Determination of absolute fluorescence quantum efficiency of quinine bisulfate in aqueous medium by optoacoustic spectrometry

3 AUTHORS, INCLUDING:

James George Highfield

Agency for Science, Technology and Researc…

61 PUBLICATIONS   **1,365** CITATIONS

Determination of absolute fluorescence quantum efficiency of quinine bisulfate in aqueous medium by optoacoustic spectrometry

M. J. Adams, J. G. Highfield, and G. F. Kirkbright

More About This Article

The permalink http://dx.doi.org/10.1021/ac50020a053 provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

LITERATURE CITED

(1) M. G. Inghram and R. Gomer, *J. Chem. Phys.*, **22**, 1279 (1954).
(2) H. D. Beckey, "Field Ionization Mass Spectrometry", Pergamon Press, Oxford, England, 1971.
(3) H. D. Beckey in "Biochemical Applications of Mass Spectrometry", G. R. Waller, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 30.
(4) S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, *Anal. Chem.*, **48**, 2105 (1976).
(5) S. E. Scheppele, G. J. Greenwood, P. L. Grizzle, T. D. Marriott, and N. B. Perreira, 24th Annual Conference on Mass Spectrometry and Allied Topics, 1976, p 481.
(6) S. E. Scheppele, G. J. Greenwood, P. L. Grizzle, T. D. Marriott, C. S. Hsu, N. B. Perreira, P. A. Benson, K. N. Detwiler, and G. M. Stewart, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **22**(2), 665 (1977).
(7) G. G. Wanless and G. A. Glock, Jr., *Anal. Chem.*, **39**, 2 (1967).
(8) H. G. Hippe and H. D. Beckey, *Erdoel, Kohle, Erdgas, Petrochem.*, **24**, 620 (1971).
(9) M. Ryska, M. Kuras, and J. Mostecky, *Int. J. Mass Spectrom. Ion Phys.*, **16**, 257 (1975).
(10) M. Kuras, M. Ryska, and J. Mostecky, *Anal. Chem.*, **48**, 196 (1976).
(11) Internal Report of the Continental Oil Company, Research and Development Department, Ponca City, Okla., Report No. 1007-4-1-73, authored by H. M. Curtis.
(12) G. J. Greenwood, Ph.D. Thesis, Oklahoma State University, Stillwater, Okla., 1977.
(13) E. M. Chait, T. W. Shannon, W. O. Perry, G. E. van Lear, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 141 (1969).
(14) C. E. Berry, *J. Chem. Phys.*, **17**, 1164 (1949).
(15) W. A. Chupka, *J. Chem. Phys.*, **54**, 1936 (1971).
(16) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci., U.S.A.*, **38**, 667 (1952).
(17) W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **47**, 2921 (1967).
(18) M. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley-Interscience, New York, N.Y., 1968, Chapter 2.

Determination of Absolute Fluorescence Quantum Efficiency of Quinine Bisulfate in Aqueous Medium by Optoacoustic Spectrometry

M. J. Adams, J. G. Highfield, and G. F. Kirkbright*

Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, United Kingdom

A method utilizing optoacoustic spectrometry is described to permit the determination of the absolute quantum efficiencies of fluorescence for compounds in solid and liquid samples. The method is demonstrated in the determination of the fluorescence quantum efficiency of quinine bisulfate in aqueous solution utilizing quenching of the fluorescence by halide ions.

In recent years there has been a rapid rise of interest in the optoacoustic effect and its application in the examination of solid and liquid samples. Harshbarger and Robin (1), Rosencwaig (2), and Adams et al. (3, 4) have demonstrated the technique of analytical optoacoustic spectrometry (OAS) in studies of a variety of sample types.

In OAS, intensity-modulated electromagnetic radiation is incident upon the sample material enclosed in a cell of constant volume. If the sample absorbs at the wavelength of the incident radiation, on subsequent de-excitation the absorbed energy may appear as heat and cause a periodic pressure rise in the gas surrounding the sample. This change in pressure may be detected and monitored by a sensitive microphone transducer enclosed within the cell. The resulting electrical signal is selectively amplified using a tuned-amplifier and phase-sensitive detector and presented as a dc potential to a potentiometric chart recorder or other voltage display system.

