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13. ABSTRACT (Maximum 200 Words)

The fluorescence properties of more than 20 aromatic hydrocarbons in aqueous solution have been characterized. The list includes benzene, toluene, ethylbenzene, and xylenes (BTEX) and naphthalene and its 1- and 2-methyl derivatives. They are found in most fuels and are sufficiently soluble to pose an environmental hazard. The fluorescence of aromatic hydrocarbons is well known, but the work reported here represents the first comprehensive characterization for the aqueous phase. BTEX fluorescence quantum yields are lower in aqueous solution than in organic solvents; a similar, but less pronounced, trend holds for the naphthalenes. Fluorescence lifetimes were determined in a fiber optic light delivery and collection mode similar to that which would be used in field measurements. Stern-Volmer analysis shows that fluorescence quenching by dissolved oxygen and anions at levels expected for environmental samples is small. Interfering fluorescence of humic substances is a greater concern.

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FLUORESCENCE OF AROMATIC HYDROCARBONS IN AQUEOUS SOLUTION

33 - 1993

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ABSTRACT

The fluorescence properties of more than 20 aromatic hydrocarbons in aqueous solution have been characterized. The list includes benzene, toluene, ethylbenzene, and xylenes (BTEX) and naphthalene and its 1- and 2-methyl derivatives. They are found in most fuels and are sufficiently soluble to pose an environmental hazard. The fluorescence of aromatic hydrocarbons is well known, but the work reported here represents the first comprehensive characterization for the aqueous phase. BTEX fluorescence quantum yields are lower in aqueous solution than in organic solvents; a similar, but less pronounced, trend holds for the naphthalenes. Fluorescence lifetimes were determined in a fiber optic light delivery and collection mode similar to that which would be used in field measurements. Stern-Volmer analysis shows that fluorescence quenching by dissolved oxygen and anions at levels expected for environmental samples is small. Interfering fluorescence of humic substances is a greater concern.

INTRODUCTION

Fiber optic spectroscopy is a promising approach for field screening of fuel contaminated groundwater and soil. Most fuels contain aromatic hydrocarbons, which can be sensitively detected via fluorescence. Our group has developed and field tested laser-based instrumentation for fiber optic fluorescence measurements. Details of the instrumentation and field results can be found elsewhere in these proceedings.^{1,2}

Ultraviolet light is required to efficiently excite the fluorescence of most aromatic hydrocarbons. The lasers that can provide the necessary ultraviolet light are generally pulsed. Fluorescence lifetimes measured with pulsed sources can be combined with the excitation and emission spectral information to distinguish the components in a complex mixture. It is not surprising, therefore, that fluorescence lifetimes have been measured in a fiber optic configuration. However, the body of work is small and little is known in general about fluorescence properties of aromatic molecules in aqueous (as opposed to organic) solutions.

Lieberman and coworkers³ give data for phenanthrene, fluoranthene, and pyrene in sea water. Niessner et al.⁴ studied about ten polycyclic aromatic hydrocarbons (PAHs), all with three or more aromatic rings. Both sets of authors used nitrogen lasers, whose output wavelength is too long (337 nm) to excite the fluorescence of benzene, toluene, ethylbenzene, and xylenes (BTEX) or naphthalenes; also, the influence of dissolved oxygen was not examined in either case. The only reported lifetime for any of the BTEX components in aqueous solution is the 2 ns value for benzene reported by Luria⁵ almost 20 years ago.

The goals of this research were to: (1) Generate a database of fluorescence lifetimes for BTEX and naphthalenes in aqueous solution; (2) Establish the accuracy and precision of lifetimes measured with a digital oscilloscope and fiber optic light delivery and collection; (3) Assess the effect of dissolved oxygen, naturally occurring anions (e.g., chloride or sulfate), and humic substances on the lifetimes.

R. Meidinger, R.W. St. Germain, V. Dohotariu and G.D. Gillispie. *"Fluorescence of Aromatic Hydrocarbons in Aqueous."* Field Screening Methods for Hazardous Wastes and Toxic Chemicals, pp. 395-403, 1993.

