength of the maximum absorption is around 600 nm to be compared to the values in aqueous solution 660 nm (monomere) and 605 nm (dimere). This result must be taken into account in any treatment of adsorption data.

- In PAS, relative concentration measurements can be performed in the range  $5.10^{-7}$  -  $10^{-9}$  mol m<sup>-2</sup> (Fig. 3) with a relative standard deviation of 0.09. Improved reproducibility is obtained when an internal standard is used since a 2 % value was reached with ZnS (see below).

- In DRS, on the contrary, if a better sensitivity was achieved, no quantitative results could be obtained and inversions in samples order or saturation were noticed (Fig. 2). This could be due to the high scattering coefficient of the matrix since good results were obtained for the ZnS calibration curve.

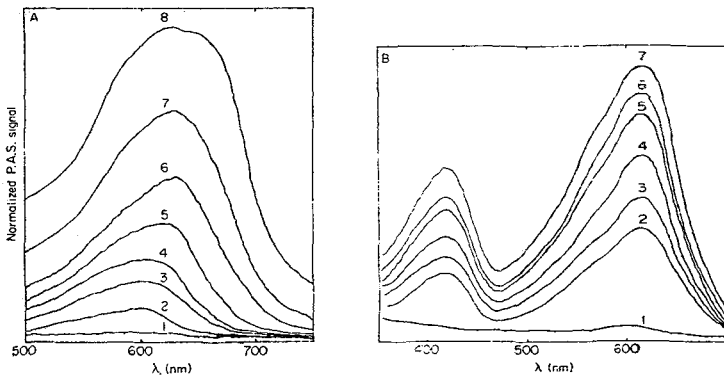


Fig. 1 - PAS spectra of the dyes adsorbed on silica (40 Hz, bandwidth 6 nm, time constant of lock-in amplifiers 1 s, 30 nm min<sup>-1</sup>, double-beam mode). A. Methylene blue : (1), 0 ; (2), 0.3 ; (3), 0.6 ; (4), 1.2 ; (5), 2.9 ; (6), 3.6 ; (7), 5.7 ; (8),  $11.3 \times 10^{-9}$  mol m<sup>-2</sup>.

B. Malachite green : (1), 0 ; (2), 0.6 ; (3), 1.0 ; (4), 1.9 ; (5), 2.8 ; (6), 3.1 ; (7),  $3.5 \times 10^{-9}$  mol m<sup>-2</sup>.

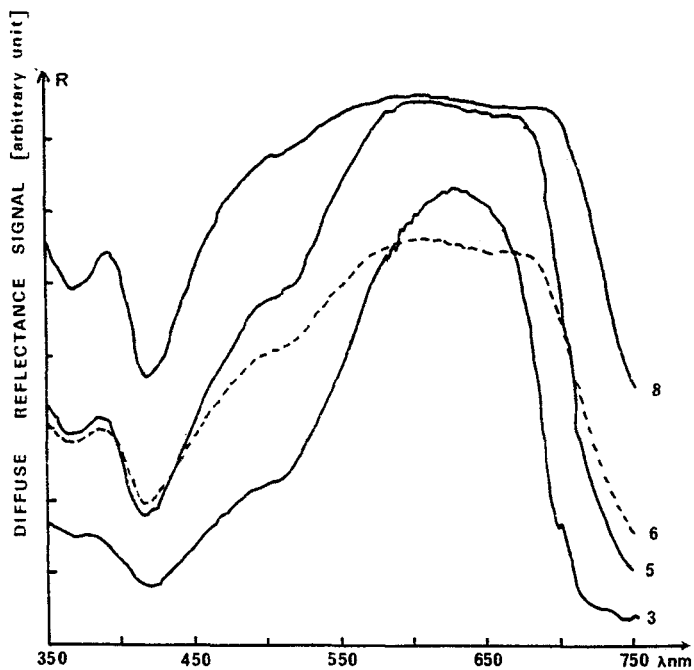


Fig. 2 - Diffuse reflectance spectra of methylene blue (for samples number, see Fig. 1)

