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**MOLECULAR OPTICAL SPECTROSCOPIC TECHNIQUES
FOR HAZARDOUS WASTE SITE SCREENING**

by

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ABSTRACT

The U.S. Environmental Protection Agency is interested in field screening hazardous waste sites for pollutants in surface water, ground water and soil. This report is an initial technical overview of the principal molecular spectroscopic techniques and instrumentation and their possible field-screening applications at hazardous waste sites. The goal of this overview is to describe the power and utility of molecular spectroscopic techniques for hazardous waste site screening and to define the main strengths, weaknesses and applications of each major spectroscopic technique. These spectroscopic methods include electronic (ultraviolet-visible absorption and luminescence) and vibrational (infrared absorption and Raman scattering) techniques. A brief discussion is also given for some other techniques that rely on spectroscopic detection (colorimetry and fluorometry as well as immunoassay and fiber-optic chemical sensors). Hyphenated techniques such as high-performance liquid chromatography and gas chromatography - Fourier transform infrared spectroscopy are discussed for applications where the simultaneous detection of the whole spectrum, rather than single wavelength detection, is involved.

The report is organized as follows: The Introduction (Section 1) is followed by a general Conclusions section (Section 2) that surveys in tabular form the applicability of each spectroscopic technique for field and laboratory use, together with classes of pollutants measured, advantages, limitations, sensitivity, and current field applicability. The cost of instrumentation and analysis and the time needed for analysis are briefly addressed, and broad guidelines are given for three categories of

instrumentation, portable, field deployable and semi-field deployable. Sections 3 through 8 discuss the specific spectroscopic areas in more detail. Each section presents a brief outline of the spectroscopic principles and instrumentation for the particular spectroscopic technique and describes the state-of-the-art approach. Advantages, limitations, sensitivities and examples of specific techniques and their applications to environmental pollutants are also discussed. Conclusions are given for each spectroscopic technique at the end of each section. The reference section (Section 9), contains all references cited, as well as a cross section of the definitive literature. This bibliography is intended to give the reader an introductory background for general principles and field applications of molecular spectroscopic techniques. The Appendix consists of a set of figures that address some of the major spectroscopic methods, including luminescence techniques such as fluorescence emission, synchronous fluorescence, room temperature phosphorescence, infrared methods, and surface-enhanced Raman spectroscopy.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASTM	American Society for Testing and Materials
CCD	Charge-Coupled Device
CARS	Coherent Anti-Stokes Raman Spectroscopy
EPA	(U.S.) Environmental Protection Agency
FIA	Fluoroimmunoassay
FOCS	Fiber-Optic Chemical Sensors
FTIR	Fourier Transform-Infrared Spectroscopy
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IR	Infrared Spectroscopy
K	Degrees Kelvin
LC	Liquid Chromatography
LC-SLM	Liquid Crystal Spatial Light Modulator
LESC-LV	Lockheed Engineering & Sciences Company - Las Vegas
LT	Low Temperature
NRS	Normal Raman Spectroscopy
ppb/ppm	part per billion/part per million
PAH	Polyaromatic Hydrocarbons
PBB	Polybrominated Biphenyls
PCB	Polychlorinated Biphenyls
RIA	Radioimmunoassay
RR	Resonance Raman
SERS	Surface-Enhanced Raman Spectroscopy
SFC	Supercritical Fluid Chromatography
SNR	Signal to Noise Ratio
SL	Synchronous Luminescence
SPR	Surface Plasmon Resonance
TIR	Total Internal Reflection
TLC	Thin Layer Chromatography
UV-VIS	Ultraviolet-Visible Spectroscopy
λ_{ex}	Excitation Wavelength
λ_{em}	Emission Wavelength

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SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is interested in field screening of hazardous waste sites for pollutants in surface and ground water as well as soil. Major reasons for this interest are to achieve improved cost effectiveness and to expedite remedial investigations at Superfund sites and thus reduce the time lag between sampling and the receipt of analytical data, which can often amount to 30 days or more. Field analytical screening can also help to confine a detailed field investigation to those areas of a site which are truly contaminated and thus reduce the number of samples sent to the analytical laboratory, thereby providing more comprehensive environmental studies as well as more relevant data with reduced cost and time.

Detailed characterization of many chemical pollutants in environmental samples from waste sites can be performed using analytical techniques such as liquid or gas chromatography and mass spectrometry. For many applications, these procedures are needlessly time consuming and expensive. Often, optical spectroscopic methods and experiments that are field deployable or portable provide attractive alternatives that permit large number of samples to be screened, characterized, and prioritized in the field with little or no sample preparation. These screening techniques permit rapid response and considerable cost savings because detailed analyses are required only for a selected subset of samples. Spectroscopic techniques may sometimes provide information on unusual sample types, or on nonvolatile compounds that are of high-molecular weight or thermally labile. For functional groups or geometrical isomers, these techniques may also provide specific information that could not be obtained by more common EPA-approved methods such as gas chromatography. Spectroscopic techniques may also offer advantages for in situ measurements

(with fiber optics), remote measurements, flow-through analyses, and nondestructive testing.

Each spectroscopic technique has certain advantages and disadvantages. Some may be more widely applicable, may be more feasible for field deployment using current technology, or may be more specific or sensitive for trace identification or classification. All of the techniques discussed in this report have the potential for field application either by themselves or in conjunction with appropriate separation or chromatographic steps. Recent rapid advances in computer hardware and software, chemometrics, and pattern recognition algorithms, although beyond the scope of this report, have also been combined with advances in spectroscopic instrumentation to improve the analysis of complex environmental pollutant mixtures and extract maximum information from data sets.

The main objective of this report is to provide a technical overview and assessment of the principal molecular spectroscopic techniques and instrumentation with applications for field screening at hazardous waste sites. These methods currently include UV-visible absorption and luminescence (electronic) spectroscopy as well as infrared absorption and Raman (vibrational) spectroscopy. For each method, a brief outline of the spectroscopic principles and instrumentation considerations is given to familiarize the reader with the present state-of-the-art approach. Advantages, limitations, sensitivities, and examples of specific techniques and their applications to environmental analyses are also discussed.

This report is intended to cover the most important spectroscopic techniques that have potential for field applications. Specific highlights are also given for adjunct techniques such as colorimetric and fluorometric analysis with chemical derivatization, spectroscopic immunoassay techniques, and fiber optic chemical sensors. The range of possible applications of

spectroscopic methods for field analysis is very broad and might include uses for identification, classification, semiquantitation, and quantitation. A direct comparison with other types of field analysis is beyond the scope of this report.

This report is meant as a technical assessment and source document. This document can provide a basis for early decision making on potential spectroscopic techniques for field surveying. It is not the intention of this document to compare specific instruments or procedures, although some references are included for information. It gives only a broad overview of time and cost considerations for various instrumental analytical procedures. The authors consider that this report will serve as a useful source of technical information and will contribute to the appreciation of the usefulness of molecular spectroscopic techniques for hazardous waste site screening. The extensive reference sections, although not comprehensive, gives the reader access to background material related to field applications of molecular spectroscopic techniques. This document can serve as a bridge leading to more detailed reviews for specific decision making.

Conclusions are given for each spectroscopic technique at the end of its section (Section 3 through 8). In the general conclusions (Section 2) a table summarizes the applicability of each spectroscopic technique for field and laboratory use, together with advantages, limitations, sensitivity, current field availability and estimated cost and time. The figures in Appendix A illustrate some of the main spectroscopic approaches as applied to specific classes of pollutants. It is hoped that this overview will allow an appreciation of the power and utility of molecular spectroscopic techniques for hazardous waste site screening.

SECTION 2

CONCLUSIONS

Field screening at hazardous waste sites for pollutants in surface water, ground water, and soil is of importance because it can expedite remedial investigations. Molecular spectroscopic analytical methods applied to field screening provide an attractive alternative to standard EPA techniques such as chromatographic and mass spectrometric procedures. Spectroscopic approaches can provide valuable qualitative and quantitative information with substantial savings of time and money. Instruments and methods are developing rapidly in this growing area, which can greatly improve environmental analytical technology.

Spectroscopic methods that are portable or field deployable permit samples to be screened and prioritized in the field with little or no sample preparation. Spectroscopic methods can sometimes provide information on unusual sample types or on non-volatile compounds that are of high molecular weight or that are thermally labile. These techniques also are advantageous for in situ or remote measurements, real-time flow-through analysis, and nondestructive testing. All of the spectroscopic methods have specific advantages and shortcomings and have potential applicability for particular environmental problems. Table 1 summarizes the advantages, limitations, and sensitivities with examples of specific techniques and their application to environmental pollutants. This table also includes definitions of portable, field-deployable and semi-field-deployable instruments and includes relative estimates of cost and time factors.

Ultraviolet-visible absorption spectroscopy is a mature technique that has good quantitative accuracy for single compounds after separation, or for simple mixtures. If it is used in conjunction with high-performance liquid chromatography using an optical multichannel analyzer as a detector, the entire spectrum for each chromatographic peak can be recorded. Its sensitivity is moderate and its specificity is low. Colorimetric reagents can greatly increase the specificity of the method and improve sensitivity by moving the spectrum of the reaction product into the visible region with high absorption coefficients. Ultraviolet-visible absorption spectroscopy is most useful for unsaturated compounds (aromatic or heterocyclic).

Ultraviolet-visible luminescence (fluorescence and phosphorescence), when applicable, can be the most sensitive spectroscopic technique for trace and ultratrace analysis, especially with laser excitation. It is useful in aqueous solutions to the part per billion to part per trillion level. Specific techniques most useful in the field include synchronous luminescence and room temperature phosphorescence. Luminescence is applicable to most polyaromatic compounds and their derivatives and can be made applied to many other compounds by using fluorometric reagents for chemical derivatization reactions. It can also be used with high performance liquid chromatography as a multichannel detector. Luminescence is much more selective for identification or classification purposes than ultraviolet-visible absorption but less selective than infrared or Raman spectroscopy. Its selectivity can be enhanced using various excitation and emission wavelengths and by time or phase resolution methods, and indirect detection methods such as fluorescence quenching or energy transfer.

Infrared absorption spectroscopy (dispersive and Fourier transform) has been used in field applications, especially for monitoring air pollutants using a gas cell, for characterizing oil or hazardous chemicals where structural information from group frequencies is useful, and where sensitivity

is not the critical factor. Infrared devices are also useful as real-time detectors with GC-FTIR and for specific quantitation applications such as oil and grease. Disadvantages include the need for sample preparation in order to eliminate water which is the major interferent, some difficulties related to quantitation and the mediocre sensitivity of the technique. Lately, more compact, rugged instruments along with better sample preparation and signal processing techniques that are designed to increase the sensitivity of this method have made it more attractive for field use.