EXPERIMENTAL METHODS

Full details on the laboratory instrumentation can be found in the M.S. thesis of Roxane Meidinger (North Dakota State University, 1993). For the work reported herein, the lifetimes were determined with 266 nm excitation from the 4th harmonic of a Nd:YAG laser. The laser was operated at 10 pulses per second and less than 100 $\mu\text{J}/\text{pulse}$ were delivered to the sample at the terminus of the fiber optic probe. Spectral grade cyclohexane was used as received. Water was passed through an activated charcoal filter to reduce fluorescence background to negligible levels. Absorbances of the samples at the 266 nm excitation wavelength were kept below 0.1/cm to eliminate reabsorption effects. For the oxygen quenching characterization, oxygen was removed by bubbling nitrogen through the solutions for approximately 6 minutes before measurements were made. The fluorescence detection system consisted of a 0.3 m monochromator, photomultiplier tube, and digital oscilloscope.

FLUORESCENCE QUANTUM YIELDS FOR AQUEOUS SOLUTION

The data in Table 1 reveal that the fluorescence quantum yields are affected by the solvent. The cyclohexane solvent data are taken from Berlman⁶ and the aqueous solution values were measured on a spectrofluorimeter in our laboratory. The aqueous solution data are reliable for comparing the relative fluorescence efficiencies of different compounds. The absolute values are tentative because there isn't an aqueous solution fluorescence standard for the ultraviolet region. We referenced our results to fluorene, for which we estimate an aqueous solution fluorescence quantum yield of 0.6. This value was deduced from Berlman's value for the fluorene fluorescence quantum yield in cyclohexane (0.80) and the ratio of the fluorescence lifetimes in cyclohexane and water (7.0 and 5.2 ns, respectively). Also note that Berlman's data are for oxygen-free solutions, whereas the aqueous solution values are for air-saturated solutions. However, the oxygen quenching effects for water as solvent are small (see below).

Table 1. Fluorescence quantum yields of BTEX and naphthalenes.

Compound	Cyclohexane ^a	Water ^b
benzene	0.07	0.01
toluene	0.17	0.04
ethylbenzene	0.18	0.01
propylbenzene	0.14	0.02
o-xylene	0.19	0.01
p-xylene	0.40	0.16
naphthalene	0.23	0.11
1-methylnaphthalene	0.25	0.15
2-methylnaphthalene	0.32	0.21

^a Quantum yields in oxygen free cyclohexane from Reference 6 based on 9,10-diphenylanthracene standard.

^b Quantum yields in air-saturated water based on estimated quantum yield of 0.6 for fluorene.

LIFETIMES FOR OXYGEN-FREE CONDITIONS

The fluorescence lifetime determinations require separate measurements of the laser excitation and fluorescence emission temporal profiles, i.e., intensity vs. time curves. The duration of the Nd:YAG laser excitation pulses is about 6 ns. Since this is comparable to or even greater than some of the lifetimes of interest, deconvolution methods are necessary to extract the intrinsic molecular decay properties. Laboratory work to produce even more accurate temporal profiles continues, but the major problems of using a digital oscilloscope in this mode have been solved. The quality of our data for fitting the calculated and observed fluorescence profiles is shown for naphthalene in Figure 1.