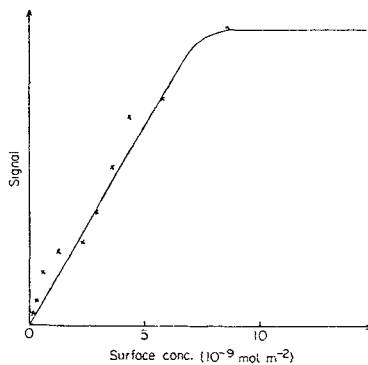


Fig. 3. Normalized p.a.s. signal vs. surface concentration of methylene blue adsorbed on silica at 610 nm (same conditions as Fig. 1).

## II - SPECTRA OF SPHALERITES ACTIVATED BY COPPER

Pure sphalerite samples coming from the mine of Reocin in Spain were powder samples with a granulometry of 50-100 microns. They were activated by contact with  $10^{-4}$  to  $10^{-3}$  M aqueous solutions of copper sulfate.

DRS and PAS spectra are represented on Fig. 4. When copper is present at the surface of ZnS, the gap of ZnS at about 400 nm is substituted by a large broadband background which does not allow any information on the nature of the surface copper. However, since its amplitude increases with the copper concentration of the activating solution, it gives a relative measure of the copper surface concentration  $\Gamma_{Cu}$ .

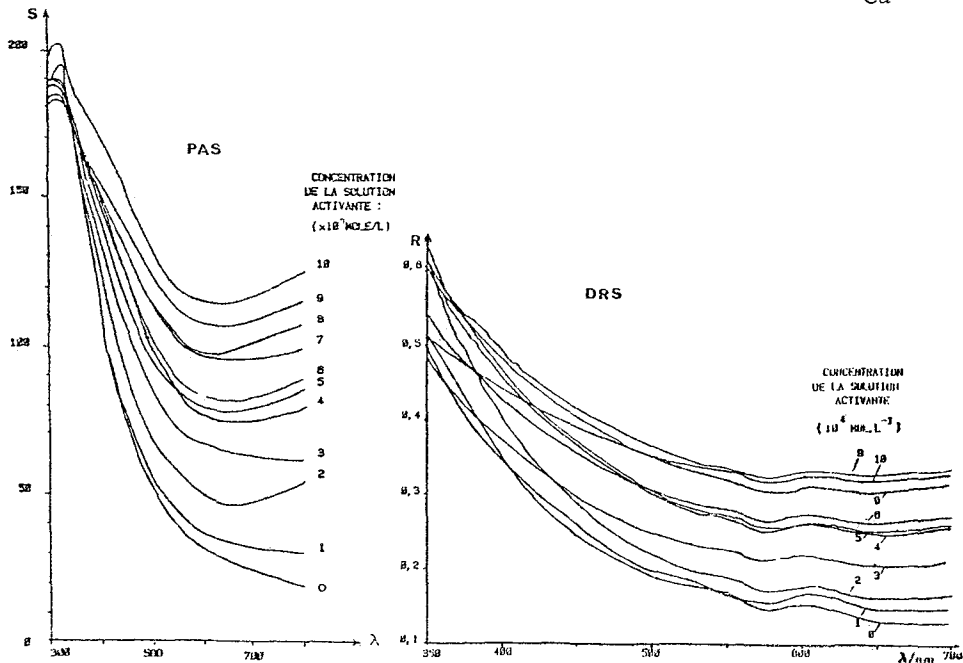


Fig. 4 - Spectra of sphalerite from Reocin (Spain) activated by  $CuSO_4$ . Numbers on curves indicate the concentration of the copper sulfate activating solutions.