Raman spectroscopy complements infrared spectroscopy because it also provides structural information but with different selection rules. Raman spectroscopy is not sensitive to water and can use visible or near-infrared optical techniques. Until recently, Raman was considered to have several disadvantages for field use including complex instrumentation, need for laser excitation and relatively low sensitivity. These disadvantages have been reduced by the advent of more compact Raman spectrometers, smaller and more rugged lasers, and special, more sensitive Raman techniques. The most promising Raman technique for field use is surface-enhanced Raman spectroscopy in which Raman scattering efficiency can be enhanced by factors of as much as 10^4 for some compounds when a chemical is adsorbed on a special roughened metal (Cu, Ag, Au) surface. Although this technique may be promising for future field applications, it is not yet fully understood or developed and may not apply to all chemicals. The advantage of the technique is that it has the potential to combine the sensitivity of luminescence with structural information similar to that provided by infrared spectroscopy.

A comparison of the main spectroscopic techniques is given in Table 1 at the end of this section.

Ancillary techniques that rely on spectroscopic detection and that greatly enhance the utility of spectroscopic methods include colorimetry,

fluorometry, immunoassay, and some fiber optic chemical sensors. Fiber optic sensors may also use some change in the optical properties of the fiber or cladding or may be used as probes for most of the spectroscopic techniques discussed.

Spectroscopic techniques are being used with increasing frequency for field screening, allowing rapid response and reduced costs for environmental monitoring programs. Such techniques also help to optimize sampling efforts and help to prioritize samples for more detailed analysis. Some spectroscopic methods can be used in place without sampling, e.g. fiber optic chemical sensors, whereas others can be used with portable instrumentation or field deployable instruments set up in a mobile laboratory. Recent instrumentation developments, such as more compact lasers, miniaturized optical hardware, new types of detectors, increased use of fiber optics, and better computer software for spectral data processing and pattern recognition have increased the utility of these spectroscopic methods.

Further research and development efforts are needed to improve the field applicability of current and new spectroscopic analytical techniques, to make instruments more portable and compact. Also, new techniques that employ field-ready instruments need to be accompanied by detailed analytical protocols, appropriate standards, calibration criteria and appropriate quality assurance for specific pollutant classes. Field spectroscopic instruments and methods are a rapidly improving and growing analytical area which can greatly improve environmental analytical technology.

A better appreciation of the conclusions, relative to the applicability of these spectroscopic techniques, can be obtained by reviewing Table 1.

TABLE 1. CHARACTERISTICS OF SPECTROSCOPIC TECHNIQUES FOR FIELD ANALYSIS

UV-VIS ABSORPTION					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
<p>POLYAROMATIC COMPOUNDS (PACs)</p> <p>DYES</p> <p>COLORIMETRIC REACTION PRODUCTS</p>	<p>MATURE TECHNIQUE</p> <p>INSTRUMENTATION READILY AVAILABLE</p> <p>GOOD QUANTITATIVE ACCURACY FOR SINGLE COMPOUNDS AND SIMPLE MIXTURES</p> <p>FEW INTERFERENCES BY NONAROMATICS</p> <p>SPECTRAL DATA AVAILABLE</p>	<p>UNSPECIFIC (COMPARED TO IR AND LUMINESCENCE)</p> <p>EXTENSIVE SAMPLE PREPARATION</p> <p>QUANTITATION MAY BE AFFECTED BY SOLVENT, POLARITY OR MEDIUM, CHEMICAL COMPLEXATION</p>	<p>MODERATE SENSITIVITY</p> <p>ppm - ppb IN FAVORABLE CASES</p>	<p>PORTABLE</p> <p>-HAND-HELD COLORIMETER</p> <p>-COLORIMETRIC KITS</p> <p>FIELD DEPLOYABLE INSTRUMENTATION WITH MULTICHANNEL DETECTORS</p> <p>HPLC DETECTORS</p>	<p>UV-VIS TECHNIQUES</p> <p>- FT</p> <p>- DERIVATIVE</p> <p>LT MATRIX ISOLATION</p> <p>REFLECTANCE</p> <p>PHOTOACOUSTIC SPECTROSCOPY</p> <p>FIBER OPTIC COLORIMETRIC SENSORS</p> <p>MULTICHANNEL DETECTORS</p> <p>- DIODE ARRAYS</p> <p>- CCDs</p>

CONTINUED

TABLE 1. CONTINUED

UV-VIS LUMINESCENCE (FLOORESCENCE AND PHOSPHORESCENCE)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
POLYAROMATIC COMPOUNDS FLUORESCENT DYES FLUOROMETRIC REACTION PRODUCTS PCBs PHENOLS PESTICIDES SEMIVOLATILES NONVOLATILES PETROLEUM OILS	MOST SENSITIVE METHOD FOR TRACE AND ULTRATRACE ANALYSIS WHEN APPLICABLE INSTRUMENTATION READILY AVAILABLE NO INTERFERENCE BY WATER FEW INTERFERENCES BY NONAROMATICS SOME STRUCTURAL SPECIFICITY - ENHANCED BY SPECIAL TECHNIQUES VERY SELECTIVE - ENHANCED BY TIME AND WAVELENGTH VARIABILITY CAN DISTINGUISH GEOMETRICAL ISOMERS	LIMITED TO COMPOUNDS WITH FAIRLY HIGH LUMINESCENCE YIELDS (USUALLY PACs, UNLESS DERIVATIZED) RELATIVELY UNSPECIFIC FOR STRUCTURAL INFORMATION (COMPARED TO IR) QUANTITATION COMPLICATED BY DIFFERENCES IN QUANTUM YIELDS, QUENCHING, MICROENVIRONMENTS LIMITED REFERENCE SPECTRA AVAILABLE	EXCELLENT SENSITIVITY ppb (ppttrillion OR LESS WITH LASER EXCITATION) DEPENDENT ON QUANTUM YIELDS	PORTABLE INSTRUMENTS AVAILABLE FIELD DEPLOYABLE INSTRUMENTS AVAILABLE FLOW-THROUGH OIL-WATER MONITORS AND HPLC WITH MULTICHANNEL DETECTORS FRONT SURFACE - RTP	LUMINESCENCE TECHNIQUES - FLUORESCENCE - PHOSPHORESCENCE - SYNCHRONOUS - TIME AND PHASE RESOLUTION - POLARIZATION - RT AND LT - 3D - MICROSCOPY FIBER OPTIC FLUOROMETRIC SENSORS MULTICHANNEL DETECTORS - DIODE ARRAYS - CCDs FLUORESCENCE QUENCHING OR ENERGY TRANSFER - INDIRECT WAYS TO MEASURE NONLUMINESCENT MOLECULES

CONTINUED

TABLE 1 CONTINUED

SYNCHRONOUS FLUORESCENCE					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
INCREASED SPECIFICITY FOR INDIVIDUAL PACs OR PAC CLASSES IN COMPLEX MIXTURE PETROLEUM OILS CREOSOTES	INCREASED SPECIFICITY LESS SPECTRAL OVERLAP CLASSIFICATION OF PAHs BY NUMBER OF RINGS USEFUL FOR SCREENING COMBINE WITH OTHER LUMINESCENCE TECHNIQUES	DECREASE IN SENSITIVITY WITH NARROWER BANDPASSES AND WAVELENGTH OFFSET LOSS OF VIBRATIONAL STRUCTURE IN SPECTRUM NEED DUAL SCANNING MONOCHROMATORS NEED POLYCHROMATIC SOURCE	GOOD SENSITIVITY SLIGHTLY LOWER THAN FLUORESCENCE EMISSION DEPENDENT ON INSTRUMENTAL CONDITIONS DEPENDENT ON STOKES SHIFT OF COMPOUND	PORTABLE INSTRUMENTS UNDER DEVELOPMENT FIELD DEPLOYABLE INSTRUMENTS AVAILABLE	LT MEASUREMENTS TIME AND PHASE RESOLUTION DERIVATIVE REMOTE MONITOR UNDER DEVELOPMENT SYNCHRONOUS PHOSPHORESCENCE
ROOM TEMPERATURE PHOSPHORESCENCE (RTP)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
MOST LUMINESCENT PACs, PCBs, PAHs DIRECTLY OR WITH HEAVY ATOM PERTURBER	EASY SAMPLE PREP ELIMINATES SCATTER AND FLUORESCENCE BACKGROUND LONGER LIFETIMES THAN FLUORESCENCE NO NEED FOR CRYOGENIC INSTRUMENTATION USEFUL FOR SCREENING ADDITIONAL SELECTIVITY DUE TO PERTURBER	OXYGEN MAY QUENCH IN SOLUTION LESS STRUCTURE THAN LTP SUBSTRATE/TECHNIQUE DEPENDENT QUANTITATION MAY BE COMPLICATED LIMITED CORRECTED SPECTRA AVAILABLE	GOOD SENSITIVITY ppb IN FAVORABLE CASES DEPENDENT ON QUANTUM YIELD OF COMPOUND DEPENDENT ON EFFICIENCY OF PERTURBER	PORTABLE INSTRUMENTS UNDER DEVELOPMENT FIELD DEPLOYABLE INSTRUMENTS AVAILABLE FRONT SURFACE RIGID MEDIUM - FILTER PAPER - TLC PLATE DOSIMETRY EASY SAMPLE PREP	CAN COMPARE WITH LT TECHNIQUES FOR OPTIMIZATION TIME RESOLUTION TLC ORGANISED MEDIUM - MICELLE SOLUTION - CYCLODEXTRIN

CONTINUED

TABLE 1 CONTINUED

LOW TEMPERATURE LUMINESCENCE (FLUORESCENCE AND PHOSPHORESCENCE)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
LUMINESCENT PACs PCBs	HIGHER SENSITIVITY, SPECIFICITY THAN RT VIBRATIONAL STRUCTURE SIMILAR TO RAMAN QUANTITATION OVER 6 ORDERS OF MAGNITUDE DISTINGUISH ISOMERS VERY SELECTIVE - ENHANCED BY TIME AND WAVELENGTH VARIABILITY	CRYOGENIC APPARATUS MORE COMPLICATED NEED SKILLED OPERATOR LESS REFERENCE SPECTRAL DATA THAN RT SOME ANALYTES MATRIX DEPENDENT	EXCELLENT SENSITIVITY pptrillion IN OPTIMAL CASES IMPROVED WITH LASER	LIMITED SEMI-FIELD DEPLOYABILITY	LT TECHNIQUES - SHPOLSKII SPECTRA - LASER-LINE NARROWING - SITE SELECTION - MATRIX ISOLATION LOW TEMPERATURES 77 K TO 4 K