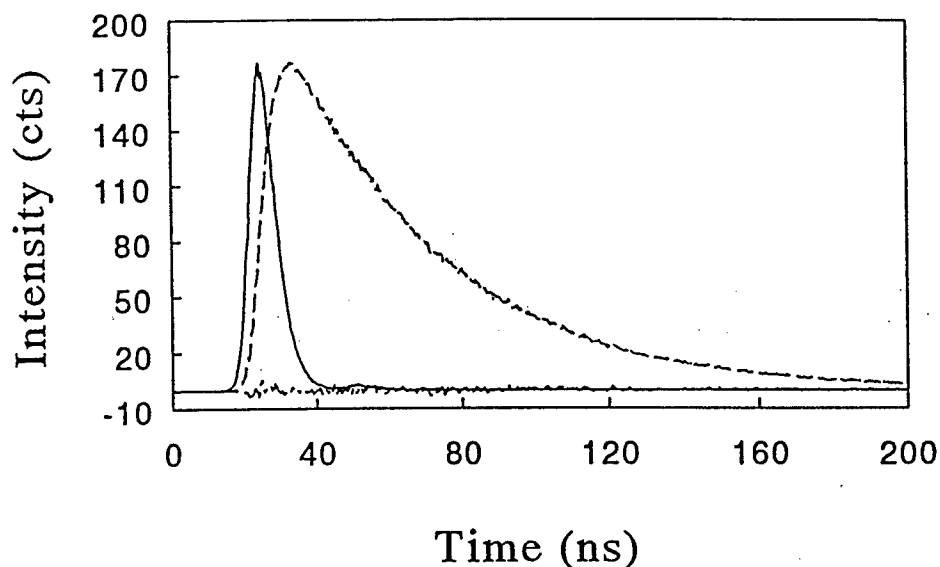


Figure 1. Typical laser-excited fluorescence temporal profiles for lifetime measurements. Sample is naphthalene in water. Solid line shows laser intensity as function of time. At the scale of this figure, the calculated and experimental fluorescence profiles are indistinguishable. The difference between them is shown along the baseline.

Fluorescence lifetime data for oxygen-free aqueous solutions are given in Table 2. The only literature values for comparison are those for benzene reported by Luria et al.⁵ Their values of 2.0 ns for benzene in deoxygenated water and 3.1 ns in D₂O are in good agreement with our value of 2.5 ns.

Table 2. Fluorescence lifetimes of BTEX and naphthalenes in deoxygenated water

Compound	Fluorescence Lifetime (ns)
benzene	2.5
toluene	4.9
ethylbenzene	4.5
o-xylene	6.1
p-xylene	11.1
propylbenzene	3.8
1,2,4-trimethylbenzene	8.6
naphthalene	40.3
1-methylnaphthalene	30.3
2-methylnaphthalene	24.6

QUENCHING EFFECTS

Owing to the fact that its ground state has a triplet spin, oxygen very efficiently quenches fluorescence. The fluorescence lifetime is consequently a function of all conditions that affect either the oxygen concentration or its diffusion rate. For solution conditions, the most important factors are temperature, solvent polarity and viscosity, and the partial pressure of oxygen over the solution. Natural groundwater also contains other potential quenchers, including metal cations and anions such as hydrogen carbonate, sulfate, and chloride.

Quenching effects on excited state decay properties are conveniently determined by comparing the fluorescence lifetimes in the presence and absence of quencher. The fluorescence lifetime in the absence of quencher, τ_0 , is represented as

$$\tau_0 = 1/(k_r + k_{nr}) \quad (1)$$

where k_r is the first-order rate constant for radiative emission and k_{nr} is the non-radiative decay rate constant. In the presence of quencher, the lifetime, τ , is further reduced according to the equation

$$\tau = 1/(k_r + k_{nr} + k_q[Q]) \quad (2)$$

in which $[Q]$ is the concentration of quencher and k_q is a second-order rate constant. Equations (1) and (2) can be combined into the Stern-Volmer equation:

$$\tau_0/\tau = 1 + \tau_0 k_q[Q] \quad (3)$$

A. Oxygen

Equation 3 indicates that a plot of $\tau_0/\tau - 1$ vs. τ_0 should give a straight line passing through the origin if the quenching efficiency per collision is the same for all compounds in the study and the quencher concentration is fixed. Berlman⁶ presented a graph of this type for the oxygen quenching of many different aromatic hydrocarbons in cyclohexane solution. We repeated much of Berlman's work and generally find longer lifetimes than he did for deoxygenated organic solutions. The trend is most obvious for molecules with long lifetimes, e.g., naphthalene and its methyl derivatives. Berlman's value for naphthalene in degassed cyclohexane is 96 ns, compared to 115 ns in our work.

