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Application of PAS to Turbid Media

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Quantitative measurement of turbid particles in liquid has been carried out with a turbidimetry, which is based on the measurement of the attenuation of transmitted light by a solution containing a finely divided precipitate. There is a direct relationship between an optical density $\log I_0/I$ (I_0 and I are the intensities of the incident and transmitted beams respectively), and the amount of material in suspension. That is,

$$\log I_0 / I = (1/2.303) K \cdot N \cdot \pi \cdot r^2 \cdot l$$

where N is number of spherical particles per unit volume, r is the radius of the particle, l is the thickness of a suspension, and K is sometimes called total scattering coefficient and is deduced from electromagnetic theory by Mie assuming uniform spherical particles. K depends upon (1) the particle size, (2) the wavelength, (3) the refractive index, and (4) the complex refractive index in the case of absorbing particles. Turbidimetry is often not very precise since it is difficult to prepare a stable and reproducible suspension of the precipitate. A precision and accuracy of ± 5 - 10 % of the amount present is usually obtained. On the contrary, as photoacoustic spectroscopy provides only information concerning light intensity absorbed by particle, the particle size distribution would affect less the photoacoustic signal intensity.

Recently, photoacoustic spectroscopy has been applied to the measurement of absorption of light by aerozols and dust in the atmosphere. Absorption measurement of ultra trace turbid or colloidal particles in liquid has been attached importance to particulary in the field of biochemistry and environmental chemistry. However, few studies have been carried out for lack of sensitivity and accuracy in their measurements. In the present investigation, applications of PAS to turbid media were attempted using $BaSO_4$ suspension and colloidal[4] tellurium produced chemically.

The apparatus used in the present investigation was shown in Figure 1. A quasi-double beam system

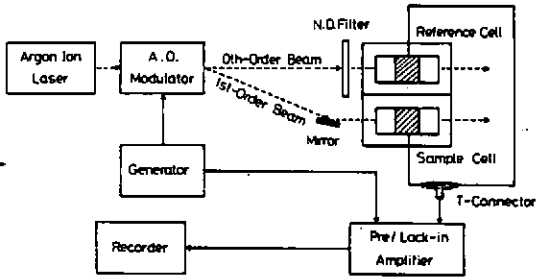

Figure 1. Block diagram of the apparatus.

was adopted to subtract the background signal due to the solvent. Laser light was expanded to about 7 mm diameter with a concave lens and was incident on a sample cell in order to lower the effect of the particle size distribution in the vertical direction upon photoacoustic signal. And a thin platinum plate (0.1 mm thickness) was adhered inside the piezoelectric ceramic (NPM, N-21, Tohoku Kinzoku Co. Ltd.), photoacoustic sensor of our cell. An argon ion laser was modulated at a given frequency in the range from a few Hz to 100 KHz with an acousto-optic light modulator. A spectrophotometer was used as a turbidimeter.

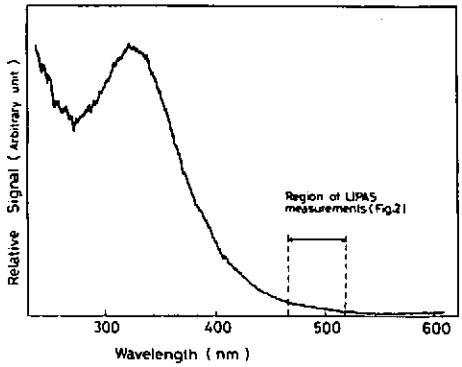

Figure 2. PA spectrum of $BaSO_4$ powder.

All reagents were of ultrapure grades. Twice-distilled water was used. Two kinds of turbid $BaSO_4$ solutions were prepared as follows. Method 1 : 10 ml of glycerine solution (1:1) and 5 ml of NaCl solution (25%, HCl_2 solution) were added to 50 ml of a known concentration of SO_4^{2-} ion solution. While stirring the solution, $BaCl_2$ powder (0.3 g) was added there. This solution was stirred for 1 min., left for 4 min. and stirred again for 15 sec. just before measurement.
Method 2 : The same concentration of glycerine solution (1:1) and NaCl solution (25%, HCl_2 solution) were added to 40 ml of a known concentration of SO_4^{2-} ion solution as was done in the method 1. While stirring the solution, 10 ml of $BaCl_2$ solution (3%) was added. The same precedure was carried out just before measurement.

Figure 2 shows the PA spectrum of $BaSO_4$ powder produced chemically. As $BaSO_4$ powder is nonfluorescent, this spectrum can be considerd to coincide with the absorption spectrum. As shown in Figure 2, the absorption spectrum of $BaSO_4$ powder has a maximum at ~330 nm.