CONTINUED

TABLE 1 CONTINUED

INFRARED (DISPERSIVE)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
ORGANIC AND INORGANIC DETERMINATION OF SPECIFIC FUNCTIONAL GROUPS	HIGHLY SPECIFIC STRUCTURAL DATA ON GROUP FREQUENCIES MATURE TECHNIQUE INSTRUMENTATION WIDELY AVAILABLE SPECTRAL LIBRARIES AVAILABLE	MID/LOW SENSITIVITY WATER IS INTERFERENT REQUIRES SPECIAL OPTICS/SOLVENTS QUANTITATION DIFFICULTIES WEAK OPTICAL SOURCES AND DETECTORS	LESS SENSITIVE THAN UV-VIS ABSORBANCE MUCH LESS SENSITIVE THAN FLUORESCENCE ppthousand to ppm IN FAVORABLE CASES	PORTABLE AND FIELD INSTRUMENTS AVAILABLE PORTABLE UNIT WITH GAS CELL QUANTITATION OF GREASE AND OIL ATR ATTACHMENTS FOR SOLIDS, OILS	FTIR GC/LC-FTIR
INFRARED (FOURIER TRANSFORM)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
ORGANIC AND INORGANIC DETERMINATION OF SPECIFIC FUNCTIONAL GROUPS ROUTINELY USED FOR REAL-TIME GC AND VAPOR ANALYSIS	HIGHLY SPECIFIC STRUCTURAL DATA ON GROUP FREQUENCIES INSTRUMENTATION WIDELY AVAILABLE REAL-TIME FLOW THROUGH VAPOR APPLICATIONS - GC-FTIR SPECTRAL LIBRARIES AVAILABLE	LESS SENSITIVE THAN LUMINESCENCE REQUIRES SPECIAL OPTICS/SOLVENTS CAN TOLERATE SOME WATER (BACKGROUND SUBTRACTION) ORGANICS DETECTION 1-10 ppthousand IN WATER	MORE SENSITIVE THAN DISPERSIVE IR - SIGNAL AVERAGING ppm to subppm IN FAVORABLE CASES	FIELD AND SEMI-FIELD DEPLOYABLE - WITH OR WITHOUT GC - VOLATILES/SEMIVOL ADAPTABLE TO USE WITH SFC	GC/LC-FTIR MATRIX ISOLATION - LT FOR SENSITIVITY MICROSCOPY

CONTINUED

TABLE 1 CONTINUED

NEAR INFRARED					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
SINGLE COMPOUNDS SIMPLE MATRICES ORGANICS OVERTONES	SOURCES AND OPTICAL MATERIALS BETTER THAN MID-IR OPTICALLY GOOD SENSOR MATERIALS CAN DISTINGUISH MAJOR COMPONENTS OF SIMPLE MATRIX FEWER INTERFERENCES THAN MID-IR	LESS SPECTRAL STRUCTURE THAN MID-IR - OVERTONE OVERLAP - LESS SPECIFICITY - INTERPRETATION COMPLICATED NOT USEFUL FOR COMPLEX MATRICES SIGNAL PROCESSING AND PATTERN RECOGNITION REQUIRED	LOW SENSITIVITY 10 - 1 ppthousand	PORTABLE NEAR-IR INSTRUMENT WITH FIBER OPTIC PROBE CHARACTERIZATION OF OIL BULK CHEMICAL ANALYSIS	SURFACE/POLLUTANT INTERACTION STUDIES NEAR IR SENSORS PROCESS CONTROL

CONTINUED

TABLE 1 CONTINUED

NORMAL RAMAN SPECTROSCOPY (NRS)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
ORGANIC AND INORGANIC AQUEOUS SOLUTIONS BIOLOGICAL MATRICES POLYMERS	SPECIFIC AS IR FOR STRUCTURAL INFORMATION DIFFERENT SELECTION RULES - COMPLEMENTS IR FEWER INTERFERENCES THAN IR IN VIS OR NEAR-IR REGIONS WATER AND GLASS NOT INTERFERENCES GOOD OPTICS AND SOLVENTS AVAILABLE CAN HANDLE UNUSUAL SAMPLE SHAPES/SIZES	FLUORESCENCE INTERFER- ENCE IN UV-VIS REQUIRES LASER SOURCE RELATIVELY COMPLEX INSTRUMENTATION REQUIRES SKILLED OPERATOR NOT AS MATURE AS IR RELATIVELY POOR LIMITS OF DETECTION	MODERATE SENSITIVITY 1000 - 20 ppm	SEMI-FIELD DEPLOYABLE INSTRUMENTS UNDER DEVELOPMENT	RESEARCH IN : - AQUEOUS SOLUTIONS - BIOLOGICAL MATRICES - POLYMERS SPECIAL RAMAN TECHNIQUES - SERS - RESONANCE - CARS - MICROPROBES - MICROSCOPY LT APPLICATIONS
SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS)					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
MANY POLLUTANTS DEMONSTRATED FOR : - PYRIDINE - HYDRAZINE - PAHS - PESTICIDES	SPECIFIC IN STRUCTURAL INFORMATION MORE SENSITIVE THAN NORMAL RAMAN AS SENSITIVE AS LUMINESCENCE IN FAVORABLE CASES NO INTERFERENCE BY WATER (SEE ALSO NRS)	RELATIVELY NEW TECH. SURFACE/SUBSTRATE MATERIAL DEPENDENT REPRODUCIBILITY REQUIRES LASER AND SPECIAL SUBSTRATE NOT ALL ANALYTES ENHANCED EQUALLY FEW SPECTRAL LIBRARIES (SEE ALSO NRS)	GOOD SENSITIVITY FOR SELECTED ANALYTES ppm - ppb IN FAVORABLE CASES	FIELD DEPLOYABLE INSTRUMENTATION UNDER DEVELOPMENT	RESEARCH TO OPTIMIZE TECHNIQUES MICROSCOPY MICROPROBES SURFACE STUDIES FIBER OPTIC SENSORS MPLC (UNDER DEVELOPMENT) MULTICHANNEL DETECTORS

CONTINUED

TABLE 1 CONTINUED

RESONANCE RAMAN					
APPLICABILITY	ADVANTAGES	LIMITATIONS	SENSITIVITY	CURRENT FIELD APPLICABILITY	RELATED LAB TECHNIQUES & SENSORS
PACs ABSORBING IN UV PHENOLS	SPECIFIC IN STRUCTURE MAY ELIMINATE FLUORESCENCE BACKGROUND (SEE ALSO NRS)	ONLY CHROMOPHORE VIBRATIONS ENHANCED LIMITED TO UV ABSORBING COMPOUNDS - MAINLY PACs QUANTITATION DIFFICULT NOT COMPARABLE TO OTHER RAMAN TECHNIQUES UV LASER SOURCE COMPLEX INSTRUMENTATION (SEE ALSO NRS)	FAIR SENSITIVITY IN FAVORABLE CASES WITH CHROMOPHORE VIBRATIONS	MANY PRACTICAL DIFFICULTIES	CHROMOPHORE CHARACTERISATION BIOLOGICAL APPLICATION

DEFINITIONS OF PORTABLE, FIELD DEPLOYABLE, AND SEMI-FIELD DEPLOYABLE AS USED IN THIS TABLE ARE:

PORTABLE:
BATTERY POWERED
ONE PERSON CAN CARRY
LITTLE SAMPLE PREP. (<10 MIN.)
INSTRUMENT COST < \$10,000.
ANALYSIS COST < \$30.

FIELD DEPLOYABLE:
GENERATOR POWERED
COMPACT, TWO PEOPLE CAN LIFT (SEVERAL INSTRUMENTS IN MOBILE LAB)
RELATIVELY SIMPLE SAMPLE PREP. (<1 HR.)
INSTRUMENT COST \$30,000. TO \$100,000.
ANALYSIS COST \$30. - \$200.

SEMI-FIELD DEPLOYABLE:
CAN FIT IN MOBILE LAB
COMPLEX OR FRAGILE INSTRUMENT
OFTEN CONSIDERABLE SAMPLE PREP. (>1 HR.)
INSTRUMENT COST > \$100,000.
ANALYSIS COST > \$200.

DEFINITIONS OF ABBREVIATIONS AS USED IN THIS TABLE ARE:

ATR Attenuated Total Reflectance
CARS Coherent Anti-Stokes Raman Spectroscopy
CCD Charge-Coupled Device
FTIR Fourier Transform-Infrared Spectroscopy
GC Gas Chromatography
HPLC High Performance Liquid Chromatography
IR Infrared Spectroscopy
LC Liquid Chromatography
LT Low Temperature
NRS Normal Raman Spectroscopy

PAC Polyaromatic Compounds
PAH Polyaromatic Hydrocarbons
PCB Polychlorinated Biphenyls
ppb/ppm part per billion/part per million (mg/mL,ug/mL)
RTP Room Temperature Phosphorescence
SERS Surface-Enhanced Raman Spectroscopy
SFC Supercritical Fluid Chromatography
TLC Thin-Layer Chromatography
UV-VIS Ultraviolet-Visible Spectroscopy

SECTION 3

ULTRAVIOLET-VISIBLE ABSORPTION SPECTROSCOPY

INTRODUCTION

Ultraviolet-visible (UV-vis) absorption spectroscopy has long been accepted as a mature "workhorse" technique especially suited for quantitative analysis in samples of limited complexity (Wehry, quoted in Bjorseth, 1983).

THEORY

The theory involved in absorption spectroscopy has been discussed in many standard texts such as Murrell (1963), Burgess and Knowles (1981) and will be mentioned only briefly here. Most of the organic molecules that absorb strongly in the UV-vis are unsaturated, aromatic, or heterocyclic aromatic molecules. The electronic transitions involve the excitation of one electron from a bonding π to an antibonding π^* molecular orbital. Most polycyclic aromatic hydrocarbons (PAHs) have spectra of this type containing considerable vibrational fine structure, but the spectra of their polar derivatives have much less well-resolved structure in liquid solution. For some heterocycles and carbonyls, an unshared electron pair occupies a nonbonding orbital on the heteroatom or carbonyl oxygen. One of the nonbonding electrons can sometimes be promoted to an antibonding π^* orbital (n to π^*). This transition, although formally forbidden by quantum mechanical selection rules, can occur, and this n to π^* transition is then often at longer wavelengths and much less intense than π to π^* transitions.

