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Ultraviolet Fluorescence Monitor

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Ultraviolet Fluorescence Monitor

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Abstract

A multispectral ultraviolet (UV) fluorescence imaging fluorometer and a pulsed molecular beam laser fluorometer were developed to detect volatile organic compounds of interest in environmental monitoring and drug interdiction applications. The UV fluorescence imaging fluorometer is a relatively simple instrument which uses multiple excitation wavelengths to measure the excitation/emission matrix for irradiated samples. Detection limits in the high part-per-million to low part-per-million range were measured for a number of volatile organic vapors in the atmosphere. Detection limits in the low part-per-million range were obtained using cryogenic cooling to pre-concentrate unknown samples before introducing them into the imaging fluorometer. A multivariate analysis algorithm was developed to analyze the excitation/emission matrix and used to determine the relative concentrations of species in computer synthesized mixtures containing up to five organic compounds. Analysis results demonstrated the utility of multispectral UV fluorescence in analytical measurements. A transportable UV fluorescence imaging fluorometer was used in two field tests. Field test results demonstrated that detection limits in the part-per-billion range were needed to reliably identify volatile organic compounds in realistic field test measurements. The molecular beam laser fluorometer, a more complex instrument with detection limits in the part-per-billion to part-per-trillion range, was therefore developed to satisfy detection sensitivity requirements for field test measurements. High-resolution spectroscopic measurements made with the molecular beam laser fluorometer demonstrated its utility in identifying volatile organic compounds in the atmosphere.

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Ultraviolet Fluorescence Monitor

Introduction

Ultraviolet (UV) fluorescence spectroscopy is generally considered a highly sensitive technique to detect organic and inorganic molecules. However, its utility as an analytical tool has been limited because of the difficulty in determining species concentrations from highly overlapped ultraviolet spectra of individual species. To take advantage of the high sensitivity of ultraviolet fluorescence spectroscopy in analytical measurements, we have developed two methods to identify species and determine their concentrations from fluorescence spectra. The first uses a *multispectral UV fluorescence imaging fluorometer* to excite fluorescence spectra with multiple excitation wavelengths, thereby producing an excitation/emission matrix which is compared to corresponding database spectra for individual species to obtain species concentrations. The second method uses a pulsed *molecular beam laser fluorometer* (MBLF) to cool species to a few Kelvins in a free-jet expansion, resulting in simplified narrow-band ultraviolet absorption spectra which are no longer highly overlapped, thereby simplifying the identification of individual species. Measurements made using the MBLF require more complex instrumentation but are more sensitive than measurements made with the multispectral UV fluorescence imaging fluorometer. MBLF measurements were found to have detection limits in the part-per-billion (ppb) to part-per-trillion (ppt) range, whereas measurements made with the multispectral UV fluorescence imaging fluorometer were found to have detection limits in the high part-per-million (ppm) to low ppm range. Because of the greater simplicity of the UV fluorescence imaging fluorometer, it was used to measure multispectral UV fluorescence spectra for a number of species and to develop analysis algorithms to determine species concentrations. A transportable multispectral UV fluorescence imaging fluorometer was also developed for field test measurements. As discussed in this report, results of two field test campaigns demonstrated the need for instrumentation based on the higher sensitivity MBLF measurements. Development of a transportable MBLF instrument is not discussed in this report.

In the remaining sections of this report, we discuss multispectral UV fluorescence measurements, the development of a laboratory fluorometer to measure the excitation/emission matrix for a number of small molecules, and measurements of detection limits using the laboratory UV fluorometer. Development of a transportable UV fluorescence imaging fluorometer and results of two field test campaigns to detect volatile organic compounds in the atmosphere are also discussed. Finally, we discuss development of the molecular beam laser fluorometer, cooling of molecules in a free-jet expansion to simplify UV spectra, and MBLF detection limits for representative volatile organic compounds.

Multispectral Ultraviolet Fluorescence Concept

Background

The high degree of overlap in ultraviolet absorption spectra is illustrated in Fig. 1 which shows absorption cross sections for six species at wavelengths between 252 and 280 nm. The cross sections in Fig. 1 for benzene, *m*-xylene, *o*-xylene, *p*-xylene, and toluene were measured with a resolution of 0.01 nm with a high resolution tunable UV dye laser. The only species in Fig. 1 which has narrow-band absorption features is benzene. Absorption cross sections for all other species are fairly broad and highly overlapped. As a consequence, light at 266 nm, for example, will excite fluorescence in all species in Fig. 1 except sulfur dioxide, which does not emit fluorescence when excited at 266 nm. Fig. 2, showing measured fluorescence quantum yields, further indicates that the resulting fluorescence spectra for benzene, *m*-xylene, *p*-xylene, and toluene are also highly overlapped. (The fluorescence quantum yield for *o*-xylene is not shown in Fig. 2.) Determining species concentrations from the resulting fluorescence spectra is thus complicated by the highly overlapped UV fluorescence spectra.

