38. *Laser-Induced Photo-Acoustic Ultra Trace Determinations of Liquid Samples*

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(Communicated by Takayuki SOMIYA, M. J. A., April 12, 1978)

Absorption spectrometry utilising the photo-acoustic effect has become of major interest. With the photo-acoustic absorption technique, it is possible to measure absorption spectra of opaque solids and liquids which previously had been extremely difficult using conventional transmission or reflectance spectrometry. Rosencwaig¹⁾ and Adams *et al.*²⁾ have been actively investigating possible applications of the technique. Lasers, used extensively as light sources in many areas of analytical spectroscopy, have a possibility of providing sensitive detection when employed in photo-acoustic absorption spectrometry. Ultra low gas concentration has been determined by this approach, while Kreuzer³⁾ has discussed photo-acoustic gas analysis in detail. Lahmann *et al.*⁴⁾ were the first workers to apply the laser-induced photo-acoustic spectrometry (LIPAS) to analysis of liquids. This technique has a possibility as a powerful tool for ultra trace determinations in liquid samples.

In the present paper, the determination of MnO_4^- in aqueous solution and cadmium in the form of dithizonate in chloroform were carried out with this new technique.

Experimental. Apparatus. A block diagram of the photo-acoustic spectrometer is shown in Fig. 1. The output beam of argon ion laser (Spectra-Physics Model 164-03), operating in a single line mode of 514.5 nm, was modulated at a given frequency by a light chopper and was directed into the sample cell through a collecting lens ($f=20$ cm).

The pressure fluctuation induced sample solution by absorbed radiation was detected by a piezoelectric ceramic (NPM, N-6 supplied by Tohoku Kinzoku Co. Ltd.). A lock-in amplifier/preamplifier (NF. Co. Ltd., Model LI-574) was used to amplify the modulated output signal.

The piezoelectric ceramic acts simultaneously as a sample cell and a pressure sensor. The middle part of the cell was of cylindrical piezoelectric ceramic (length 50 mm and inner diameter 24 mm) which was sealed on both sides by pyrex tubes incorporating a stopcock and a

Fig. 1. Block diagram of the apparatus.

quartz window. The cell was placed inside an airtight chamber which was secured to a vibration free stand to prevent pressure fluctuations caused by vibrations from external sources.

Reagents and procedure. Standard solution of MnO_4^- was prepared by dissolving potassium permanganate (1.5804 g) in distilled water, boiling for several minutes and diluting to 1 litre accurately with water. The concentration of this stock solution was 1×10^{-2} M. This solution was diluted to a given concentration for the measurements of the LIPAS.

Cadmium was extracted into chloroform as cadmium dithizonate according to Saltzman's procedure.⁵⁾ A stock solution of cadmium dithizonate ($0.5 \mu\text{g ml}^{-1}$ Cd) was prepared by diluting cadmium solution (10 ml, $1 \mu\text{g ml}^{-1}$ Cd) to 20 ml with chloroform. The calibration graph was obtained for standard cadmium solutions which were prepared by appropriate dilution of the stock cadmium solution ($0.5 \mu\text{g ml}^{-1}$ Cd).

Results and discussion. The laser-induced pressure fluctuations Δp in the photo-acoustic cell depend upon some physical constants of the solvent according to Kohanzadeh *et al.*⁶⁾

$$\Delta p \sim \frac{\alpha_T}{K \cdot \rho \cdot v^2 \cdot C_p} \cdot \epsilon \cdot C \cdot P. \quad (1)$$

Where K =compressibility, α_T =thermal expansion coefficient, ρ =density, v =velocity of sound, C_p =specific heat, ϵ =molar absorptivity, C =molar concentration and P =average laser power output. In very dilute solution, however, the photo-acoustic signal intensity is considered to be proportional to the incident laser power, the absorptivity of the sample at different wavelengths and the concentration of the solute. In a given solvent, the photo-acoustic signal intensity is proportional to the concentration of the solute, if the laser power is constant.

At 400 mW laser power and 300 Hz chopping frequency, the relationship between the photo-acoustic signal intensity and the concentration of MnO_4^- in aqueous solution was linear beyond a range of two orders of magnitude, that is, from 1×10^{-7} M to 1.5×10^{-5} M. The results show in Fig. 2. The photo-acoustic signal intensity for MnO_4^- was obtained by subtracting that of the solvent. The intensity exhibited a little saturation beyond 1.5×10^{-5} M, and the saturation was considered to be caused by an increase in the temperature of solution. In fact, at laser power less than 400 mW, the linear range was extended to concentrations greater than 1.5×10^{-5} M.