The likely explanation is that our deoxygenation procedure is more effective than was Berlman's. We tested degassing efficiency with pyrene, because its unusually long-lived lifetime makes it extremely susceptible to oxygen quenching. For a cyclohexane solution purged by nitrogen gas bubbling for six minutes, we found a pyrene fluorescence lifetime of 458 ± 15 ns, in good agreement with literature values.

The graphs of equation 3 for data taken for water and heptane solvents are shown in Figure 2. Our correction of Berlman's organic solvent data doesn't affect his conclusion that quenching efficiency per collision is nearly the same for all the compounds; fluoranthene is a notable exception for its near immunity from oxygen quenching.

The oxygen quenching for air-saturated aqueous solutions is nearly negligible. The slope of the line through the data is 40 times smaller than for the heptane solvent quenching line. Only for the longest-lived compounds could the effect even be discerned. For example, the lifetime of naphthalene increases only about 10% (from 36 to 40 ns) when the oxygen is removed. As was the case above, pyrene is the most sensitive probe. Our value of 127 ns for an air-saturated distilled water solution of pyrene agrees well with Lieberman's report³ of 129 ns in air-saturated sea water. Oxygen removal extends the pyrene fluorescence lifetime to 194 ns. The aqueous solution quenching was calculated with just the naphthalene and pyrene data.

The nearly negligible fluorescence quenching by oxygen in aqueous solution compared to organic solvents is readily understood from the data of Table 3. First, note that the solubility of oxygen in water is an order of magnitude lower than in aliphatic solvents. This accounts for the majority of the difference. A secondary contribution arises from the higher viscosity of water, which in turn means a

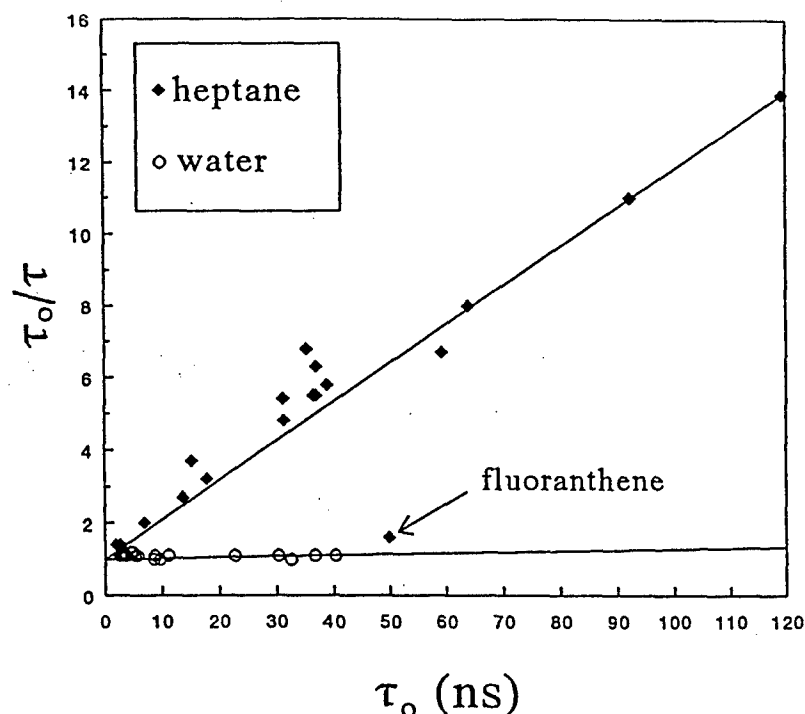


Figure 2. Graphs of degree of oxygen quenching (τ_o / τ) for air saturated solutions vs. lifetime in oxygen free solutions (τ_o). Oxygen quenching is approximately 40 times greater for heptane solvent, mostly owing to higher oxygen solubility (see text). Fluoranthene is anomalously immune to oxygen quenching.

slower diffusion-controlled rate constant, k_d . The product of the oxygen solubility and k_d (last column in Table 3) is a measure of oxygen quenching in a given solvent under air-saturated condition, if the quenching efficiency per collision is independent of solvent. Our data shows this to be so to a good approximation.