Good calibration curves were obtained with the same standard deviation for DRS and PAS leading to the following equations ( $R$  for DRS in % ;  $S$  for PAS in mV ;  $\Gamma_{Cu}$  in  $\mu mol m^{-2}$ ) :

$$\Gamma_{Cu} = 9.46 \cdot 10^{-5} R - 1.22 \cdot 10^{-5} \quad (r^2 = 0.98 \quad \lambda = 700 \text{ nm})$$

$$\Gamma_{Cu} = 1.43 \cdot 10^{-7} S - 2.51 \cdot 10^{-6} \quad (r^2 = 0.98 \quad \lambda = 800 \text{ nm})$$

However this reproducibility does not allow measurements on sphalerites highly colored by impurities, which almost present a photoacoustic saturation. Improved reproducibility was reached by using an internal standard, which was the value of the signal on the saturation plateau below the gap. Since there is photoacoustic saturation this value is independent of the copper fixation if one assume that thermal properties of the sample do not change with activation by copper.

Let us call  $S$  the normalized PAS signal at 983 nm and  $S_0$  the normalized signal at 395 nm on the sphalerite spectrum illustrated on Fig. 5. The 983 nm value was chosen in the absorption broadband of copper at a peak of the xenon source in order to have the maximum light power, and the 395 nm value at an arbitrary value below the ZnS gap around 400-450 nm.

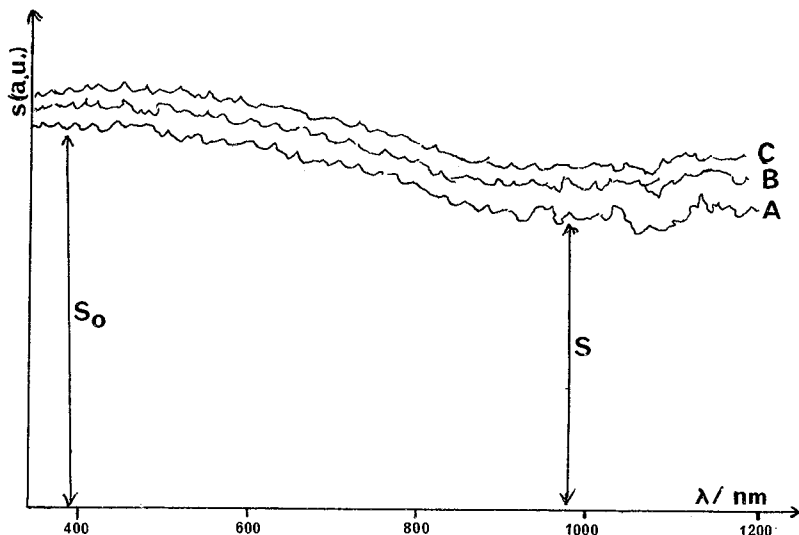


Fig. 5 - PAS spectra of sphalerites from Saint Salvat (France). A : natural sphalerite. B : sphalerite activated by a  $10^{-3}$  M  $\text{Cu SO}_4$  solution. C : sphalerite activated by chalcoppyrite. (40Hz, 80 nm/mn, time cte 1s)

The reproducibility of the corrected signal  $S_{\text{cor}}$  :

$$S_{\text{cor}} = \frac{S}{S_0}$$

measured on a quite brown sphalerite from Saint Salvat (France) (Fig. 5) is better than 2 % and allows a distinction between an untreated sphalerite and a sample activated by copper sulfide  $10^{-3}$  M or by chalcoppyrite as shown in the table :

Repetitive measurements of  $S_{\text{cor}}$

sample A	: 0.72 - 0.73 - 0.72 - 0.78 - 0.72	mean : 0.73 $\pm$ 0.01
sample B	: 0.77 - 0.78 - 0.75 - 0.75	" : 0.76 <sub>5</sub> $\pm$ 0.015
sample C	: 0.76 - 0.77 - 0.77 - 0.76	" : 0.76 <sub>5</sub> $\pm$ 0.01

In conclusion, PAS seems well suited for analytical studies of sphalerites activation.

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#### REFERENCES

- (1) PLICHON V., LELIEVRE D., LE LIBOUX M., FOURNIER D., CECILE J.L. and BOISSAY S., Anal. Chim. Acta 138 (1982) 349.