Fig. 3 shows the relationship between the average laser output power and the photo-acoustic signal intensity at 6×10^{-6} M MnO_4^- . The photo-acoustic signal intensity is proportional to laser power within the range of the experiment. This linear relationship are expected to hold until the absorption of radiation is saturated.

The dependence of the photo-acoustic signal intensity upon chopping frequency was investigated. The results are shown in Fig. 4. The photo-acoustic signal intensity decreased beyond 200 Hz. Adams *et al.*²⁾ observed a similar relationship in the measurement of solid samples and pointed out that it is due to the $1/f$ thermal lag. However, this explanation seems hard to be accepted for liquid samples. This may be due to the frequency characteristics of the piezoelectric ceramic. Further theoretical estimates are necessary concerning the mechanism for generating photo-acoustic waves in liquid. At the

Fig. 2

Fig. 3

Fig. 2. Response of photo-acoustic signal in the wide range of MnO_4^- . Laser power: 400 mW. Chopping frequency: 300 Hz.

Fig. 3. Effect of laser power on photo-acoustic signal intensity. Concentration of MnO_4^- : 6×10^{-6} M. Chopping frequency: 300 Hz.

Fig. 4

Fig. 5

Fig. 4. Relation between photo-acoustic signal and chopping frequency. Concentration of MnO_4^- : 6×10^{-6} M. Laser power: 600 mW.

Fig. 5. Calibration curve of cadmium.

present stage, this relationship in liquid samples cannot be clarified yet.

The detection limit for MnO_4^- in aqueous solution was calculated to be 5×10^{-8} (6 ppb), based on a limiting photo-acoustic signal to noise ratio of 2:1. This value was about sixty fold lower than that for conventional colorimetric analysis (360 ppb).⁸⁾

The LIPAS was also applied to ultra trace determination of cadmium as a practical sample. Cadmium was extracted as cadmium dithizonate into chloroform, as mentioned previously. Fig. 5 shows the calibration curve obtained for ultra-low concentrations of cadmium. Laser power used was 700 mW. For 0.5 ng ml^{-1} Cd (as cadmium dithizonate solution), the coefficient of variation was 1.3% (8 determinations). The detection limit was calculated to be 0.02 ng ml^{-1} Cd (14 ppt).⁹⁾ This value was about two orders of magnitude lower than that for colorimetric analysis (3 ng ml^{-1})⁵⁾ and for conventional flame atomic absorption measurement (10 ng ml^{-1}).¹⁰⁾

As shown in equation (1), the laser-induced pressure fluctuations in a sample cell depend upon several physical constants of the solvent and the absorptivity of the solute in very dilute solution, if the concentration of the solute, the laser power and other experimental conditions are constant. The molar absorptivity of MnO_4^- in aqueous solution is $\sim 1800 \text{ (L mol}^{-1} \text{ cm}^{-1})$ for 514.5 nm. On the other hand,

cadmium dithizonate has a molar absorptivity of ~ 79000 ($\text{L mol}^{-1} \text{cm}^{-1}$) at 514.5 nm. The ratio of the pressure fluctuation of chloroform in comparison with water is 16:1 according to equation (1). From the above results, using a detection limit for MnO_4^- (5×10^{-8} M, 3 ng ml^{-1} Mn), a detection limit of cadmium dithizonate was estimated to be 0.008 ng ml^{-1} Cd. Our experimental results agree roughly.

Conclusion. The LIPAS exhibited a remarkable enhancement of the detection sensitivity in comparison with the conventional colorimetric spectrometry. Both the linear concentration range of photo-acoustic signal intensity and the reproducibility were practically satisfactory. Significant differences between the LIPAS and the conventional colorimetric spectrometry are as follows. a) Photo-acoustic signal intensity is proportional to incident radiation power. Therefore, the use of lasers is recommended. In the colorimetric spectrometry, the increase of incident radiation intensity has no influence upon the absorbance, unless the cell length is varied. On the other hand, photo-acoustic signal intensity does not depend upon the cell length as indicated in equation (1). b) The photo-acoustic signal intensity depends upon several physical constants of the solvent. Accordingly, an appropriate selection of the solvent improves the detection sensitivity.

The LIPAS is applicable to a wide range of liquid samples and application of lasers operating in the uv, visible and IR is recommended. Further development in surface pretreatment of piezoelectric ceramic is needed in order to measure materials in concentrated acidic or basic media. Then, ultra trace determinations of various kinds of metals and organic compounds would become possible utilising the LIPAS.

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