Table 3. Solvent data relevant to the quenching efficiency of oxygen

Solvent	Molar Solubility ^a	Viscosity ^b (cP)	k_d ($M^{-1} s^{-1}$)	$k_d[O_2]$ (s^{-1})
cyclohexane	2.28×10^{-3}	0.98	6.7×10^9	1.5×10^7
heptane	2.69×10^{-3}	0.42	1.6×10^{10}	4.3×10^7
hexane	3.02×10^{-3}	0.31	2.1×10^{10}	6.3×10^7
water	2.56×10^{-4}	1.00	6.6×10^9	1.7×10^6

^a Calculated using data from reference 7 for organic solvents and reference 8 for water;

^b Reference 9.

There is also an intrinsic solvent dependence of τ_o . Consider the lifetime data in Table 4 for naphthalene in air-saturated and deoxygenated cyclohexane, heptane, and water. The lifetimes in degassed cyclohexane and heptane are identical to within experimental error. The only definite conclusion that can be drawn is that the ratio of radiative and non-radiative decay rate constants is the same in both solvents. In principle, both k_r and k_{nr} could be affected proportionately by a change from cyclohexane to heptane solvent, but there is no reason to expect that to be the case. On the other hand However, the much shorter τ_o value in water requires that either the radiative decay rate is lower or th

radiationless decay rates is higher than in the aliphatic solvents. It is likely that k_{nr} , determined predominately by intersystem crossing, is faster in water than in the organic solvents.

Table 4. Fluorescence lifetime of naphthalene in different solvents

Solvent	Lifetime (ns)-undegassed	Lifetime (ns)-degassed
cyclohexane	16.7	120
heptane	9	119
water	36	40

B. Dissolved Ions

The prospects for quantitative fluorescence measurements under field conditions are enhanced by the demonstration that oxygen has only a minor effect. However, dissolved ions in natural waters are also potential quenchers. Just as oxygen can enhance the intersystem crossing rate, so can other species via the phenomenon known as the "heavy atom effect." The incorporation of high atomic weight atoms in a molecule is well known to enhance spin-orbit coupling between the S_1 and T_1 states and thereby speed-up intersystem crossing; the phenomenon is referred to as the internal heavy atom effect. The presence of high atomic weight atoms in the solvent or in ions dissolved in solution gives rise to an analogous external heavy atom effect. Owing to their relatively high concentrations in natural waters, chloride and sulfide are the most likely quenchers. We also studied bromide, even though its concentration in natural waters is quite low, because it will provide an upper-limit to the magnitude of the heavy atom effect.

We measured the fluorescence lifetime of naphthalene in deoxygenated aqueous solutions containing different concentrations of dissolved sodium salts. The data in Table 5 show that there is a marked lifetime decrease with increasing bromide ion concentration. Chloride ion has a much smaller effect. Even for 1 M NaCl, only about 20% of the fluorescence is quenched and the effect is barely noticeable at 0.1 M quencher concentration. The Stern-Volmer plots in Figure 4 clearly reveal the expected linear relationship.

Table 5. Anion effect on naphthalene fluorescence lifetime

Concentration [M]	Lifetime (ns) in NaCl(aq)	Lifetime (ns) in NaBr(aq)
0	40.3	40.3
0.05		26.4
0.1	40.1	18.1
0.4		6.8
0.5	35.2	
0.7		4.2
1.0	32.9	2.9

The lifetime of naphthalene in oxygen-free water is 40 ns with an experimental uncertainty of about 1 ns. The concentration of quencher that reduces the lifetime by an amount equal to the uncertainty defines an approximate threshold for the quenching effect to be considered significant. For our data, the quenching of naphthalene by Br^- is insignificant at concentrations below 0.02 M (≈ 2000 ppm) while the limit for Cl^- is about 0.1 M (≈ 6000 ppm). Since these values are much higher