Figure 1. Absorption cross sections measured with a high-resolution dye laser are highly overlapped but show distinct spectral features which can be used to identify individual species. The SO_2 absorption cross section is taken from Ref. 1.

Figure 2. Relative fluorescence quantum yields were measured for benzene, *m*-xylene, *p*-xylene, and toluene. Absolute quantum yields were obtained by normalizing the relative measurements to previous measurements by Suto *et al.*²

Even though the spectra in Figs. 1 and 2 are highly overlapped, unique spectral features associated with each molecule are apparent. In the next two sections we show that the spectral differences evident in Figs. 1 and 2 allow us to use measurements made with multiple absorption (or fluorescence excitation) wavelengths to identify species and determine their concentrations.

Multispectral UV Fluorescence Imaging Fluorometer

A low-resolution multispectral UV fluorescence imaging fluorometer was developed to study the fluorescence properties of volatile organic compounds. A schematic diagram and photograph of the fluorometer are shown in Fig. 3. The fluorometer uses a high-pressure xenon arc lamp source and an intensified multichannel detector to measure the excitation/emission matrix. The excitation/emission matrix is measured by using the broadly tunable xenon arc lamp UV light source to excite fluorescence. Fluorescence spectra are measured by sequentially scanning the wavelength of the xenon arc lamp from 200 nm to 400 nm in 5-nm steps using a scanning monochromator to spectrally filter the broadband light from the xenon arc lamp. The spectral resolution of the filtered xenon arc lamp was measured to be 15 nm full-width-half-max (FWHM). The spectrally filtered light from the xenon arc lamp is imaged onto a sample chamber where it excites fluorescence in irradiated samples. Fluorescence excited by the xenon arc lamp is reimaged onto the entrance slit of a imaging spectrometer and dispersed onto an intensified diode-array multichannel detector. The multichannel detector covers the spectral range from 200 nm to 800 nm with a spectral resolution of about 7 nm FWHM. At each

excitation wavelength, the dispersed fluorescence spectrum detected with the diode-array detector is digitized and recorded for subsequent off-line data analysis. The *excitation/emission matrix* of the sample is a composite fluorescence spectrum made up of the fluorescence spectrum excited at each excitation wavelength. For the measurements discussed in this report, it thus consists of the 41 fluorescence spectra excited at wavelengths from 200 to 400 nm in 5-nm increments. A typical excitation/emission matrix is measured in about 10 minutes with the low-resolution UV fluorescence imaging fluorometer.

An example excitation/emission matrix for a 10^{-4} molar solution of rhodamine-6G in methanol is shown in Fig. 4. Fig. 4 is a hidden-line 3-d plot showing the series of 41 discrete dispersed fluorescence spectra which make up the excitation/emission matrix - one fluorescence spectrum for each of the 41 excitation wavelengths. Peaks and valleys in the fluorescence spectra in Fig. 4 correspond to peaks and valleys in the absorption and fluorescence spectrum of each component in the mixture. Changes in, for example, the rhodamine-6G fluorescence spectrum as the excitation wavelength increases are due to changes in the rhodamine-6G absorption cross section (The fluorescence signal from methanol is due to impurities in the methanol.). The composite spectrum in Fig. 4 is also referred to as the *multispectral fluorescence spectrum* or the *dispersed fluorescence excitation spectrum* of the sample.

Schematic Diagram of UV Fluorometer

(a)

(b)

Figure 3. Schematic diagram (a) and photograph (b) of the multispectral UV fluorescence imaging fluorometer used to measure the excitation/emission matrix.

The data in Fig. 4 illustrate the utility of multispectral UV fluorescence measurements in the identification of species. The excitation/emission matrix spreads out the individual spectra, making it relatively easy to identify each species. Assuming all measurements are made in the linear absorption range, species concentrations can be determined from the intensity of the fluorescence peaks.

Figure 4. Excitation/emission matrix for rhodamine-6G in reagent grade methanol. Fluorescence wavelengths along the x-axis range from 200 nm to 700 nm; excitation wavelengths along the y-axis range from 200 nm to 400 nm. Peaks and valleys in the rhodamine-6G fluorescence spectrum correspond to changes in the rhodamine-6G absorption spectrum. The methanol fluorescence signal is due to impurities.

Multispectral UV Fluorescence Spectra

Excitation/emission matrices for a number of small molecules of interest in environmental monitoring and drug interdiction are shown in Figs. 5 to 11. Neat samples were irradiated for the measurements in Figs. 5 to 11. In each case, the excitation wavelength was scanned from 200 nm to 400 nm in 5-nm steps. In each figure, the fluorescence band corresponding to the neat sample is identified. Other prominent features in Figs. 5 to 11 are the first-order and second-order scattered light peaks arising from a combination of Rayleigh scattering from the neat sample and stray light not rejected by the imaging system. First-order and second-order scattered light peaks as well as second-order spectra of the fluorescence band are identified in Figs. 5 to 11.