Clearly, optoacoustic spectrometry relies on the radiationless conversion of absorbed energy for the production of an acoustic signal and, hence, is complementary to the conventional techniques of luminescence spectrometry. As a pressure transducer is employed to monitor, indirectly, the temperature of the absorbing species, optoacoustic spectrometry may be considered as a calorimetric method for the detection and study of excited states. Rosencwaig (2) suggested that the technique might be useful for these purposes but presented no data relating to liquid samples. Callis (5) has reviewed some modern calorimetric techniques for examining radiationless deactivation in solid and liquid samples employing both microphones and piezoelectric crystals as heat-flow transducers. More recently, Lahmann and Ludewig (6) have employed the optoacoustic technique using a piezoelectric transducer immersed in the sample solution to determine the absolute fluorescence quantum efficiency of rhodamine 6G in aqueous solution. Such calorimetric methods of studying excited states are reported to be rapid, simple, and sensitive.

In the work described here the single-beam optoacoustic spectrometer described earlier (3, 4) has been employed for the determination of the absolute quantum efficiency of quinine bisulfate in aqueous solution and examination of the quenching effect on this species observed upon the addition of chloride ions to the sample solution.

EXPERIMENTAL

Apparatus. The single-beam optoacoustic spectrometer employed for the work discussed here has been described elsewhere (3, 4). Radiation from a 1-kW high-pressure, xenon short-arc illuminator was focused through a rotating sector onto the entrance-slit of an $f/4$ monochromator. The optoacoustic cell (4), containing the sample, was positioned at the exit slit of the monochromator. The signal from the sensitive capacitor microphone in the cell, was led to a lock-in amplifier unit and

compared with the reference signal generated by the rotating sector unit. The voltage output from the synchronous detector was applied to a conventional potentiometric chart recorder. All results described here were obtained with a modulation frequency of 30 Hz and a spectral half-band width of 20 nm.

Reagents. The analytical solutions were prepared by dissolving quinine bisulfate dihydrate (fluorescence standard purity, J. T. Baker Chemical Co.) in 0.1 N sulfuric acid and 0.1 N hydrochloric acid solutions. The test solutions were prepared by dilution and mixing of these stock solutions. Optoacoustic measurements were recorded at the excitation maximum for quinine bisulfate, 366 nm (7), for a 0.5-mL aliquot pipetted into the sample tray of the optoacoustic cell.

Procedure. Solution transmittance spectra were obtained using a silica cuvette positioned between the exit slit of the monochromator and the optoacoustic cell containing a carbon-black sample. In this mode of operation, the optoacoustic cell served as a black-body energy detector and transmittance spectra were obtained under identical optical conditions to the optoacoustic signals (8). The cuvette comprised two silica windows (20-mm diameter, 2-mm thickness) separated by a polyethylene ring spacer (i.d. 15 mm, thickness 0.025 mm). This cell path-length was chosen to provide acceptable transmittance over the solution concentration range employed.

RESULTS AND DISCUSSION

In order to estimate the absolute quantum efficiency of fluorescence, Q, for a compound from the experimental data, it is necessary to derive a theoretical expression for the magnitude of the optoacoustic signal. For constant experimental conditions and assuming no optical or thermal saturation,

$$P(OAS) = P_{abs} \cdot \beta \tag{1}$$

where $P(OAS)$ is the magnitude of the OAS signal at wavelength λ, P_{abs} is the radiant power absorbed at this wavelength by the sample, and β is an efficiency factor which is a measure of the conversion efficiency of absorbed power into heat by nonradiative mechanisms.

For a sample capable of fluorescence it can be shown that,

$$\beta = 1 - Q + Q \left(\frac{\nu_0 - \nu_F}{\nu_0} \right) \tag{2}$$

where Q is the quantum efficiency, ν_0 is the frequency of the exciting radiation and ν_F is the mean frequency of the fluorescent radiation.

In Equation 2, the term $(1 - Q)$ accounts for the absorption of radiation by nonfluorescing molecules and the second term corrects for the radiationless fraction of energy produced in the sample in the fluorescence process (i.e., the Stokes shift).

Thus, combining Equations 1 and 2, for a fluorescent compound

$$P(OAS)_F = P_{abs} \left[1 - Q + Q \left(\frac{\nu_0 - \nu_F}{\nu_0} \right) \right] \tag{3}$$

and for a nonfluorescent compound, i.e., $\beta = 1$,

$$P(OAS)_{NF} = P_{abs} \tag{4}$$

Assuming the absorptivity of both the fluorescent and nonfluorescent compounds to be identical, and the thermal characteristics of the solutions to be similar, then P_{abs} is constant for both samples and Equation 3 may be expressed upon rearrangement as,

$$Q = \frac{\lambda_F}{\lambda_0} \left[1 - \frac{P(OAS)_F}{P(OAS)_{NF}} \right] \tag{5}$$

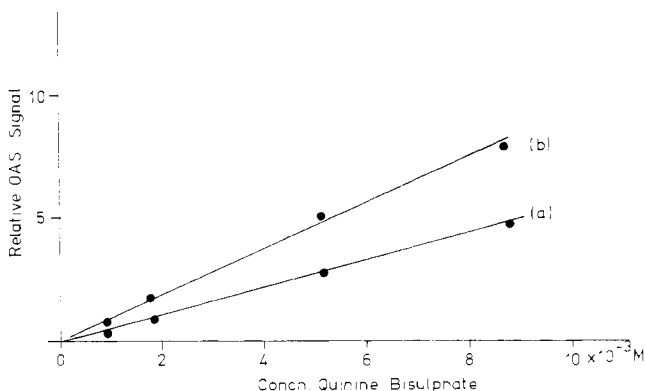where λ_F is the mean wavelength of fluorescence and λ_0 the wavelength of excitation.