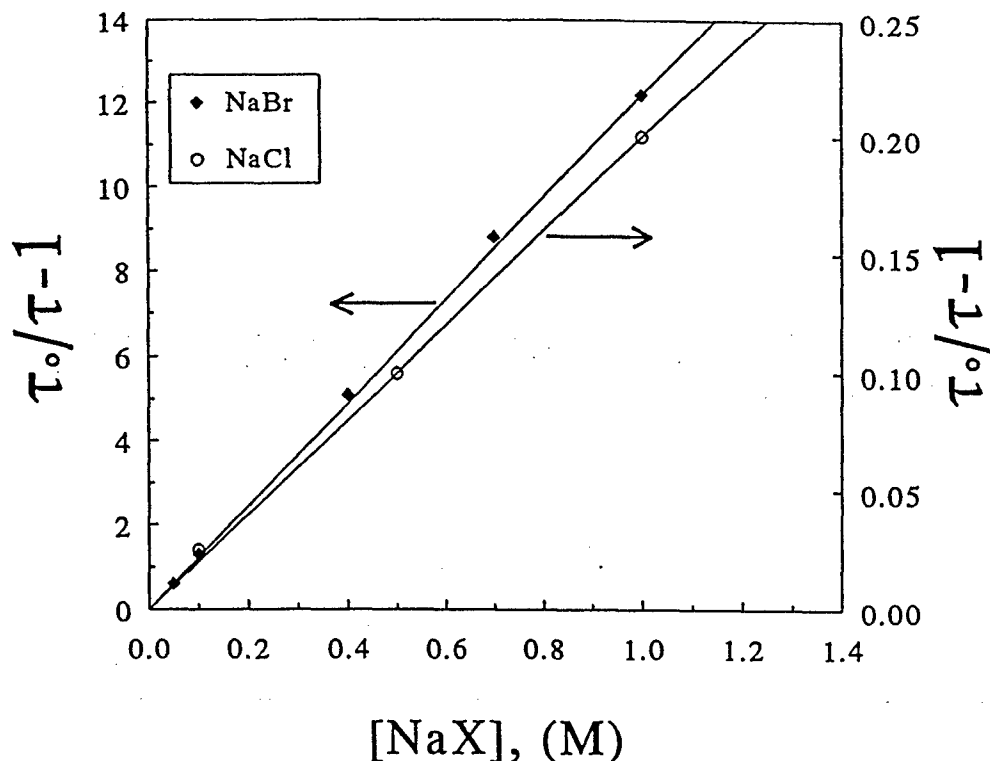


Figure 3. Fluorescence quenching of naphthalene by bromide and chloride ion. Note that the ordinate scales are different by a factor of approximately 50.

than levels normally found, these ions should not interfere with lifetime data from groundwater environments. Stumm and Morgan report chloride concentrations of ≈ 4 to 20 ppm for groundwater in a variety of environments.¹⁰ Faure¹¹ gives the concentration of Br^- in streams at 20 ppb while Krauskopf¹² reports a concentration of Br^- in seawater of 67 ppm.

C. Humic Substances

Humic substances are formed by bacterial and chemical degradation of plant tissue. High concentrations of these species are commonly found in soil and in groundwater and their effect on aromatic hydrocarbon fluorescence must be determined. Even tapwater can show an appreciable humic fluorescence, as is illustrated in Figure 4. The signal in distilled water is much lower, but can be reduced still further by passing the water through a charcoal column. We examined the fluorescence of naphthalene in such filtered distilled water and in water which had been equilibrated with uncontaminated soil from Tinker AFB. A large humic substance fluorescence was observed in the 400-500 nm range for the latter sample. In addition, the naphthalene fluorescence was reduced substantially. The naphthalene fluorescence lifetime was determined and a value of ca. 35 ns was found in each case. Since the lifetime was not affected in the presence of humic materials, the reduction in fluorescence intensity must be due to static quenching. This is consistent with previous reports in the literature.