The excitation/emission matrix makes differences in the fluorescence band shape, band location, and band asymmetry of each species more apparent. It is these spectral differences which make it possible to identify species and determine their concentrations using multivariate analysis algorithms. The algorithm is used to analyze excitation/emission spectra from an

unknown sample to determine species concentrations. The analysis is carried out by comparing the excitation/emission matrix for the unknown sample to excitation/emission matrices for database spectra. Representing the excitation/emission matrix for the unknown by U and the database matrix for species i by D^i , the excitation/emission matrix for the unknown can be written as a linear combination of the database matrices:

$$U = \sum_{i=1}^N C_i \cdot D^i, \quad (1)$$

where the coefficients C_i are proportional to the concentration of species i and N represents the number of database species. The coefficients C_i are obtained by least squares minimization of Eq. (1):

$$\chi^2 = \sum_{k,l} (U_{kl} - \sum_{i=1}^N C_i \cdot D_{kl}^i)^2, \quad (2)$$

where the subscripts k,l represent matrix elements of the U and D^i excitation/emission matrices. Differentiating Eq. 2 and setting the result equal to zero gives

$$\frac{\partial \chi^2}{\partial C_j} = 2 \cdot \sum_{k,l} (U_{kl} - \sum_{i=1}^N C_i \cdot D_{kl}^i) \cdot D_{kl}^j = 0 \quad (3)$$

The coefficients C_i are obtained by solving the N simultaneous equations

$$\sum_{k,l} (U_{kl} - \sum_{i=1}^N C_i \cdot D_{kl}^i) \cdot D_{kl}^j = 0. \quad (4)$$

Equation 4 is used to identify species in unknown chemical mixtures by calculating relative concentration coefficients C_i for each database species. The procedure was tested using computer synthesized data to generate an excitation/emission matrix for a mixture of acetone, benzene, methanol (impurities), toluene, and xylene in relative concentrations of 1:1:1:1:0.01. Individual excitation/emission matrices in Figs. 5, 6, 9, 10, and 11 were multiplied by 1, 1, 1, 1, and 0.01, respectively, and added together to generate the mixture data, U , in Fig. 12. Excitation/emission matrices in Figs. 5, 6, 9, 10, and 11 were also used as database spectra, D^i , to solve Eq. 4 for the relative concentration C_i of each species. Only those matrix elements containing spectral information about species concentrations were used to solve Eq. 4. For example, matrix elements associated with scattered light peaks were not used. The solution in Table 1 shows that excellent agreement was obtained between the computer synthesized and calculated concentrations. In a more stringent test of Eq. 4, the five database spectra were used to calculate relative concentrations for a computer synthesized mixture of benzene and xylene, species with somewhat similar low-resolution fluorescence spectra. As shown in Table 2, calculated relative concentrations for species not in the mixture are in the 10^{-5} to 10^{-7} range.

Even in the presence of as much as 50% rms noise numerically added to the synthesized mixture spectrum, Eq. 4 could still be used to calculate the correct relative concentration of each species. Results obtained analyzing computer synthesized spectra suggest that multispectral fluorescence measurements are robust enough to analyze the noisy data often encountered in field measurements.

Table 1. Calculated concentrations for a computer synthesized mixture of acetone, benzene, methanol (impurities), toluene, and xylene.

Species	Computer Synthesized Relative Concentration	Calculated Relative Concentration
Acetone	1.00	1.00
Benzene	1.00	1.00
Methanol (impurities)	1.00	1.00
Toluene	1.00	1.00
Xylene	0.01	0.01

Table 2. Calculated concentrations for a computer synthesized mixture of benzene and xylene.

Species	Computer Synthesized Relative Concentration	Calculated Relative Concentration
Acetone	0.00	$9.4 \cdot 10^{-7}$
Benzene	1.00	1.0
Methanol (impurities)	0.00	$-3.5 \cdot 10^{-5}$
Toluene	0.00	$-4.5 \cdot 10^{-7}$
Xylene	0.01	$1.0 \cdot 10^{-2}$

Figure 5. Excitation/emission matrix for neat acetone.

Figure 6. Excitation/emission matrix for neat benzene.

Figure 7. Excitation/emission matrix for neat biacetyl.

Figure 8. Excitation/emission matrix for gasoline.

Figure 9. Excitation/emission matrix for methanol impurities.

Figure 10. Excitation/emission matrix for neat toluene.

Figure 11. Excitation/emission matrix for neat xylene.

Figure 12. Excitation/emission matrix for a computer synthesized mixture of acetone, benzene, methanol, toluene, and xylene.

Fluorescence Detection Limits

The excitation/emission matrix was also measured for volatile organic vapors. Results for acetone, benzene, biacetyl, methanol (impurities), toluene, and xylene are shown in Figs. 13 to 18, respectively. Vapor-phase multispectral UV fluorescence detection limits ($S/N=3$) were obtained by comparing the peak fluorescence intensity to the rms fluctuations in the baseline. Detection limits, listed in Table 3, range from 2000 ppm for acetone to 5 ppm for xylene.

Table 3. Gas-phase detection limits measured with the multispectral UV fluorescence imaging fluorometer.

