Detection of Trace Amounts of Sodium by Fluorescence Emission Excited by a Continuous Wave Organic Dye Laser

Sir:

Organic dye lasers have been used by several workers to increase the detectability of trace amounts of materials.[1–6] The high intensity of a continuous wave (cw) dye laser concentrated in a line width comparable to atomic and ionic absorption widths combined with its highly directional properties and tunability makes it an excellent source for fluorescence excitation.[7] In this communication, we describe the use of a cw organic dye laser to detect 0.016 fg (1 fg = 10^{-15} g) of sodium vapor.

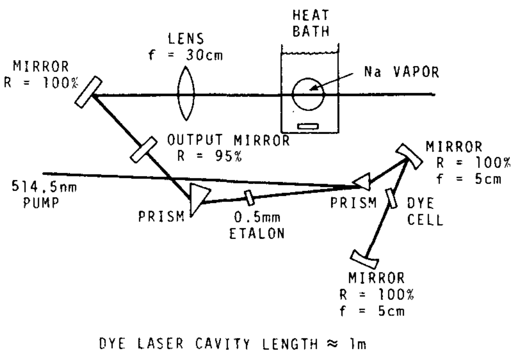

Figure 1. Block diagram of experimental apparatus showing cw dye laser configuration and sodium vapor cell for observing the sodium fluorescence.

The apparatus used in these experiments is shown in Figure 1. The laser configuration is similar to that described by Dienes, *et al.*[8] Two prisms and a 0.5-mm uncoated etalon in the cavity reduced the band width of the laser emission to 3 GHz (0.03 Å). The wavelength used in these experiments was 5896 Å and corresponds to the longest wavelength member of the sodium doublet. An output power of approximately 50 mW was obtained when the laser was pumped with 1.7 W of 5140-Å radiation from the Ar ion laser. The laser emission was focused into the sodium cell with a 30-cm focal length lens to give a beam diameter inside the cell of approximately 0.5 mm. The sodium was contained in an evacuated 2-in. spherical flask completely submerged in a well-stirred glycerine temperature bath. The pressure of the sodium vapor was obtained by measuring the temperature of the bath at its coldest point and using the vapor pressure *vs.* temperature data of Gordan.[9] Temperature gradients in the cell were less than 5°. Fluorescence from the sodium vapor in the cell was easily detected by visually observing the narrow line source excited by the passage of the laser beam through the sample cell.

The lowest temperature at which sodium fluorescence is visible was [illegible]. At this temperature, the vapor pressure of sodium is 1.5×10^{-8} mm.[9] The laser power used in these experiments was sufficient to saturate the sodium transition. This was demonstrated by observing that the intensity of the sodium fluorescence was not appreciably changed when the excitation beam intensity was attenuated by 90%. In this range of excitation intensities, the fluorescence intensity depends only upon the concentration of sodium atoms and not upon the light intensity.

The concentration of sodium atoms at a vapor pressure of 1.5×10^{-8} mm is 4.2×10^{8} atoms/cc. Detection of the fluorescence was actually made in a volume of approximately 1 mm^3 which contained 4.2×10^{5} molecules or 0.016 fg of material. Comparison of these data with other fluorescence excitation techniques is shown in Table I. Most of the data for Table I were taken from the recent work of Kuhl and Marowsky.[6] Inspection of Table I shows that the use of a cw organic dye laser as an excitation source for fluorescence analysis decreases the amount of sodium necessary for detection by two orders of magnitude.

Table I. Detectability Limits of Sodium by Different Analytical Techniques[a]

Technique	Limit[b]
Atomic absorption	
Hollow cathode lamp	12 ng/cm^3
Pulsed dye laser (sample inside cavity)[c]	2.0 pg/cm^3
Atomic fluorescence	
Hollow cathode lamp	33 ng/cm^3
Sodium vapor lamp	0.5 ng/cm^3
Pulsed dye laser (estimated)[d]	3 pg/cm^3
cw dye laser (present work)	16 fg/cm^3

[a] See ref 6. [b] Defined by Kuhl and Marowsky[6] as at a concentration where the signal to noise ratio is 2. The limit expressed in the present work is not a true limit in the sense that no signal to noise ratio was determined. [c] See ref 1: 10-cm path with pressure 3×10^{-7} mm ~ 2.0 pg/cm^3. [d] Estimated by multiplying 12 ng/cm^3 by the ratio of the laser power necessary to obtain a minimum detectable signal in a 12-ng cm^3 sample to the maximum laser power available.[6] This assumes that the sodium absorption will not be saturated at the higher laser powers.

Photoelectric detection of fluorescence excited by cw dye lasers will permit quantitative determination of atomic and ionic species in amounts well under a femtogram. Corresponding improvements in the ability to detect molecular species are expected.

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