As described above, the light absorbed corresponds to electronic transitions from the ground state to different excited states of the molecule, usually in the 10^{-15} second time span. Usually, a double beam instrument is used and light is simultaneously transmitted through the sample and through a reference cell containing solvent. The basic equation for light transmission (sometimes called the Beer-Lambert Law) can be expressed as:

$$I = I_0 10^{-\epsilon cd}$$

where

I = intensity of the transmitted radiation

I_0 = intensity of incident radiation

ϵ = molar absorptivity ($\text{LM}^{-1}\text{cm}^{-1}$)

C = molar concentration (ML^{-1})

d = thickness of sample (cm)

Absorbance, transmittance and intensity can then be related as:

$$\text{absorbance} = A = \log_{10} \frac{I_0}{I} = \epsilon Cd$$

$$\text{transmittance} = T = \frac{I}{I_0}$$

INSTRUMENTATION

UV-vis double beam absorption spectrophotometers, usually using deuterium sources for the UV spectral region and tungsten sources for the visible region and photomultiplier or photodiode detection, have been discussed in many standard texts (Burgess and Knowles, 1981) and will not be treated in detail here. The increased availability of multichannel detectors such as photodiode array detectors (PDAs) with millisecond responses has led to increased use of these devices with high performance liquid chromatography (HPLC) or supercritical fluid chromatography (SFC) on a real-time basis. These rapidly developing techniques have potential for increased use in field laboratories.

PRACTICAL APPLICATIONS

Polynuclear aromatic hydrocarbons (PAHs), in particular, have well-structured UV-vis absorption spectra which are useful for identification purposes. UV-vis absorption has the disadvantages of relatively low sensitivity and selectivity, as compared with luminescence techniques. UV absorption spectroscopy can be useful for nonfluorescent compounds or for dyes absorbing in the near UV or visible region of the spectrum. Recent uses have generally included low-temperature matrix isolation or Shpol'skii applications (Meyer, 1971; Nakhimovsky, 1989), (much more commonly used with UV-vis luminescence for analytical applications) which are not practical for field use, or computer derivatization, which enhances the observed spectral structure for the analyst.

Second derivative spectrometers have been available for almost two decades (see Hager, 1973; Hawthorne, 1980). Haas et al. (1988) have developed and field-tested a portable spectrometer for second derivative absorption spectrometry for the screening of aromatic contaminants in ground water. Benzene and other aromatics such as phenols have been analyzed at the ppm ($\mu\text{g/mL}$) level in a shallow ground-water well by using a prototype instrument with a 5-m fiber optic probe. In comparison, a more sensitive fluorescence method, also in the second derivative mode, can monitor benzene and phenols to the ppb (ng/mL) level (Vo-Dinh, in Eastwood, 1981). The second derivative absorption technique has limited applicability for complex mixtures because so many compounds absorb in the same region, but may be satisfactory for relatively simple mixtures at the ppm level.

Colorimetric techniques using chemical derivatization to move the absorption spectrum of the complex into the visible region have long been used for quantitation. For screening purposes, a field kit has recently proven useful for PAHs, and a separate kit is available for polychlorinated biphenyls

(PCBs). The field method for analysis of aromatics at the sub-ppm level developed by Hanby (1988) uses the Friedel-Crafts reaction. An alkyl halide extractant and the polyaromatic pollutant form electrophilic aromatic substitution products with the Lewis acid catalyst, which also serves as the dehydrant necessary for this Friedel-Crafts reaction. These products are very large molecules that have a high degree of electron delocalization. Hence, they are intensely colored and can be compared with appropriate color charts. A variation of this method can be used for analysis of trichloroethylene. Hanby (1988) states that this method is more accurate than direct-injection gas chromatography, but that it has the disadvantage of being relatively cumbersome in the chemicals and equipment required.

Several kits have been developed that rely on colorimetric spot tests or sensitive papers for selected environmental analyses (Leichnetz, 1979; Hach, 1988). These established techniques have limited applicability to complex environmental samples but can be used for field-monitoring specific major pollutants, especially when they have been verified by other techniques. Hand-held colorimeters have proven useful, but their applicability does not extend into the UV region. Colorimetric techniques are also being applied to fiber-optic chemical sensors, but the required chemistry is more complex because the reagent should be stable for long periods of time, and must be immobilized on the fiber. In addition, the chemical reactions involved should be easily reversible for some sensors, yet other sensors, designed to be integrating probes, would require nonreversible reactions.

Woolerton et al. (1988) discussed a qualitative KWIK-SKRENE[®] colorimetric method for PCBs in dielectric oils or soil. This method can detect approximately 10 ppm of Aroclor 1260, but the chemical equipment may be cumbersome and some interferences may occur.

Colorimetric detection is also used with bioassay and immunoassay techniques. Sellers (1979) reported the detection of numerous pesticides including Baygon[®], carbaryl, diazinon, Dursban[®], and malathion in water to 10 ppm or less using enzyme test tickets and pretreatment with bromine. The method works by measuring the inhibition of the enzyme cholinesterase in solution by organophosphate and carbamate pesticides with colorimetric detection (absence of color indicating a positive test). The bromine serves to improve the sensitivity of diazinon, Dursban[®], and malathion by converting them from phosphorothionates to phosphates by oxidative desulfurization. The tickets are stable under field conditions between 4°C and 40°C for as long as 8 months.

This discussion does not attempt to give a comprehensive survey of the colorimetric literature; it presents highlights and references for colorimetric reactions and biomarker reactions that use colorimetric detection.

CONCLUSIONS

UV-vis absorption is a mature technique for quantitating and semi-quantitating pollutants after separation or in relatively simple mixtures. Because it is relatively insensitive (as compared to UV-vis luminescence), relatively unstructured (as compared to infrared), and subject to interferences, at least in the UV region, it is most useful for pollutants where alternative luminescence techniques do not exist or for compounds that absorb strongly in the visible region, such as non-fluorescent dyes or colorimetric reaction products.

Hand-held colorimeters are potentially useful for screening, but currently do not extend to the UV region. The use of UV-intensified diode

optical multichannel devices for absorption detection is increasing for EPLCs and for real-time, flow-through applications.

For field use, colorimetric applications, either as sensitive papers, tubes, or spot-tests, or as colorimetric fiber-optic sensors deserve more attention. However, these methods are usually designed to apply to specific pollutants and therefore will lack general applicability. Although colorimetric reagents were extensively discussed in the older literature, many had unstable chemistries, numerous interferences, or were not sufficiently specific. For example, metal chelate reagents often produce products that have similar spectra for many different metals in addition to the target metal. Also, some potentially useful colorimetric reagents which are not commercially available or have undesirable characteristics (instability, toxicity, mutagenicity, etc.) rendering their use by unskilled personnel difficult. Seawater may also be an interferent for some colorimetric methods (Eastwood, private communication). Colorimetric reagents were formerly not required to be stable for long periods of time under field conditions. A new look at colorimetric reagents to supplement fluorometric reagents is needed, if better colorimetric sensors are to be developed.

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SECTION 4

ULTRAVIOLET-VISIBLE LUMINESCENCE SPECTROSCOPY

INTRODUCTION

Ultraviolet-visible (UV-vis) photoluminescence (fluorescence or phosphorescence) has become a well-established technique for field and laboratory screening and for specific quantitation applications using both scanning and filter spectrofluorometers. Luminescence has the advantages of very high sensitivity for some classes of pollutants, good selectivity, relative freedom from interferences by water and non-fluorescing chemicals, ease of sample preparation, and availability of field-deployable instrumentation. Disadvantages include: wide variability in fluorescence yields, matrix and microenvironment effects, and quenching effects. Since the mid-1970s, the United States Coast Guard has been using standard fluorescence techniques in mobile laboratories for oil spill identification (U.S. Coast Guard, 1977). These procedures also served as the basis for American Society for Testing and Materials (ASTM) methods such as ASTM D3650-78. The EPA in Edison, NJ has developed similar methods for monitoring oils and hazardous chemicals at spills and at Superfund sites (Remeta and Gruenfeld, 1987). In addition to aromatics, PAHs, and oils, luminescence has been shown to be useful for pollutants such as phenols, PCBs, and some pesticides, heterocycles, and metal complexes.

These methods are still being used, for the most part with standard fluorescence emission techniques. Significant developments have taken place in sources, such as lasers and miniaturized lamps, and in detectors, with near-infrared detectors becoming more common. Of special importance is the

increased use of photodiode arrays, and more recently, CCDs, which have allowed real-time spectra to be generated for use with hyphenated techniques such as HPLC, SFC, and time-resolved measurements. Increased use of computer automation, signal processing, and computerized library search routines, together with commercially available spectrofluorometers that yield corrected fluorescence spectra, has allowed for intercomparison of fluorescence spectral data. Libraries of corrected fluorescence spectra have, until recently, been unavailable, with exceptions such as Berlman (1971) and Brownrigg et al. (1979).

THEORY

Conventional luminescence spectroscopy uses either a fixed wavelength excitation (λ_{ex}) to produce an emission spectrum or, less commonly, a fixed emission wavelength (λ_{em}) to record an excitation spectrum. Excitation spectra are occasionally used for comparison with UV-vis absorption spectra for the identification of unknown compounds.

In the last section, the Beer-Lambert Law was stated to be $I = I_0 10^{-\epsilon c d}$ where I was the transmitted light. The following discussion is based on Miller (1981):

$$I_f = I_0 \phi_f = I_0 \phi_f (1 - 10^{-\epsilon c d}) = I_0 \phi_f \left[1 - \left\{ 1 - 2.303 \epsilon c d + \frac{(2.303 \epsilon c d)^2}{2!} \dots \right\} \right]$$

assuming that $I_a = I_0 - I_t$

I_a = intensity of the absorbed light

I_f = intensity of the fluorescence

and

ϕ_f = quantum yield of fluorescence for the analyte

This equation for I_f can be separated and if $\epsilon c d \leq 0.05$ the terms in the expansion after $-2.303 \epsilon c d$ can be neglected so that:

$$I_f = 2.303 I_0 \phi_f \epsilon c d$$

Assuming the assumptions above are valid, this equation is frequently used to show that:

- (1) the intensity of the fluorescence is directly proportional to the intensity of the exciting light, so that the more intense the light source, the more intense the fluorescence (hence the advantage of lasers assuming that photodecomposition does not take place);
- (2) fluorescence intensity for a compound depends on ϵ at the exciting wavelength as well as on the quantum yield;
- (3) the intensity of fluorescence is directly proportional to concentration of the analyte.