Compound	Detection Limit (ppm)
Acetone	2000
Benzene	40
Biacetyl	300
Methanol (Impurities)	400
Toluene	100
Xylene	5

Figure 13. Excitation/emission matrix for 194 torr acetone vapor in air at room temperature.

Figure 14. Excitation/emission matrix for 77 torr benzene vapor in air at room temperature.

Figure 15. Excitation/emission matrix for 40 torr biacetyl vapor in air at room temperature.

Figure 16. Excitation/emission matrix for 105 torr methanol vapor (impurities) in air at room temperature.

Figure 17. Excitation/emission matrix for 23 torr toluene vapor in air at room temperature.

Figure 18. Excitation/emission matrix for 7 torr xylene vapor in air at room temperature.

DEA Field Test

Background

The UV fluorescence imaging fluorometer was used in a Drug Enforcement Agency (DEA) drug lab simulation field test from May 20 to May 23, 1991. This was the first DEA operated test and the second in a series of tests to evaluate the ability of advanced chemical sensors to identify drug-related chemical vapor plumes. The field test was focused on the detection of plumes associated with the production of cocaine, heroin, and methamphetamine laboratories. Plumes of acetone, acetic acid, diethyl ether, sulfur hexafluoride (simulant to calibrate FTIR instruments), and biacetyl (simulant to calibrate UV imaging fluorometer) were produced. Organizations participating in the field test are listed in Table 4.

Field Test Goals

Our primary purpose at the field test was to obtain information needed to evaluate the capability of the UV fluorescence imaging fluorometer to detect drug-related plumes and to access its reliability under field test conditions. Data of interest in evaluating the performance of the imaging fluorometer were: 1) plume concentrations and 2) the detectability of plume vapors using the UV fluorescence imaging fluorometer. Component parts for the UV imaging fluorometer were designed, built, and put together on a tight six-week time schedule which included debugging new software written to automate the collection of fluorescence spectra.

Table 4. Organizations participating in the May 1991 field test.

Organization	Activity
Drug Enforcement Agency	Lead laboratory and organizer
Federal Bureau of Investigation	Infrared imaging
ERDEC (Army)	Infrared spectroscopy (two FTIR systems)
Los Alamos National Laboratory	Ion mobility mass spectrometer
Night Vision Laboratory (Army)	Infrared Spectroscopy (FTIR)
Sandia National Laboratories NM	UV imaging fluorometer
Sandia National Laboratories CA	Air sampling and plume characterization
Atmospheric Sciences Lab (Army)	Meteorology
Naval Ocean Systems Command	Observers
Naval Ordnance Tech Center	Observers

Field Test Results

Concentrations of vapors released at the field test ranged from about 1 ppm to 300 ppm. The UV fluorescence imaging fluorometer was set up about 25 m from the plume release point. In order to sample plume vapors, a Teflon[®] tube was run to the release point and a pump was used to draw vapors through the Teflon tube into the sampling chamber at atmospheric pressure with no pre-concentration. Comparing vapor detection limits for acetone and biacetyl in Table 3 to the released vapor concentrations shows that the sensitivity of the UV imaging fluorometer was, at best, marginal to detect the vapor plume. Folding in higher-than-expected vapor losses in the tubing used to transport sampled vapors from the release point to the fluorometer, we estimate that the fluorometer sensitivity needed to be about a factor of 10 to 100 lower to reliably detect the vapor plume. This was borne out by the fluorometer measurements which did not detect an unambiguous fluorescence signal. In reassessing the measurements after the field test, it was concluded that excellent results would have been obtained using xylene or benzene as simulant vapors for the UV imaging fluorometer.

Throughout the field test, the UV fluorescence imaging fluorometer operated flawlessly, with no down time, giving us confidence in the feasibility of developing a reliable instrument to sample vapor plumes. After the field test, a transportable platform was developed for the UV fluorescence imaging fluorometer and a scheme was devised to improve the detection limits of the fluorometer a factor-of-10 by using a cryogenic trap to concentrate and subsequently expand the vapors into an evacuated sampling chamber. The transportable UV fluorescence imaging fluorometer with enhanced detection limits is discussed in the next section of this report.

Transportable Multispectral UV Fluorescence Imaging Fluorometer

Background

A transportable UV fluorescence imaging fluorometer system was developed to sample and measure volatile organic vapors in the air. As shown in the previous sections, when sampled gases are excited by ultraviolet light, the irradiated gases emit a luminous or fluorescent light that can then be analyzed to identify organic vapors. The UV fluorescence imaging fluorometer system is totally self contained and is intended to be transported to landfills or similar sites. The fluorometer fits on a 3 foot by 3 foot optical breadboard. Assembly and testing were done in the laboratory before the complete system was reduced in size and placed on the transportable table.

Construction

There were three major concerns when designing the transportable UV fluorescence imaging fluorometer system: 1) the optical system needed to be compact, 2) the fluorometer and all its supporting equipment had to be mounted on one platform, and 3) the fluorometer needed to be easily transportable. The transportable system was designed on a personal computer using CAD software, which provided flexibility to accommodate changes to the fluorometer layout.

