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SONOLUMINESCENCE FOR WATER DETERMINATION

Masaaki YAMADA,* Toshiyuki HOBO, and Shigetaka SUZUKI
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

Sonoluminescence, ultrasonically induced luminescence, is described for the determination of water in methanol. It is based on the measurement of emissions from OH^*, H_2O^*, etc. produced when ultrasonic waves is propagated through methanol containing water. The method is unique in capable of determining water with no use of reagents.

Sonoluminescence(SL) is a weak emission of light observed when ultrasonic waves is passed through a liquid containing dissolved gases; its spectrum and intensity vary with kinds of dissolved gases. The SL is caused by acoustic cavitation responsible for many of the chemical reactions which occur in an ultrasonic field. The SL spectrum of air-saturated water shows the emission extending from 240 nm to the near-infrared region with broad peaks having maxima around 310(H_2O^* and OH^*), 360(radiative recombination, HO_2+H), and 400 nm(NO_2^*). All these emissions are overlaying a broad continuum arising from the radiative recombination, H+OH.[1)] From the viewpoint of analytical chemistry, it is likely that the SL from water is usable to estimate water content in organic solvents. This paper demonstrates preliminary investigations on a simple and rapid determination of water by SL method. Methanol was selected as a solvent in relation to the Karl Fisher(KF) method, although it sonoluminesces *per se*.

A schematic diagram of the experimental arrangement is depicted in Fig. 1. Stainless steel tubing(1 mm i.d.) was used for flow lines except the pump tubes, the diameters of which were chosen so that the methanol volume within the cell was kept constant(ca.2 ml). Methanol solution in an insonation cell with a quartz window at the bottom was insonated at 28 kHz by means of an exponential horn(cross section, 0.05 cm^2), oscillated with Handy Sonic Model UR-20P(max.20 W, Tomy Seiko Co.). The resultant SL from the cell was observed directly by a photomultiplier tube(PM)(Hamamatsu TV-R453) with no wavelength discrimination. Water methanol solution prepared by diluting 10-ml water to 100 ml with commercially available dehydrated-methanol was used through most of the experiments.

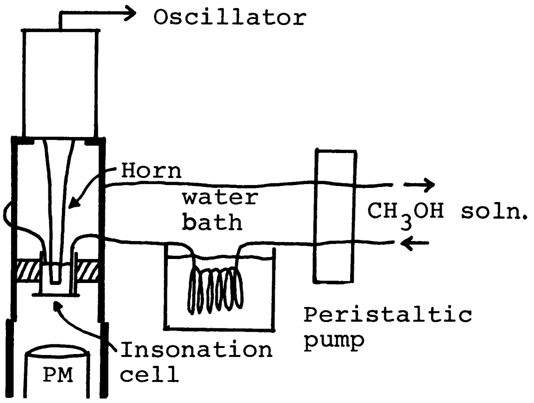
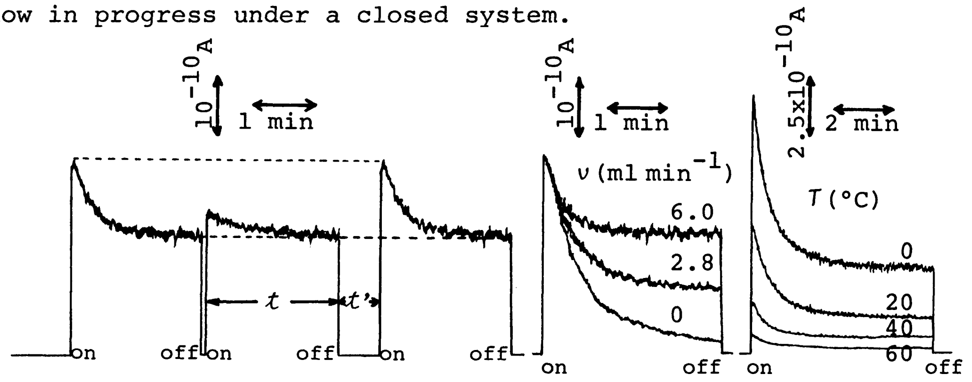


Fig. 1. Experimental arrangement

Typical SL signals are shown in Fig. 2, indicating that the insonation initially gives rise to a maximum emission followed by a constant emission after its gradual decay. In order for the maximum emission intensity to be reproduced, a certain insonation interval(t') is required after insonation(time, t); under a given pumping speed of the methanol solution(ν), the gradual decay of emission eventually leads to a definite intensity regardless of the lengths of t and t' (Fig. 2A). This behavior is explicable in terms of a rise of the methanol solution temperature(water bath temp., T) during insonation as stated later. Accordingly, the length of t' giving reproducible maximum emission intensity is closely related to ν. The maximum emission intensity obtained is independent of ν if a sufficient t' is taken(Fig. 2B). Fig. 2C indicates that T greatly influences the emission intensity. This is ascribable to the idea that the intensity attenuation is largely due to a decrease in the degree of cavitation with elevating T. The stronger insonation power(E) gave the higher degree of cavitation, resulting in the stronger SL, but it caused the higher noise.

The maximum emission intensity is preferred as SL signal for the water determination because it does not depend on ν and allows a short t', namely, short analysis time. Operating conditions for the water determination, t=5 s, t'=30 s, ν=6 ml min^{-1}, T=0°C, and E=8(reading, max.10), provided a calibration graph to be linear between 0 to 0.2 g ml^{-1} and a detection limit(S/N=3) of 0.005 g ml^{-1}. The detection limit depends strongly on how thoroughly methanol used is dried and to what extent it absorbs moisture from surroundings during measurement.

Through this preliminary experiment, it was proved that the SL phenomenon was applicable to determination of water in methanol. Although the present method is much inferior to the KF method in sensitivity, it posseses an excellent feature that simple and rapid water determination is feasible with no use of reagents. The lack of sensitivity will be overcome by: i)the use of a solvent which is not emissive itself, ii)exhaustive dehydration of the solvent, iii)the block of moisture absorption into the solvent, and iv)the replacement of dissolved gas, air by Ar.[1] In addition, the use of interference filter for monitoring the OH emission alone will be effective for selective detection of water. For these improvements, experiments are now in progress under a closed system.



(A) ν=6 ml min^{-1}, T=room temp., E=8(reading, max.10) (B) T=room temp. E=8 (C) ν=2.8 ml min^{-1} E=8

Fig. 2. Typical SL signal profiles

Reference

1) C.Sehgal, R.G.Sutherland, and R.E.Verrall, J.Phys.Chem., 84, 388(1980).

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