The assumptions and approximations involved in deriving this equation are often overlooked.

For organic molecules in solution or solid state, the following general theory applies: the essence of photoluminescence spectroscopy is that a molecular sample, excited by light from an external source, emits light at different wavelengths (usually longer than the excitation wavelength) as fluorescence or phosphorescence. In luminescence spectroscopy, the observed transitions are electronic transitions with vibrational structure; the selection rules for the vibrational structure are the same as those in Raman spectroscopy, that is, allowed vibrational transitions are those which correspond to changes in polarizability of the molecule.

Usually, on excitation with ultraviolet or visible light, the decay of the molecule to the lowest excited singlet is radiationless. Radiative transitions from the lowest excited singlet to different vibrational levels of the ground state give rise to fluorescence emission. The lifetimes for these fluorescence decays are usually from 10^{-10} to 10^{-7} seconds. Mixing of the

singlet states with the lowest multiplet (usually triplet) states permits radiative transitions (phosphorescence) from the lowest triplet state to the ground state to occur. This transition is usually forbidden to occur due to spin-selection rules. The lifetime of the phosphorescence decay can vary from 10^{-4} seconds to several seconds. Phosphorescence, as will be discussed later, is easily quenched because of its longer lifetime and therefore is usually observed only at low temperatures, in rigid matrices or in organized media, or in the absence of oxygen. Because light must be absorbed and then re-emitted radiatively, in competition with radiationless deactivation processes, molecules with high luminescence quantum yields on excitation in the near-ultraviolet or visible regions are normally those with aromatic or heterocyclic structures (with extended π or conjugated-bonding). In-depth discussion of the theory of photoluminescence is available in standard texts such as Parker (1968), Becker (1969), Miller (1981), and Vo-Dinh (1984).

INSTRUMENTATION

For most commercial spectrofluorometers, xenon arc lamps are used as excitation sources, although mercury or other line sources or lasers with fixed or tunable wavelengths may be used. Although some types of lasers, such as diode lasers, nitrogen-dye lasers and even excimer lasers, are being made more compact and rugged to be more suitable for field deployment, there are also disadvantages for field use such as relatively high cost, relative fragility and frequent lack of tunability. Probably lasers should be used only when their special features are required or when factors such as limited sample size or restricted detection volume are involved. For scanning spectrofluorometers, the continuous spectrum of the light source is dispersed by using an excitation monochromator, which can be scanned mechanically to choose the excitation wavelength region with a selected bandpass. The emitted light originating from the sample is usually detected at right angles to the exciting light by an emission monochromator coupled to a detector.

Photomultiplier tubes are the most commonly used detectors, but multichannel detectors are gaining popularity. Further discussions of instrumental considerations for photoluminescence are available in standard texts (Miller, 1981; Schulman, 1985). A portable luminescence device with a fiber optic probe has recently become commercially available for field measurements using a fixed excitation wavelength (Environmental Systems Corporation, 1988) and is being modified to allow synchronous luminescence measurements. This instrument was used for sensitized fluorescence spot tests of PAHs (Vo-Dinh and White, 1986).

TOTAL LUMINESCENCE SPECTROSCOPY

Total luminescence (also called contour luminescence or excitation-emission arrays) contains all of the information in the excitation and emission spectra of the mixtures. A total luminescence spectrum can be computer-derived by using consecutive emission spectra generated at different excitation wavelengths. The complexity of the observed arrays, which are generally instrument dependent and often contain more information than is needed, has led to relatively little use of this technique. Christian et al. in Wehry (1981) showed that such arrays could be generated in seconds using a videofluorometer. Warner et al. (1979) discussed the design of such a system and multicomponent data reduction schemes. Although the feasibility of analyzing environmental samples by HPLC with this technique has been demonstrated, it has not been used in the field. Denton et al. (1987, 1988, 1989) has demonstrated CCDs in spectroscopic detection. This technology promises to greatly improve spectroscopic instrumentation. When used for complex mixtures, it should be combined with appropriate feature extraction techniques to eliminate redundant information and to select the most important features. It is most useful for feasibility studies on new analytes or sample types.

SYNCHRONOUS LUMINESCENCE SPECTROSCOPY

Synchronous luminescence (SL) spectroscopy, introduced by Lloyd (1971), generates spectra which are more simplified cross-sections of excitation-emission arrays. These spectra can be rapidly and easily produced by commercial spectrofluorometers. SL procedures have advantages over conventional luminescence for environmental screening procedures because they reduce or eliminate the frequent overlap of various emissions from the numerous compounds in complex mixtures. Another unique feature of the SL technique is the capability to provide spectral information in one measurement scan, for PAH compounds with different numbers of fused rings. This technique has been discussed in detail by Vo-Dinh, in Wehry (1981) and elsewhere.

With synchronous spectroscopy, the luminescence signal is recorded while both λ_{ex} and λ_{em} are simultaneously scanned (Lloyd, 1978; Vo-Dinh, 1978). A constant wavelength interval is maintained between the excitation and the emission monochromators throughout the spectrum. As a result, the intensity of the synchronous signal I_{ss} , can be written as a product of two functions as follows:

$$I_{ss}(\lambda_{ex}, \lambda_{em}) = kc E_x(\lambda_{ex}) E_e(\lambda_{em})$$

where:

k = a constant

c = concentration of the analyte

E_x = excitation function

E_e = emission function

For a single molecular species, the observed intensity I_{ss} is simplified, often to a single peak, and the bandwidth of the peak is narrower than for the conventional emission spectrum. Even for broad and featureless excitation and emission spectra of molecules such as phenol, the synchronous signal will be narrow. This feature can significantly reduce spectral overlap in multi-

component mixtures. Correlation of the signal wavelength position with the structure of the compounds becomes easier. For example, the spectrum of an aromatic compound with a larger number of rings occurs generally at a longer wavelength than the spectrum of a compound with a smaller number of rings. With conventional spectroscopy, this basic rule cannot often be utilized advantageously due to severe spectral overlap. By confining each individual spectrum to a narrow and definite spectral band, the synchronous method offers the possibility of identifying specific compounds or a class of compounds in a mixture.

A synchronous spectrum can be visualized on an excitation-emission matrix (EEM) as a 45° line parallel to, and to the red of, the scattered excitation light (an emission spectrum would be represented as a horizontal line on the same matrix). For a small wavelength offset, similar to the Stokes shift, the resulting spectrum contains only a few peaks corresponding to zero-zero transitions of fluorescent compounds in the mixture. For pattern recognition in complex mixtures, larger wavelength offsets may also be used on an empirical basis. Variable SL, scanning the excitation and emission monochromators at different speeds, was used by Kubic et al. (1980) to get other cross-sections of the contour array. Another version of SL uses a constant ΔE rather than $\Delta \lambda$, which is more theoretically significant.

Synchronous techniques work especially well to produce simple spectra for PAH mixtures whose components have spectra with well-defined vibronic bands. The technique may be less specific for spectra with asymmetric or unstructured peaks or where the zero-zero transition is not strong.

SL offers instrumental simplicity. Devices intended for conventional fixed-excitation spectra can often be employed for synchronous measurements with little or no modification. Several spectrometers are available with provision for interlocking the excitation and emission monochromators. A variety

of environmental samples has been analyzed to illustrate the applicability of the SL techniques for screening PAH compounds in waste waters. (Abbott et al., 1986).

The simple method of SL analysis opens up many possibilities for monitoring organic pollutants by luminescence spectroscopy. The SL technique can be applied to obtain not only spectroscopic fingerprints from complex samples, such as oil spills as discussed by Eastwood in Wehry (1981), but also specific information of analytical interest regarding individual pollutants or pollutant classes. The synchronous fluorescence technique has already been used for some field applications and, because of its simplicity, has immediate applicability for use in mobile field laboratories and potential applicability for use with portable instruments that have fiber optic probes. Vo-Dinh and Abbott (1984) have successfully used this technique to rank relative amounts of different PAH classes as compared to other more standard methods of analysis. A protocol for total PAH characterization and quantitation based on fluorescence emission and synchronous spectra is now under development at EPA-Las Vegas (Eastwood et al., 1989).

The derivative technique, usually but not always the second derivative, can be used to enhance the selectivity of photoluminescence techniques including synchronous fluorescence. In this mode of data representation, the signal produced is proportional to the second-derivative (d^2) of the spectrum with respect to wavelength. Second-derivative signals can be obtained by numerical differentiation, modulation techniques, or direct electronic differentiation. (Green and O'Haver, 1974). In the d^1 mode the measurement is of the rate of change of curvature of a peak. Broad peaks are eliminated in the recording, but sharp spectral features are intensified; hence, this technique provides improved compound selectivity and quantitation.

The synchronous and derivative techniques can be combined for many of environmental sample analysis applications. Purcell et al, in Cline-Love and Eastwood (1985), successfully separated the SL peaks of phenol, o-cresol, m-cresol, and p-cresol by taking the fourth derivative (applying the second derivative twice) of the SL system.

Luminescence spectroscopy is especially well-suited for determination of chemicals that fluoresce in complex mixtures, due to the multidimensional nature of the information available in the luminescence spectrum. For analytical purposes, luminescence excitation and emission spectra, lifetimes, polarization, and quenching or enhancement by perturbers are some of the independent dimensions of analytical information.

As an example, fluorescent compounds with highly overlapping emission and excitation spectra may have different fluorescence lifetimes so that their relative intensity contributions can be resolved in the lifetime domain. Even with HPLC analysis, separation of PACs in complex real-world samples can be difficult. McGown (1989) has used the fluorescence lifetime information provided by phase-modulation fluorescence to strengthen the quantitative analysis of fluorescence detection for HPLC. For on-line detection, fluorescence lifetime heterogeneity of chromatographic peaks are used as an indicator of the purity of the peaks.

Phase-resolved fluorescence spectroscopy (PRFS) has not yet been used in the field, but is under consideration for use with HPLC and with fiber-optic remote sensors. Commercial instrumentation for PRFS is compact enough to fit in a mobile laboratory.

These techniques are most valuable in situations where the variations in the composition of complex samples (containing a large number of organic compounds, e.g., oil spills [Eastwood in Wehry, 1981], exhaust soot, by-product

water [Vo-Dinh in Wehry, 1981]) fail to provide significant changes in the conventional fluorescence spectrum.