A schematic diagram of the imaging fluorometer is shown in Fig. 19. An MDC Corp. model-150 six-way cross functions as the sample measurement chamber. Magnesium fluoride windows are installed on the chamber because of their ability to transmit ultraviolet light and their relatively low fluorescence yield when illuminated by UV light. A compact, tunable monochromatic light source with sufficient energy is necessary to excite fluorescence in the gas sample. The light source used in the fluorometer is an Oriel model 66057 lamp housing with a 150-watt high-pressure xenon arc lamp. Filtering the light through an ISA model H-10 monochromator enables the light to be tuned from 200 nm to 400 nm with a 15-nm FWHM bandwidth. Since sample vapor concentrations can be small, the detection system needs to be very sensitive. Therefore, a multichannel detection system with single-photon sensitivity was selected. An ISA model CP-200 imaging spectrometer capable of 10-nm FWHM resolution, and an ITT model 1024-SA gated, intensified diode-array detector met the detection requirements without the need to cool the array detector. A Tektronix model 2430A oscilloscope acquires and displays spectral data from the fluorometer. Spectral data is collected using an 80486-66 DX2 computer interfaced to the oscilloscope using software developed at Sandia.

Supporting equipment also had to be transported with the system on a platform designed to carry the entire system. A 3' x 4' table was designed to mount a optical breadboard, and instrumentation racks were installed at two ends to hold supporting equipment. A Newport model XS-33 optical breadboard with micro-lock tie downs is attached to the table. A hole drilled through the table allows the sample chamber to be held at a specific height with its associated vacuum plumbing mounted under the breadboard (see Fig. 20). The base of the table is equipped with a steel plate to carry an Alcatel model 2010 vacuum pump and a Neslab model RTE recirculating chiller.

Figure 19. Schematic diagram of the transportable multispectral UV fluorescence imaging fluorometer system.

Figure 20. Schematic diagram showing the layout of plumbing and support equipment used to operate the transportable UV fluorescence imaging fluorometer.

Six-inch casters made of polyurethane are mounted on the bottom of the table. The size and material of the casters provide ample ground clearance, support a three-hundred-pound load, and provide mobility on almost any terrain. Leveling feet are installed so the table can be leveled on uneven ground (see Fig. 20).

Solid aluminum mounting plates and bases were made for all the optical components so they could be mounted at the same optical height (see Fig. 21). All optical components are securely attached to mounting holes built into the optical table. Lenses, mounted in Newport LP1 mounts which have ϕ -x-y-z adjustments, were used to transport the excitation light to the sample chamber and to image the resulting fluorescence onto the multichannel detector. These lens mounts enabled precise alignment of the fluorescence images on the spectrometer entrance slits. Black tubing is installed along the entire optical path to prevent stray light from entering the detection system.

Figure 21. Photograph of optical components mounted on solid aluminum bases for optical stability.

The vacuum system is almost entirely constructed with various standard stainless-steel vacuum flanges and parts. Metal seals are used throughout the vacuum system. The vacuum system is able to reach a base pressure of $3 \cdot 10^{-9}$ torr when pumping through the entire gas

manifold. A Perkin Elmer digital ion gauge and controller are used to measure the base pressure. Operating pressures are measured with MKS 1000-torr and 10-torr baratron transducers. The baratron transducers are read by an MKS model PDR-C-2C readout controller. An MKS model 253A-1 throttle valve is placed in-line as shown in Fig. 20. The throttle valve is controlled by an MKS model 252 exhaust valve controller used to set the desired operating pressure. The pumping system consists of a Balzer model TPU050 turbo pump backed by an Alcatel model 1012 mechanical pump that is also used for roughing the vacuum system. Oil de-misters and traps are installed on the system to minimize back-streaming of oil into the sampling chamber.

The gas manifold is designed to deliver a concentrated sample of gas to the center of the sample measurement chamber. A stainless-steel cylinder is used to collect the sample and store it. Two other small cylinders are installed and contain known materials that are used to calibrate the fluorometer (see Fig. 22).

Figure 22. Photograph of the stainless-steel sample cylinder used to concentrate volatile organic compounds and of two stainless-steel cylinders containing reference materials used to calibrate the response of the fluorometer.

Operation

The sample gas enters the system and is first collected in a stainless-steel sample cylinder which is cooled with liquid nitrogen to freeze out the volatile vapors. After an adequate amount of gas has been collected, the sample cylinder is evacuated. After the sample cylinder is evacuated, a concentrated slug of the sampled gas is left frozen in the sample cylinder. The sample cylinder is then heated to release the frozen vapors. The sample gas is released into the evacuated UV fluorescence imaging fluorometer sample chamber where light from the xenon arc lamp is used to excite fluorescence. A motor controller is installed on the monochromator so that the monochromator can be stepped in 5-nm increments. Fluorescence from the chamber is collected using the CP-200 imaging spectrometer and its output is detected by a diode-array detector. The diode-array output is connected to an oscilloscope that is used for data collection. Data is automatically collected by a computer using software written specifically for this system. The program steps the monochromator while the oscilloscope displays and records the fluorescence images. This system can scan from the far ultraviolet to the near infrared in a few minutes. Fluorescence data profiles are then saved to a disk for further analysis.