Gauthier et al.¹³ measured the fluorescence of aqueous solutions of phenanthrene, anthracene, and pyrene and found that the fluorescence intensity decreased with an increase in humic materials. To maximize fluorescence relative to background from the humic material they used concentrations near the solubility limit. The PAHs they investigated have moderate solubilities in water. An interesting note is that PAHs with lower solubilities tend to bind more strongly to humic substances so that the humic concentrations required for the binding constant measurements are lower. Williams¹⁴ also

predicts that the quenching mechanism for the presence of dissolved humic materials is static. He determined the fluorescence lifetimes of 1-naphthol, napropamide, and fluoranthene in aqueous solutions and found that the lifetimes did not shorten with increasing humic acid concentration.

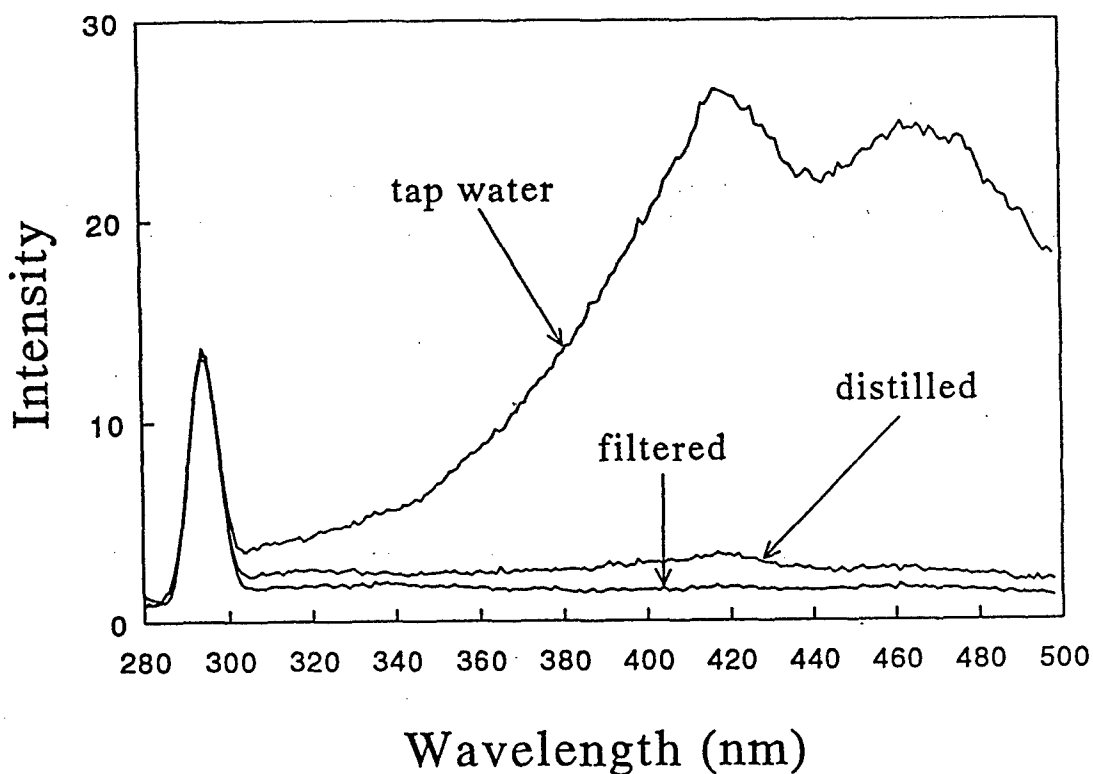


Figure 4. Background fluorescence spectra of water samples. Feature at 295 nm is a water Raman band. Emission in tap water is ascribed to humic substances. The small background for distilled water can be reduced further by filtering the water through a column of charcoal. Fluorescence spectra similar to those for tap water are also found for natural water samples.

CONCLUSIONS

Quenching of fluorescence by oxygen or anions in solution is of only minor consequence and does not pose a problem for quantitative in-situ fluorescence analysis. The fluorescence lifetimes of benzene, toluene, p-xylene, and naphthalene are significantly different, so lifetime data will likely prove helpful for speciating these compounds. Humic substances represent a greater complication.

ACKNOWLEDGMENTS

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