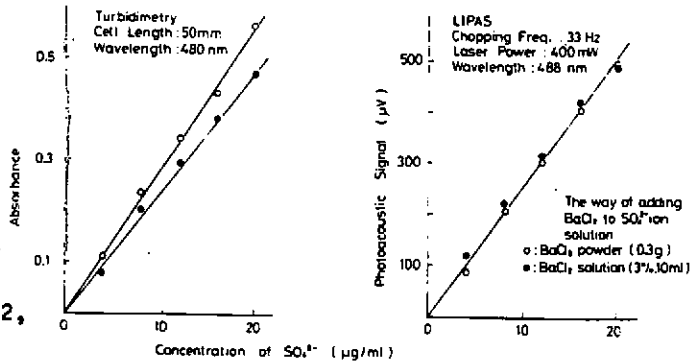

Figure 3. Calibration graphs obtained from turbidimetric and photoacoustic measurement.

At present, an assignment of this absorption band is not clear. Its trail is extended to the visible region. Though the color of $BaSO_4$ powder is white, it absorbs some of visible light.

The effect of the particle size diameter upon photoacoustic and turbidimetric signal intensity were investigated. According to Turnbll (1), the way of adding $BaCl_2$ to SO_4^{2-} ion solution is greatly dependent upon the size distributions of $BaSO_4$ particles produced chemically in solution. In order to make a particle size smaller, the formation of local supersaturation is required during a mixing process. That is, the addition of $BaCl_2$ powder makes the particle size smaller (0.5-6 μm) than that of $BaCl_2$ solution(2-20 μm). Figure 3 shows the calibration graph obtained from photoacoustic and turbidimetric measurement of various concentrations of $BaSO_4$ particles produced chemically in solution by using $BaCl_2$ powder and solution respectively. In a turbidimetry two different calibration graphs were obtained, while only one in PAS. The turbidimetric measurement reflects clearly the difference of the size distribution by means of the two different ways of adding $BaCl_2$. On the other hand, in PAS the photoacoustic signal intensity was not affected by the difference of the size distribution.

The detection limit was calculated to be 0.03 μg/ml $BaSO_4$, based on a limiting signal to noise ratio of 2:1. As the result of calculation with extinction coefficient k (defined by $I = I_0 \exp(-4\pi kx/\lambda_0)$, x : effective thickness, λ_0: wavelength in vacuo) of $BaSO_4$ from the literature (1), the value of the detection limit was found out to correspond to an optical density of 1.6×10^{-2}.

As an application to practical purpose of this PAS method, an analysis of tellurium in waste water in the campus of our university was carried out.

10 ml of stannous chloride solution (5 %, 5N hydrochloric acid solution) was added to sample solution (25 ng～10 μg, Te), and diluted exactly to 100 mL with twice distilled water. When the solution is permitted to stand for 40 ～ 60 min., colloidal tellurium is formed. The distilled water, which the same procedures were done, was used as a reference solutions. Figure 4 shows the PA spectrum of colloidal tellurium. As its color was black, the spectrum exhibited almost flat over the visible wavelength region. By using an argon ion laser line of 514.5 nm (400 mW), the concentration of hydrochloric

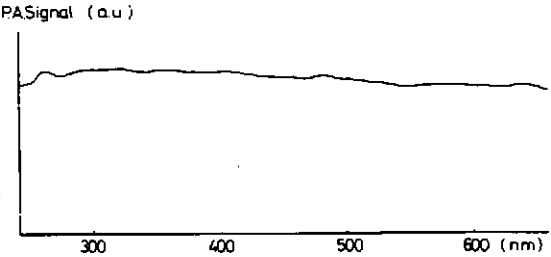

Figure 4. PA spectrum of colloidal tellurium.

acid, the amount of stannous chloride, and the standing time were investigated in order to obtain most suitable conditions for reduction reaction. Figure 5 shows the calibration graph. The detection limit was calculated to be 2.5 ppb, and its value was about three orders of magnitude lower than that by an ordinary turbidimetry.

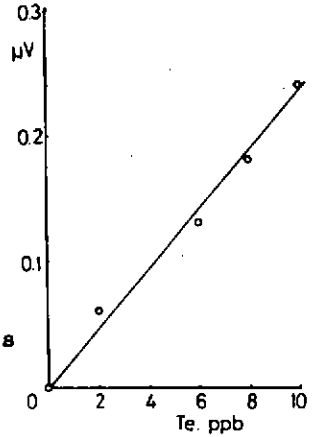

Figure 5. Calibration graph for tellurium.

The preliminary analysis of this waste water were as follows; 150 ppm (BOD), 120 ppm (COD), 24.8 ppm (SS), and 0.5 5 ppm of Fe, Cu, Mn, Pb, and Zn. Though most of these coexisting materials did not interfere the determination of tellurium, The existence of colored ions such as cobalt (II) interfered.

In comparison with AAS (Atomic Absorption Spectrometry), and ICP (Inductively Coupled Plasma Spectrometry), the present method, only to hold the concentration of hydrochloric acid and stannous chloride constant, and to measure after a definite standing time, simplified greatly the analysis of tellurium. This method is applicable and recommendable enough to the analysis of practical samples in many fields.

REFERENCES

(1) D. Turnbll, Acta, Mettalug., 1, 684 (1953).