Figure 1. Optoacoustic signal magnitude, at 366 nm, vs. concentration of quinine bisulfate in (a) 0.1 N sulfuric acid solution, and (b) 0.1 N hydrochloric acid solution

Previous studies concerning the determination of absolute quantum efficiencies of fluorescent materials utilizing the optoacoustic effect have employed pressure transducers immersed in the analyte and nonfluorescent materials as reference solutions (5, 6). This is achieved by ensuring that the reference material and the fluorescent compound to be examined have comparable absorption coefficients and equating the difference in magnitude of the optoacoustic signals from the two solutions to the efficiency of fluorescence of the sample. The method described here in the study of quinine bisulfate employs this compound as both the sample and the reference. This is achieved by monitoring the OAS signals from the fluorescent quinine sulfate solution and subsequently the signals obtained from nonfluorescent sample solutions after addition of chloride ions to promote quenching.

Halide ions are efficient fluorescence quenching agents and there are several references in the literature pertaining to the total quenching of quinine bisulfate aqueous solutions in the presence of excess chloride ions (9, 10).

To ensure that the addition of chloride ions to the quinine bisulfate solutions did not affect the absorptivity of the solutions in the concentration range of interest, absorbance vs. analyte concentration plots were obtained using the optoacoustic spectrometer in the transmittance mode. The plots obtained are linear in accordance with Beer's law and of equal molar absorptivity irrespective of whether the quinine bisulfate is present in sulfuric acid (i.e., fluorescent) or hydrochloric acid (quenched).

Employing a similar range of concentrations of quinine bisulfate in these acids, optoacoustic signals were recorded at an excitation wavelength of 366 nm; the graphs obtained are shown in Figure 1. The effect of the chloride ion on increasing the magnitude of the optoacoustic signal is clearly evident and the linearity of the graphs ensures that in the concentration range examined no interfering effects due to optical absorption saturation or thermal saturation (11) were present. The effect of varying the chloride ion concentration on the fluorescence efficiency of the quinine bisulfate was also examined; the results are shown in Figure 2 for a 5 × 10⁻³ M solution of quinine bisulfate in the acid mixture employed. These mixtures were prepared to ensure a constant pH for the solution under study. As Figure 2 demonstrates, at these concentrations of quinine bisulfate the use of 0.1 N hydrochloric acid solution was sufficient to quench totally the fluorescence; this acid concentration was employed as the medium for the observation of the optoacoustic signals on excitation at 366 nm under quenched conditions in the presence of chloride ions (Figure 2).

To determine Q from Equation 5, a value for λ_F of 459 nm was employed (12). The term $P(OAS)_F / P(OAS)_{NF}$ was evaluated from the ratio of the gradients of the graphs shown
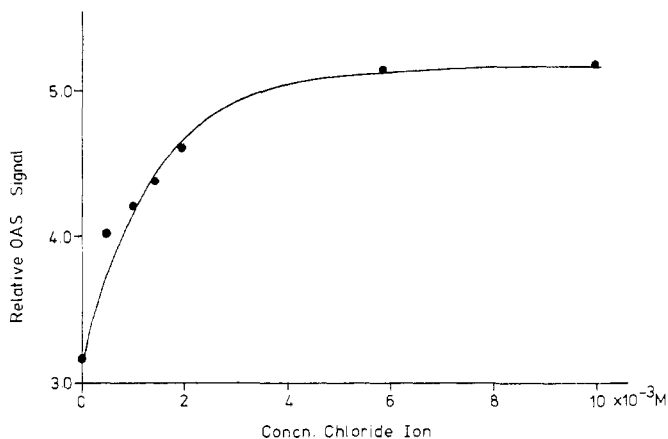
Figure 2. Effect of chloride ion concentration on the optoacoustic signal magnitude for a 5 × 10⁻³ M quinine bisulfate solution at pH 1

in Figure 1. By this technique, a value for Q for quinine bisulfate (in 0.1 N sulfuric acid) over the concentration range 10^{-3} to 10^{-2} M was found to be 0.53 ± 0.02. This value is in good agreement with the accepted literature value of 0.51 (7).