ROOM TEMPERATURE PHOSPHORESCENCE

Phosphorescence has an advantage in that many interferences, such as fluorescence emission as well as Rayleigh and Raman scattering, can be eliminated either by wavelength or lifetime selectivity. Although low-temperature luminescence techniques such as laser-excited Shpol'skii, line-narrowing fluorescence, or matrix isolation spectroscopy appear to be more suitable for laboratory applications, room temperature phosphorescence (RTP) enhancement is gaining increased interest for field applications (Vo-Dinh, 1984). RTP techniques usually require adsorption on solid substrates or stabilization in organized media such as micelles (Cline-Love and Skrilec, 1981) or cyclodextrins (Warner in Eastwood and Cline-Love, 1988) to avoid quenching by intermolecular collisions or by oxygen processes that might lead to the deactivation of the phosphorescent triplet state.

The following is a brief discussion of the theory of phosphorescence (for further discussion see Vo-Dinh [1984]). From the first excited singlet S_1 , the molecule may undergo transition to some vibrational level of the triplet manifold via a mechanism known as intersystem crossing (ISC). Intersystem crossing is possible because of the coupling of the electron spin with the orbital angular momentum which produces a quantum mechanical mixing of states of different multiplicities. The molecule then relaxes to the lowest vibrational level of T_1 by radiationless vibrational relaxation processes. From T_1 , the molecule may return to the different vibrational levels of the ground state S_0 either by a radiationless deactivation process or by the emission of a photon (phosphorescence). A less common emission process, delayed fluorescence, can also occur by repopulation of the S_1 state by thermal activation or by triplet-triplet interaction.

Because of its spin-forbidden nature, phosphorescence emission exhibits typically longer decay times than the spin-allowed fluorescence process. In liquid solutions at room temperature, bi- and mono-molecular quenching processes usually cause nonradiative deactivation of the triplet state. The presence of oxygen, an efficient triplet quencher, is also a major contributor to the radiationless deactivation of the triplet level. The radiationless deactivation process for most molecules in the triplet state is so efficient that phosphorescence can normally be observed only when the solution is frozen into rigid matrices (Birks, 1970). Conventional methods in phosphorimetry, therefore, involve: (1) careful preparation of oxygen-free solutions, (2) insertion of analyte compounds into polymer samples, or (3) use of rigid matrices of frozen organic solvent. The first two techniques involve tedious and time-consuming preparation, the third requires experiments at low temperatures, usually 77 to 4.2 K.

Intense phosphorescence at room temperature has been observed from various salts of polyaromatic compounds (PACs) adsorbed on solid supports, such as silica, alumina, paper, and asbestos (Shulman and Walling, 1972; Vo-Dinh, 1984). This type of phosphorescence is assumed to originate from surface-adsorbed molecules, because none could be observed from finely ground samples of free crystalline compounds. Numerous ionic compounds were found to show strong phosphorescence, especially when they were spotted onto substrates following dissolution in strongly acidic or basic solvents. As a consequence, the ionic state of the molecules may have resulted in an increased molecular rigidity via adsorption to the substrate, thus reducing the effect of collisional deactivation. Hydrogen bonding was also found to be responsible for phosphorescence of adsorbed compounds at room temperature.

Unlike conventional phosphorimetry, RTP does not require cryogenic equipment and involves simple experimental steps such as: (1) substrate

preparation (optional pretreatment), (2) sample delivery, (3) drying process, and (4) spectroscopic measurement.

The versatility of sampling procedures is one of the main advantages of the method. Various sample collection methods are possible, including spotting, leaching, swipe techniques, and liquid filtration. The use of filter paper or filter membranes as direct sample support broadens the type of samples that can be monitored and is advantageous in performance, reproducibility, convenience and low cost.

Although some luminescent chemicals such as PCBs have higher phosphorescence than fluorescence quantum yields, others such as PAHs require the enhancement of the triplet emission by the external heavy atom effect, which perturbs the electronic levels of the analyte and hence increases ISC between the singlet and triplet states, leading to enhanced phosphorescence. Numerous heavy atom salts such as thallium and lead acetate, silver perchlorate, cesium or methyl iodide and sodium bromide have been found to be efficient in enhancing the phosphorescence quantum yields of PAHs selectively (Vo-Dinh and Hooyman, 1978). RTP signals can be selectively enhanced by several orders of magnitude by pretreating the matrix or premixing the sample with the heavy atom perturber.

Two types of external heavy-atom perturbers are commonly used for RTP. Type A perturbers such as thallium acetate form phosphorescent ground state charge-transfer complexes with the aromatic compound. Type B perturbers such as methyl iodide do not associate with the compound. Type B perturbers normally give multi-exponential decay curves, whereas Type A perturbers, depending on the concentration of the perturber, will give mono- or bi-exponential decay curves. Because the perturbers not only increase the phosphorescence quantum yields but do so with different enhancement factors, depending on perturbers used and their concentrations, the selectivity of the

technique can be increased. (Vo-Dinh and Hooyman, 1978; Jakovljevic, 1978; White and Seybold, 1977).

Synchronous phosphorescence may also be used with the optimum $\Delta\lambda$ determined by the singlet-triplet energy difference, which might range from 100 to 300 nm.

These RTP techniques have been successfully used to analyze for individual chemicals in complex environmental mixtures containing polyaromatic hydrocarbons such as benzo(a)pyrene, benzo(e)pyrene, chrysene, fluoranthene, fluorene, pyrene and phenanthrene. (Vo-Dinh, 1984; Cline-Love and Skrilec, 1982; Bower and Winefordner, 1978; Ford and Hurtubise, 1979).

CHEMILUMINESCENCE

Chemiluminescence occurs when a chemical reaction produces an electronically excited state to emit light on returning to the ground state. As recently shown by Fernandez-Gutierrez and Munoz de la Pena in Schulman (1985), the chemiluminescence intensity can be expressed as:

$$I_{\text{cl}} = \phi_{\text{cl}} Z$$

where:

Z = rate of the chemical reaction

ϕ_{cl} = chemiluminescence quantum yield of the excited product

$$\phi_{\text{cl}} = \frac{\text{number of emitted photons}}{\text{number of reacting molecules}}$$

Chemiluminescence can be measured as a function of time with the maximum intensity usually proportional to the concentration of analyte, or by mixing the reactants in a flowing system.

Usually, for inorganic analyses, concentrations between 10^{-4} and 10^{-5} $\mu\text{g/mL}$ can be measured, requiring relatively simple equipment. Chemiluminescence has been most often used for biochemical analyses, such as adenosine triphosphate (ATP) using the oxidation of luciferin catalyzed by the luciferase enzyme, or for air pollutant analysis. The development of chemiluminescence for analytical purposes has been limited because few molecules demonstrate this phenomenon in solution and also chemiluminescence methods tend not to be very selective. Chemiluminescence reactions may be catalyzed by low levels of ions. Chemiluminescence assays have therefore been developed for ions such as Cu^{2+} and Co^{2+} based on their catalytic effect on the oxidation of luminol. Several other inorganic ions or gases have also been determined by chemiluminescence methods involving luminol or luciferin.

CONCLUSIONS

UV-vis luminescence (fluorescence and phosphorescence), when applicable, is potentially the most sensitive spectroscopic analytical method, especially when laser excitation is available. Therefore, luminescence is the method of choice for field use for trace or ultratrace analysis for classes of pollutants with appreciable luminescence yields, such as most polyaromatic compounds (PACs), both aromatic and heterocyclic. At higher levels, or where extensive sample preparation is needed, other methods become competitive with luminescence. Luminescence is especially applicable for water samples, where little or no sample preparation may be involved, and for real-time flow-through applications either direct or with HPLC multichannel detection.

As compared to UV-vis absorption, luminescence is potentially more sensitive and subject to fewer interferences. As compared to infrared and Raman, this technique is more sensitive, but spectra are less specific and structured. Vibrational structure in luminescence spectra is found, however, for certain classes of compounds such as PAHs. Additional spectral structure

can be introduced by use of rigid media, low temperature, site-selective laser excitation, or derivative techniques. Specificity in complex mixtures without separatory or chromatographic procedures can be improved by techniques such as synchronous luminescence, luminescence lifetime techniques or special low temperature methods.

Fluorometric reagents can be extremely sensitive and specific, but many have the same problems as colorimetric reagents, namely interferences, lack of specificity, and chemical instability, especially for use with fluorometric fiber-optic sensors. Other possible disadvantages include fluorescence background such as that from fulvic or humic acids, scatter from excitation light, quenching, or self-absorption. Quenching and self-absorption can usually be avoided by dilution and scatter can be minimized by use of RTP, life-time discrimination, or appropriate filters. Fluorescence from fulvic or humic acids is usually a problem only at the low ppb level and then could be avoided by separatory methods, time-resolved techniques, or background subtraction.

Field-deployable scanning and filter spectrofluorometers have been available and in use for some time, primarily for petroleum oil and PAH analyses, and by hydrologists who use fluorescent dyes to trace ground water movement. At least one portable fluorescence instrument has been developed, and another portable spectrofluorometer with a fiber optic probe and synchronous capability is under development. The main obstacle has been the apparent lack of a market, because, until recently, attention was not focused on this promising technique for environmental applications. Now ASTM and EPA analytical methods are being developed for PAHs, PCBs, and phenols, which should stimulate the use of luminescence in environmental analysis.

Classes of compounds for which fluorescence is especially applicable include petroleum oils and PAHs. Fluorescence has also been found useful for

other polyaromatic compounds including phenols, some pesticides and heterocycles. RTP is potentially applicable to important pollutants such as PCBs and PBBs, and chlorinated dibenzodioxins and dibenzofurans.

For field use, fluorescence can be used to characterize oils and creosotes, quantitate total PAHs and rank relative amounts of different PAH classes using synchronous techniques. PCBs and some pesticides can be detected and quantitated by RTP, possibly in conjunction with thin layer chromatography (TLC). Soluble aromatic compounds such as phenols and chlorinated phenols can be measured even in mixtures in aqueous solution using synchronous-derivative methods. Use of fluorometric reagents can greatly extend the range of pollutants that can be studied by this technique to include non-fluorescent species such as chlorinated alkanes, metal ions, and anions such as cyanide.

Luminescence techniques are probably less important for volatiles and more so for semivolatiles and nonvolatiles such as the heavier PAHs, PCBs, chlorinated dibenzofurans, and dioxins. Luminescence may also be useful for the more polar or thermally labile compounds or those luminescent compounds of higher molecular weight (or compounds which form fluorescent derivatives) which can be measured in conjunction with HPLC, SFC, or, for field applications, TLC. For screening and semiquantitation, synchronous fluorescence and RTP are especially applicable for chemical classes such as PAHs and PCBs.