In a typical operating procedure, 1) gas is injected into the analysis chamber, 2) the excitation light is tuned from 200 nm to 400 nm in 5-nm steps, 3) at each excitation wavelength the fluorescence is displayed on the 2430A oscilloscope, digitized and stored in the computer, and 4) the stored spectra are then analyzed to identify organic vapors and to determine vapor concentrations. A typical calibration spectrum for 100 ppm of toluene vapor in the sample chamber is shown in Fig. 23.

Figure 23. Calibration spectrum for 100 ppm toluene in the sample chamber.

Mixed Waste Landfill (MWL) Field Test

Background

The transportable UV fluorescence imaging fluorometer was transported to Sandia's Mixed Waste Landfill (MWL) on September 28, 1993 and measurements were carried out at LCAP3. Fluorometer measurements were made on gases sampled through the SEAMIST borehole instrumentation and fluid sampling system from depths of 6, 51, and 81 feet. Our results from the MWL measurements suggest that the sensitivity of the transportable UV fluorescence imaging fluorometer must be further improved an order of magnitude to detect low concentration toluene vapors from LCAP3.

Apparatus

The transportable UV fluorescence imaging fluorometer used for measurements at the MWL was described in the previous section. Briefly, the fluorometer uses a 150-W high-pressure xenon arc lamp to obtain tunable UV light between 200 nm and 400 nm with a spectral bandwidth of ~15 nm FWHM. Tunable UV light is obtained by using a computer-controlled 1/8-meter monochromator to filter the broadband xenon lamp output. The average power of the tunable UV light was measured with a Laser Precision model RK-3240 average power meter and a Scientech model 361 thermopile detector. Average power increases from ~0.05 mW at 200 nm to a peak of ~0.6 mW at 300 nm dropping to ~0.4 mW at 400 nm. The tunable UV light is imaged onto a vacuum cell containing the gas sample. Fluorescence radiation from the irradiated sample is imaged onto a second imaging spectrometer used to disperse the fluorescence radiation. Fluorescence spectra are measured between 200 nm and 700 nm with a resolution of ~7 nm FWHM. Fluorescence radiation is detected by a gated 1024-element diode-array detector that is fiber-optic coupled to a dual-microchannel plate image-intensifier with single-photon sensitivity. The output from the diode-array is displayed on a digital oscilloscope used to digitize the fluorescence signal and transfer the data to a computer for subsequent processing and display. A measurement sequence consists of stepping the tunable UV radiation between 200 nm and 400 nm in 5-nm steps and digitizing the dispersed fluorescence radiation excited at each excitation wavelength.

Gas Chromatography Measurements

Gas chromatography measurements made at LCAP3 by Laguna^{3,4,5} were used to access sensitivities needed to detect volatile organic compounds at the MWL. Measurements made at LCAP3 with an automated gas chromatograph (GC) are summarized in Table 5. Of the compounds listed in Table 5, the enhanced UV fluorometer is only sensitive to toluene. However, toluene concentrations measured with the automated GC are more than an order of magnitude lower than toluene detection limits listed in Table 3. It was therefore necessary to operate the fluorometer in the "enhanced detection mode" with cryogenic pre-concentration of the sample to improve the detection limit at least an order of magnitude.

Table 5. Summary of gas chromatography measurements at the MWL.

Compound	Measurement Date		
	8/6-8/9 (ppm)	8/13-8/16 (ppm)	8/20-8/23 (ppm)
Dichlorobenzene (1,2-)	4	1	2
Freon-113	15	15	22
Pentane	12	13	18
Tetrachloroethylene	5	6	10
Toluene	6	--	--
Trichloroethane (1,1,1-)	23	25	40
Trichloroethylene	120	110	240

Enhanced UV Fluorescence Imaging Fluorometer

Detection limits listed in Table 3 are primarily limited by oxygen and water vapor quenching of the fluorescence signal. Improved detection limits can therefore be obtained by minimizing quenching effects. A scheme to minimize quenching effects by selective cryogenic trapping of volatile compounds in an incoming air stream was therefore included in the transportable imaging fluorometer. An incoming air stream is first passed through a liquid nitrogen cold-trap which freezes out volatile compounds and water vapor. Nitrogen and oxygen, which are not trapped, are pumped off. The frozen vapors in the cold trap are then thawed and allowed to expand into an evacuated sampling chamber where they are irradiated with UV light and the subsequent fluorescence signal detected. The resulting analytical detection curve for toluene vapors shows that detection limits in the low ppm range can be obtained for sampled toluene vapors. Since the detection limit in Fig. 24 is comparable to the toluene concentrations measured with the GC, the transportable UV imaging fluorometer was moved to the MWL for a demonstration measurement.