CONCLUSION

OAS provides a rapid and accurate technique for the determination of absolute quantum efficiencies of solutions; the apparatus described is capable of use with solid, liquid, or gel type samples.

Calorimetric techniques have been reported for triplet formation quantum yields and photochemical reaction studies (5), and the applications of OAS to obtain not only spectral data but also information about transient excited states for solid and solution samples should be of growing interest.

LITERATURE CITED

(1) W. R. Harshbarger and M. B. Robin, Acc. Chem. Res., 6, 329 (1973).
(2) A. Rosencwaig, Anal. Chem., 47, 592A (1975).
(3) M. J. Adams, A. A. King, and G. F. Kirkbright, Analyst (London), 101, 73 (1976).
(4) M. J. Adams, B. C. Beadle, A. A. King, and G. F. Kirkbright, Analyst (London), 101, 553 (1976).
(5) J. B. Callis, J. Res. Natl. Bur. Stand., Sect. A, 80 (3), 413 (1976).
(6) W. Lahmann and H. J. Ludewig, Chem. Phys. Lett., 45, 177 (1977).
(7) W. H. Melhuish, J. Phys. Chem., 65, 229 (1961).
(8) M. J. Adams, B. C. Beadle, and G. F. Kirkbright, Analyst (London), 102, 569 (1977).
(9) E. Lette and W. West, Proc. R. Soc. (London), Ser. A, 121, 294 (1928).
(10) J. Eisenbrand and M. Raisch, Fresenius' Z. Anal. Chem., 179, 352 (1961).
(11) A. Rosencwaig and A. Gersho, J. Appl. Phys., 47, 64 (1976).
(12) W. H. Melhuish, J. Phys. Chem., 64, 762 (1960).

Determination of Boron Isotope Ratios by Atomic Absorption Spectrometry

Peter Hannaford* and R. Martin Lowe

CSIRO, Division of Chemical Physics, P.O. Box 160, Clayton, Victoria, Australia 3168

Isotopic analysis of boron by atomic absorption methods is possible if neon-filled (but not argon-, krypton- or xenon-filled) discharge lamps are used as the source of boron resonance lines. For accurate measurement of the isotope ratio, it is advantageous to use enriched isotope sources and a sharp-line absorber, such as a water-cooled sputtering cell, and to make the absorption measurements on the 2088.9/2089.6 Å doublet, which has a considerably larger isotope shift than the main 2496.8/2497.7-Å resonance-line doublet. The ¹⁰B abundance of a sample of natural boron, determined with a sputtering absorption cell, was found to be 20.0 ± 0.2%. A less accurate determination of boron isotope ratios is possible using a nitrous oxide–acetylene flame absorption cell with the enriched isotope sources. A very simple, approximate method, which uses a commercial natural-boron source and the nitrous oxide–acetylene flame, is also described.

The isotopic composition of elements can in some cases be determined by spectroscopic techniques, such as atomic emission or atomic absorption. The atomic absorption technique, which was suggested some time ago as a possible method of isotopic analysis (1), is applicable to those elements for which the isotope shifts of the resonance lines are comparable to or greater than the widths of the emission- and absorption-line profiles defined by the experimental condi-

tions. For conventional atomic absorption measurements, in which uncooled sources and uncooled absorption cells are used, the elements having suitably large isotope shifts are: (i) the very light elements, for which the large relative mass difference of the isotopes can result in large isotopic mass shifts, and (ii) the heavy elements, for which differences in the nuclear charge distribution of the isotopes can result in large isotopic field shifts. Thus, to date, the only successful reported determinations of isotope ratios by atomic absorption (or fluorescence) measurements have been for lithium (2–6), mercury (7), lead (8, 9) and uranium (10, 11).

After lithium, the next light element having a natural isotope is boron, for which the natural abundance is usually 20% ¹⁰B to 80% ¹¹B. The determination of boron isotope ratios is of interest for a number of reasons: (i) the natural abundance of the isotopes is known to be variable (12), (ii) the large relative mass difference of the isotopes can lead to separation during the manufacture of boron compounds, and (iii) ¹⁰B-enriched materials, which are commonly used as neutron absorbers in reactor technology, can become depleted in ¹⁰B during exposure to high fluxes of neutrons. For the main boron resonance line, 2497.7 Å, the isotope shift (of the ¹¹B component relative to ¹⁰B) is +0.0085 Å (13), which is comparable to the typical widths of emission lines from hollow-cathode lamps (14). This suggests that boron should be a suitable element for isotopic analysis by atomic absorption methods. In an attempt to determine boron isotope ratios