Low temperature (77 K to 4.2 K) luminescence methods are useful in the laboratory for backup and for comparison with RTP used in the field. Also, these high resolution techniques could complement gas chromatography-mass spectrometry (GC-MS) by distinguishing important geometric isomers, even in complex environmental matrices, without separatory or chromatographic

procedures. Research efforts are also desirable to advance several of these promising low-temperature approaches.

Chemiluminescence is a sensitive but specialized technique that should be utilized along with other luminescence procedures, when applicable.

Analytical protocols need to be developed for more naturally fluorescing species and better fluorometric reagents for nonfluorescing species, especially for use with spot tests for field instruments and for fiber optic chemical sensors (FOCS). Better portable spectrofluorometers need to be developed with capability for synchronous measurements. Also needed are smaller lasers (the development of which is proceeding rapidly), especially for the UV range, better UV optical fibers having higher transmittance in the UV, miniaturized sources, and other optical components. More research is needed in solid surface spectroscopy to better understand the theory in order to optimize experimental conditions and improve phosphorescence yields for RTP.

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SECTION 5

INFRARED ABSORPTION SPECTROSCOPY

INTRODUCTION

Vibrational spectroscopy has traditionally been of importance for qualitative identification because of its specificity. Many sharp peaks may be present in vibrational spectra, which can be related to molecular structure. The frequencies of most molecular vibrations occur generally in the infrared region of the electromagnetic spectrum. These vibrations may be detected and measured either directly in an infrared (IR) spectrum or indirectly in a Raman inelastic scattering spectrum.

THEORY

Quantum mechanical selection rules permit only discrete vibrational energy levels. The selection rule for a vibration to be infrared active is that the vibration must result in a change in the electric dipole moment. The number of modes of vibration is $(3N - 6)$ for a molecule consisting of N atoms ($3N - 5$ if the molecule is linear). For large molecules there are thus many vibrational transitions. Many vibrations can, however, be localized to particular bonds or groupings, such as the $-C=O$ (carbonyl) group, forming the basis of characteristic group frequencies. Also, vibrational modes are observed relating to the skeletal vibrations of the molecule.

A simplified example can be given for a diatomic molecule (with 2 atoms of mass m_1 and m_2) connected by an elastic spring with force constant k . This system can be considered to represent a harmonic oscillator in the classical

physics approach. According to this model, the vibrational frequency ν of the bond connecting the two atoms can be approximately described by the formula:

$$\nu_{\text{vib}} = \frac{1}{2\pi} \left[\frac{k}{\mu} \right]^{\frac{1}{2}}$$

where:

k = force constant of the spring

μ = reduced mass of the molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

A quantum mechanical treatment of the same system will show that a harmonic oscillator will have the energy levels E_v given by $E_v = (v+1/2)h\nu$, where $v = 0, 1, 2, 3, \dots$ is the vibrational quantum number, h is Planck's constant and ν is the classical vibrational frequency of the harmonic oscillator. The vibrational selection rules are $v = 0$ or ± 1 . In the real world, oscillators will be found to have anharmonic components, which can be thought of, in the classical physics approach, as due to inelasticity or friction in the spring. See treatment in Griffiths and de Haseth (1986).

INSTRUMENTATION

A common dispersive grating instrument for measuring IR spectra is the double-beam spectrophotometer. The light source is usually a heated filament (or metal carbide rod) that emits a continuous spectrum of a "black body" exhibiting considerable intensity in the IR region. The excitation beam is split in two with one beam passing through the sample and the other through a reference cell. Both beams then pass through a chopper, which allows alternate sampling of the two beams. These beams then pass through a monochromator to the detector, which measures the difference in intensities between the two beams. Two types of infrared detectors have been commonly used: quantum detectors and thermal detectors such as the Golay detector and the

pyroelectric bolometer. Because thermal detectors respond relatively slowly, solid-state semiconductor quantum detectors such as mercury cadmium telluride (MCT) or PbS and PbSe are increasingly used. For good sensitivity, lead sulfide must be chilled with a thermoelectric cooler below ambient temperature, and MCT must be maintained at 77 K.

An IR spectrum usually consists of a plot of the absorbance as a function of wavenumber (cm^{-1}) and is characterized by the positions of the maxima of each of the absorption bands ν_{max} expressed in cm^{-1} . Within the IR region of the spectrum, the range from 1400 to 4000 cm^{-1} is especially useful for identifying frequencies for characteristic groups, e.g., -C=O . The region from 600 to 1400 cm^{-1} contains many bands, including those from skeletal vibrations, so that it is especially useful for "fingerprinting" of aliphatic and aromatic hydrocarbons and petroleum oils. Dispersive mid-IR spectroscopy has long been used by organic chemists for structural determinations. Its use as an analytical procedure has never been fully developed due mainly to its lack of sensitivity. Qualitative (e.g., for oil identification, Grant and Eastwood, 1983) and a few specific quantitative (e.g., oil and grease) methods have already been employed for field use.

The near IR region from roughly 780 nm to 1600 nm (12,800 to 6250 cm^{-1}) contains many broad, overlapping harmonic and overtone peaks. Computer pattern recognition and signal processing techniques are used to deconvolute the broad spectral peaks. This spectral region has recently proven useful for process control and for monitoring selected environmental pollutants (including the use of near IR sensors), but would prove less useful for trace analysis, because it is sensitive only to major components, down to 1 to 0.1%.

The specificity of IR is an advantage in comparison with UV-vis absorption and luminescence spectroscopies. Disadvantages include relatively low sensitivity due to relatively weak bands, the fact that IR band strengths may

not appear to be directly proportional to concentration if measurements are made at low spectral resolution, and special optical and solvent requirements. In particular, absorption bands of water in IR spectra are a serious limitation of this technique for trace analysis for hazardous waste applications. FTIR spectral subtraction techniques using a circle cell can be used down to the part per thousand level in water, but often ppm or lower is desired.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform IR (FTIR) spectroscopy uses an interferometer in conjunction with Fourier transform mathematical techniques and a dedicated computer. This technique is especially useful for real-time or flow-through gas phase measurements although it is also applicable to solids, films and liquids.

The theory behind FTIR was discussed by Griffiths and de Haseth (1986). Most interferometers are based on the same principle as the Michelson interferometer, which divides a beam of light into two parts and recombines them after a path difference has introduced interference between the beams. Intensity variations can be measured by the detector as a function of path difference. The interferometer consists of two plane mirrors, one of which is moved with a drive mechanism in a direction perpendicular to the plane of the other fixed mirror, with a beam splitter between them.

For a monochromatic light source, the theory can be described briefly as follows: The optical path difference between the beams introduced by the fixed and movable mirrors is called the retardation δ . The amplitude of the interferogram after detection and amplification is proportional to the intensity of the source, the beam splitter efficiency, the detector response, and the amplifier characteristics.

$I(\delta)$ is the modulated ac component of the intensity, usually called the interferogram.

For a monochromatic source and an ideal interferometer, the equation for the interferogram is:

$$I(\delta) = 0.5 I(\bar{\nu}) \cos 2\pi \bar{\nu} \delta$$

For a polychromatic source and a nonideal interferometer, where the beamsplitter efficiency, detector efficiency, etc. are given as a function of wavelength, $I(\delta)$ can be expressed as:

$$I(\delta) = 0.5 H(\bar{\nu}) I(\bar{\nu}) \cos 2\pi \bar{\nu} \delta$$

where: $H(\bar{\nu})$ = wavelength-dependent correction factor

$B(\bar{\nu})$ is the parameter describing the intensity of the source as a function of wavenumber $\bar{\nu}$ as modified by the instrumental characteristics.

$$B(\bar{\nu}) = 0.5 H(\bar{\nu}) I(\bar{\nu}) = \text{single beam spectral intensity}$$

So that:

$$I(\delta) = B(\bar{\nu}) \cos 2\pi \bar{\nu} \delta$$

where: $I(\delta)$ = cosine Fourier transform of $B(\bar{\nu})$

Usually, the moving mirror is scanned at a constant velocity, v (cm/sec) so that the retardation at t seconds can be thought of as:

$$\delta = 2vt$$

then:

$$I(t) = B(\bar{\nu}) \cos 2\pi \bar{\nu} 2vt$$

For a continuous polychromatic source:

$$B(\bar{\nu}) = 2 \int_0^\infty I(\delta) \cos(2\pi \bar{\nu} \delta) d\delta$$

Other factors as discussed by Griffiths and de Haseth (1986) include resolution, phase errors, and beam divergence.

The simultaneous measurement of all spectral elements by an interferometer is called the multiplex or Fellgett's advantage, allowing for rapid spectral acquisition. The multiplex advantage can be expressed as a sensitivity advantage, comparing the signal-to-noise ratio (SNR) of a spectrum measured on a Fourier transform instrument to the SNR of the same spectra on a dispersive spectrometer. If the resolution, acquisition time, and all other instrumental conditions are equivalent, the SNR for the FT instrument will be increased by a factor equal to M^2 , where M is the number of resolution elements assuming detector dark noise is dominant. The time advantage of an FT spectrometer, allowing complete spectra to be recorded in milliseconds, is even greater, being directly proportional to M . A smaller advantage is Jaquinot's advantage, which stems from increased throughput of Fourier spectrometers as compared to IR grating spectrometers. The increased throughput is dependent on the optics and resolution used, so that the total advantage of the FTIR over dispersive instruments is small in this regard. Another, the Connes advantage, is that the IR spectral frequency in the FTIR is precisely referenced by laser lines. This feature enables the spectra to be independent of the instrument and useful for interlaboratory comparison and spectral library collection.

Griffiths and coworkers have compared FT and grating IR spectrophotometers from a theoretical viewpoint in terms of the multiplex advantage of FT spectrometers, relative optical throughput, and the comparative performance of the detectors used with each type of system (Griffiths et al., 1977).

Recently, FTIR, especially used as GC-FTIR for complex environmental samples, has become accepted as a laboratory technique. Gurka (1988) has developed standard protocols for EPA analytical applications.

For satisfactory GC-FTIR analysis, the interface is most important. Most commonly, heated light pipes have been used. Basically this involves a long narrow flow cell coated with gold, with IR-transparent windows and with transfer lines for the GC effluent. Matrix-isolation capillary GC-FTIR has been commercially developed, and a real-time cold finger cryotrapping approach has been reported by Griffiths. In their present form, these systems would be complex instrumentally for field use, but offer advantages for higher sensitivities and lower detection limits, as compared to the more common GC-FTIR systems that use light pipes.