Results

Setup of the UV fluorescence imaging fluorometer at the MWL took about 60 minutes. Measurements were carried out between about 1400 and 1700 hours. Background measurements showed that background light intensities were several orders of magnitude higher than in the laboratory. The increased background signal was traced to solar background radiation which was entering the sampling chamber through an exhaust vent in the xenon arc lamp housing. The background signal was reduced about an order-of-magnitude using a sun-shade to block the solar radiation. Background light levels were, however, still too high to obtain good spectra from toluene vapors in the 10 ppm range. Even though the UV imaging fluorometer was not able to detect a reliable toluene signal, the field test provided valuable data on the field performance of the fluorometer. Except for the problem with the background solar radiation, the fluorometer operated flawlessly and the cryogenic trapping scheme worked as expected. The MWL measurements further emphasized the need to develop even higher sensitivity fluorescence

measurements. This need led to the development of a molecular beam laser fluorometer (MBLF) as a ultrahigh sensitivity detection method for volatile organic compounds in the atmosphere. The MBLF is discussed in the next section.

Figure 24. Toluene analytical curve measured with cryogenic trapping of the volatile vapors.

Molecular Beam Laser Fluorometer (MBLF)

Background

Room temperature UV absorption spectra of volatile compounds are in part highly overlapped and relatively featureless because of the spectral congestion which results from hot bands which are populated at room temperature. Cooling the molecules in a free-jet expansion collapses the ground state population to only a few vibrational states, thereby greatly simplifying the UV absorption spectrum. Prior work on the use of free-jet expansions for ultrasensitive detection by Tanada, et. al.⁶ used a relatively large, complex time-of-flight mass spectrometer to detect ions which are produced by the interaction of laser radiation with molecules in the free-jet

expansion. The work in this report discusses the use of a compact, simplified channeltron detector and a photomultiplier tube (PMT) to detect fluorescence radiation. The results show, for example, that the channeltron and PMT give comparable detection limits to mass spectrometer systems for those molecules which emit fluorescence or are ionized. In addition, the channeltron can detect ionization signals from molecules such as trichloroethylene which do not emit fluorescence but are ionized. The MBLF can thus be used to detect a large number of molecules which can not be detected with the UV imaging fluorometer.

Apparatus

A photograph of the vacuum chamber used for the free-jet expansion measurements is shown in Fig. 25. The photomultiplier tube and channeltron detector are each labeled in Fig. 25. Gas is expanded into the center of the chamber through a pulsed nozzle where the gas is irradiated by a high resolution (0.001 nm FWHM spectral bandwidth) tunable UV dye laser. Fluorescence radiation is detected with the PMT and ionization signals are detected with the channeltron detector.

Fig. 26 shows a photograph of the high-resolution tunable UV dye laser used to irradiate molecules in the free-jet expansion. The tunable dye laser is pumped by a frequency-doubled Nd:YAG laser operating at a pulse repetition rate of 10 Hz. The light from the dye laser is converted to the UV in a frequency doubler and its wavelength monitored with a pulsed wavemeter used to calibrate the wavelength of the UV light. UV light is transported to the vacuum chamber where it irradiates molecules in the free-jet expansion. Care was taken to minimize stray laser light inside the chamber by passing the incoming laser beam through a series of specially constructed tapered light baffles inside the chamber and using Brewster-angle windows on the vacuum chamber. This was necessary to keep stray laser light from saturating the photomultiplier tube and channeltron detector.

Cooling

The effect of the free-jet expansion on the fluorescence excitation spectrum of acetone is illustrated in Figs. 27 and 28. Fig. 27 shows a high-resolution fluorescence excitation spectrum of acetone at 300 K. Highly overlapped broadband spectral features are seen in the spectrum at 300 K. When the acetone is cooled to a temperature of about 4 K in the free-jet expansion, the broad spectral features in Fig. 27 coalesce into relatively sharp non-overlapping bands which give a "fingerprint" pattern that can be used to identify acetone. Similarly, cooling xylene isomers in a free-jet expansion results in "fingerprint" patterns that can be used to identify the various isomers. This is illustrated in Fig. 29 which shows high-resolution fluorescence excitation spectra of the xylene isomers and of a mixed xylene sample. Comparing the spectrum from the mixed xylene sample to the individual spectra for each isomer, it is clear that the mixed xylene sample is predominantly composed of *m*-xylene with only small amounts of *o*-xylene and *p*-xylene. The spectra in Fig. 29 can be compared to the corresponding room temperature absorption spectra in Fig. 1 for *m*-xylene, *o*-xylene, and *p*-xylene to illustrate the power of MBLF measurements in identifying volatile organic compounds.

Figure 25. Photograph of the vacuum chamber used to detect volatile organic vapors in a free-jet expansion.

Figure 26. Photograph of the high-resolution (0.001 nm FWHM spectral bandwidth) tunable UV dye laser used to detect volatile organic vapors in a free-jet expansion.

Figure 27. High-resolution fluorescence excitation spectrum of acetone vapor at 300 K.

Figure 28. High-resolution fluorescence excitation spectrum of acetone vapor in a free-jet expansion at 4 K.

Figure 29. High-resolution fluorescence excitation spectra of *m*-xylene, *p*-xylene, *o*-xylene, and mixed xylenes in free-jet expansions.

Fluorescence and Ionization Detection

A number of volatile organic compounds can be detected in a free-jet expansion using either the fluorescence signal or the ionization signal. Since both are related to the absorption spectrum of the species, they should each produce the same spectral signature. As part of a plan to move detection from the photomultiplier tube to the channeltron detector, excitation spectra for benzene were simultaneously measured with both the photomultiplier tube and the channeltron. Fig. 30 shows that similar spectral features are measured for benzene with fluorescence detection and ionization detection. Similarly, Fig. 31 compares fluorescence and ionization signals for toluene. In the case of Fig. 31, excellent agreement is obtained with both methods of measuring the excitation spectrum, giving us confidence in the ability to use either method of detection.

Figure 30. High-resolution excitation spectra of benzene in a free-jet expansion measured with ionization and fluorescence detection.

(a)

(b)

Figure 31. High-resolution excitation spectra of toluene in a free-jet expansion measured with ionization and fluorescence detection.

Detection Limits

Figure 32 shows an analytical calibration curve for detecting toluene in a free-jet expansion. Linear signals are obtained down to a detection limit of somewhat less than 30 ppb toluene in 1000 torr helium. (The calibration curve was unaffected when the measurement was repeated with toluene in dry air.) An analytical curve for detecting trichloroethylene in a free-jet expansion is shown in Fig. 32. In the case of trichloroethylene, the detection limit is a somewhat higher 200 ppb because of the two-photon excitation scheme needed to ionize trichloroethylene.

Comparing the detection limits for toluene and trichloroethylene to the concentrations measured at the MWL (see Table 5), we see that MBLF measurements provide a highly sensitive way to characterize volatile organic compounds. Further improvements in MBLF detection were obtained using a gated channeltron detector to detect the ionization signal.

Figure 32. Analytical curve for detecting toluene in a free-jet expansion with a channeltron detector.

Figure 33. Analytical curve for detecting trichloroethylene (TCE) in a free-jet expansion with a channel detector. The tunable UV dye laser excited the 0_0^0 origin band 2+1 REMPI 3d-p Rydberg transition at 310.7 nm.

Gated Channeltron Detection

The use of a gated channeltron to detect ionization signals from molecules in a free-jet expansion is discussed in a previous Sandia report.⁷ For completeness, we show one ionization signal from 53 ppb toluene in 1000 torr helium. With the use of a gated channeltron, the toluene detection limit is reduced from about 30 ppb to about 0.25 ppb, almost a two-order-of-magnitude increase in sensitivity for equivalent sampling and averaging conditions. Increasing the averaging time from 1 to 100 pulses, results in a detection limit of about 0.035 ppb, another order-of-magnitude increase in sensitivity.

Figure 34. REMPI 1+1 wavelength scan of the toluene 0^0_0 origin band using a gated channeltron detector to detect the ionization signal. The single-shot signal-to-noise-ratio of 206 from 53 ppb toluene in 1000 torr helium gives a detection limit ($S/N=1$) of 257 ppt. The detection limit for a 100 laser shot average was measured to be 35 ppt. The width of the vertical lines indicates the spectral resolution of the tunable UV dye laser.

Summary

In this report, we have shown that a multispectral ultraviolet (UV) fluorescence imaging fluorometer and a pulsed molecular beam laser fluorometer can be used to detect volatile organic compounds of interest in environmental monitoring and drug interdiction applications. The UV fluorescence imaging fluorometer is a relatively simple instrument which uses multiple excitation wavelengths to measure the excitation/emission matrix for irradiated samples. Detection limits in the high part-per-million to low part-per-million range were measured for a number of volatile organic vapors in the atmosphere. Detection limits in the low part-per-million range were obtained using cryogenic cooling to pre-concentrate unknown samples before introducing them into the imaging fluorometer. A multivariate analysis algorithm was developed to analyze the excitation/emission matrix and used to determine the relative concentrations of species in computer synthesized mixtures containing up to five organic compounds. Analysis results demonstrated the utility of multispectral UV fluorescence in analytical measurements. A transportable UV fluorescence imaging fluorometer was used in two field tests. Field tests results demonstrated that detection limits in the part-per-billion range were needed to reliably detect and identify volatile organic compounds in realistic field test measurements. The molecular beam laser fluorometer, a more complex instrument with detection limits in the part-per-billion to part-per-trillion range, was therefore developed to satisfy detection sensitivity requirements for field test measurements. High-resolution spectroscopic measurements made with the molecular beam laser fluorometer demonstrated its utility in identifying volatile organic compounds in the atmosphere. Current laser technology now makes it possible to develop a transportable version of the pulsed molecular beam laser fluorometer which can be used for field test measurements.

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