Although GC-FTIR offers advantages for field analysis of volatile pollutants, analytical techniques for nonvolatiles by hyphenated-FTIR techniques are in a less advanced stage of development. HPLC-FTIR techniques are currently being studied by the EPA. Supercritical fluid chromatography (SFC) has also been combined with FTIR, and Liebman et al. (1989) have reported the possibility of combining such analytical techniques with fiber optics and expert systems for field use. Although some of these methods may remain primarily laboratory methods, FTIR and hyphenated FTIR methods are increasingly being considered for field conditions. Fateley et al. (1989) has recently explored the use of long path length FTIR in a mobile field laboratory to measure air emissions of volatile organic compounds from soil.

Computers are integral parts of FTIR instruments, although they are being increasingly used with dispersive IR instruments also. Although extensive IR library data bases exist, many of the spectra for dispersive IR are old and are not equivalent to spectra analyzed under modern spectroscopic and sampling conditions. Yet, for many field applications, dispersive IR spectrometers with a minicomputer-based data system may also be used at lower cost. The choice of the type of instrument is best decided by the users to satisfy their particular needs.

In general, the use of an FTIR spectrometer is strongly favored for most measurements in which the time to acquire data is limited by the type of experiment (e.g., on-line gas chromatography-infrared (GC-IR) or for techniques in which the time needed for absorption spectroscopy is very long, as with absorption spectroscopy of samples with very high absorbance).

FTIR has several other advantages over conventional methods. It is much less susceptible to stray radiation. In addition, because a computer is already used to obtain the Fourier transform, it is easy to add multiple scans to improve the signal-to-noise ratio (for Poisson's distribution-type noise, noise adds up as the square root of the number of scans, whereas signal adds linearly). Digital subtraction (useful for subtracting water background to obtain infrared spectra in aqueous solutions) can produce difference spectra. This method has advantages in obtaining infrared spectra in aqueous solutions.

Although IR is a very specific technique, like other absorption methods, it lacks the potential real-time sensitivity for ultratrace measurements as compared to UV-vis luminescence. Special techniques have been used to improve detection limits of IR including tunable laser diode infrared absorption spectroscopy. FTIR, in particular, is now sensitive enough for many environmental applications.

CONCLUSIONS

Dispersive and FTIR instruments have already been used in the field, especially for total hydrocarbon and oil quantitation and characterization. The advantages of IR are largely that it is a mature technique with commercially available spectral libraries and that it is specific for characterization, because functional groups can be identified even for unknown compounds. Quantitation is also performed, although some difficulties have been reported. Disadvantages have included relative lack of sensitivity,

solvent interferences, and need for special solvents and optics. One of the greatest limitations of IR for in situ field analysis of liquids and solid wastes is interference from water, which necessitates more complicated sample preparation. For this reason it has been used in the field mainly for vapor phase applications (either remotely or with long-path length gas cells).

EPA has used infrared primarily as GC-FTIR, with vapor phase detection in a light pipe, or for front surface measurements on a cryostat cold finger. Fateley et al. (1989) are also studying FTIR for soil gas emissions with vapor phase detection. Liebman (1988) has reported FTIR detection of pollutants combined with supercritical fluid extraction (SFE) and fiber-optic light-pipe interfaces. IR used with HPLC and flow-through applications is less developed. For EPA, the future seems to hold increased use of GC-FTIR and vapor phase long-path length IR, including field deployment. FTIR, with attenuated total reflectance (ATR) attachments, is also applicable for characterization of bulk pollutants and front surface measurements on complex matrices such as oil-soaked soils. Portable IR instruments exist and are used in the field especially for gas analysis, but they should be miniaturized to a greater extent. Near-IR portable instruments and sensors are under development, but are mainly useful for relatively simple, highly concentrated mixtures, for process control, and for oil characterization. Mid-IR sensors are limited by the lack of inexpensive fiber optic materials for the mid-IR region and by interference from water.

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SECTION 6

RAMAN SPECTROSCOPY

INTRODUCTION

Raman spectroscopy has been used much less than IR spectroscopy due to its relatively complex instrumentation, relatively low sensitivity and interferences in the visible from fluorescence. Recent improvements in near-infrared lasers sources to reduce interferences from fluorescence and in signal processing have made Raman techniques potentially more promising for field applications. Raman spectra are due to inelastic scattering processes and the Raman-active vibrations are those which cause changes in the polarizability of the molecule. Therefore, Raman spectroscopy is complementary to IR because Raman-active vibrations are often IR-inactive and vice versa.

THEORY

In general, scattering is produced when electrons in a molecule oscillate under the influence of an applied electromagnetic wave. The extent of the scattering depends on the polarizability of the electrons in the molecule (i.e., the dipole moment induced by the electric field).

When a molecule with a spherical, symmetric electron cloud is placed between the plates of a charged condenser, the electrons are pulled toward the positive plate and the protons toward the negative plate. The molecule is said to be polarized, and has an induced dipole moment. Representing the vector of the electric force of the external field as E , and the induced dipole

moment oriented parallel to the direction of \mathbf{E} as μ , μ can be defined as $\mu = \alpha E$, where α is the polarizability of the atom. Using Cartesian coordinates to resolve the electric field, this equation can be rewritten as:

$$\mu_x = \alpha E_x$$

$$\mu_y = \alpha E_y$$

$$\mu_z = \alpha E_z$$

For an asymmetric molecule, α may be different for the x, y, and z directions; for the anisotropic case, the polarizability is described by a tensor

$$\mu_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$

$$\mu_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$

$$\mu_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z$$

where α_{xx} , α_{xy} , . . . α_{zz} , are proportionality constants between μ_x and E_x , μ_x and E_y , . . . μ_x and E_z , etc.

When light of frequency ν_0 impinges on a molecule, the electronic cloud of the molecule develops an induced frequency. An induced dipole moment vibrates at frequency ν_0 , and its amplitude is proportional to the polarizability of the molecule. As a result, the molecule emits Rayleigh radiation, the frequency of which is ν_0 .

The polarizability of the molecule depends on its size, shape, and orientation; and it can be viewed as a polarizability ellipsoid. The polarizability ellipsoid may be modified as a result of change in the shape of the molecule due to vibrations of the atomic nuclei. Therefore, radiation from the molecule contains not only ν_0 , the exciting frequency, but also the sum and difference of the exciting and vibrational frequency ν , i.e., $\nu_{\pm} = \nu_0 + \nu$, and $\nu_{\pm} = \nu_0 - \nu$.

The frequency shifts ν_{a} and ν_{s} are called anti-Stokes and Stokes Raman lines (or bands), respectively. The Stokes Raman radiation is of lower frequency (energy) than the anti-Stokes and is usually the only spectrum recorded. Anti-Stokes bands are due to thermally excited ("hot") states and will decrease in intensity at lower temperatures.

In Raman spectroscopy a powerful laser source scatters light inelastically from the sample. The scattered light, usually collected at right angles, reaches a spectrometer: preferably one with high stray light rejection, high resolution, and high throughput.

Raman instruments require a powerful source, preferably monochromatic. Most Raman spectrometers currently use argon or krypton ion lasers. Light scattering increases as ν' , leading to a gain in Raman intensity at higher frequencies (shorter wavelengths). For resonance Raman analysis of pollutants, usually UV sources are required. For this application excimer lasers such as KrF or frequency doubling or tripling a visible light source is required.

Raman spectrometers require high resolution, low stray light spectrometers; usually double or triple monochromators are used. Concave holographic gratings also are more nearly perfect and improve throughput and stray light rejection. Other optics and detectors are similar to those needed for luminescence measurements.

A near infrared solid-state laser source is now used on one commercial FT Raman system. This avoids fluorescence background, an important consideration for most Raman measurements, at the cost of some sensitivity.

Raman suffers from relative insensitivity (20 - 1000 ppm even with argon ion laser excitation) as compared to UV-vis fluorescence and absorption,

although the optical and solvent problems are reduced if excitation in the UV or visible is involved. Water, for example, is not an interferent. If lasers with excitation wavelengths in the visible or UV region are used, background fluorescence may be a serious problem, although there are ways to avoid this (such as use of a large quantity of a fluorescence quencher, or time resolution).

For environmental use the relative insensitivity of the normal Raman technique coupled with the greater instrumentation complexity required for its performance has so far limited this technique to a few feasibility studies: its use in the field still appears to be premature.

Tilotta et al. (1987) demonstrated a new signal processing approach which involved optical multiplexing with Hadamard transform Raman spectroscopy in the visible and near-IR spectral region. This spectrometer utilizes a liquid crystal spatial light modulator (LC-SLM) in its exit focal plane. In this instrument, the dispersed radiation is focussed onto an encoding mask where resolution elements are transmitted or rejected by absorption, depending on electronically controlled encodement which makes individual elements of the mask opaque or transmitting. This instrument allows the rejection of Rayleigh scattering and allows spectral and background subtraction with simultaneous observation of multiple Raman levels for pollutants such as 2-nitropropane. Although this relatively new technique has not yet been field tested, it offers obvious advantages of increased experimental simplicity and time savings for on-the-fly or time-resolved studies.

As stated by Gerrard and Bowley (1988), for most common analytical applications involving routine qualitative and quantitative analysis of unknowns, better established methods are available that are more rapid, are more sensitive, or have larger data bases. In general, other techniques are preferred to normal Raman spectroscopy, when available, for environmental

analytical applications unless special, more sensitive Raman techniques can be employed such as resonance Raman (using a tunable UV laser) or surface-enhanced Raman, or unless the special sampling advantages of Raman are needed.

RESONANCE RAMAN SPECTROSCOPY

Normal Raman spectroscopy (NRS) is induced by excitation far removed from any electronic transitions of the molecule, i.e., a virtual transition. In the Resonance Raman (RR) effect, the frequency ν_0 is allowed to be near an electronic absorption ν_{abr} . In this preresonance region, a marked enhancement of intensity can result due to a mechanism involving a single excited electronic state. In this case the intensity I of the resonance Raman signal can be given with several simplifying approximations (see discussion in Carey, 1982) as:

$$I \propto (\nu_0 \pm \nu_{\text{vib}})^4 \left[\frac{\nu_{\text{abr}}^2 + \nu_0^2}{(\nu_{\text{abr}}^2 - \nu_0^2)^2} \right]^2$$

A smaller term arising from the vibronic mixing of two excited states is not shown. This is the resonance Raman effect, and the advantage is in its great sensitivity and selectivity as a tool for investigating chromophore structure, because only vibrational modes directly associated with the chromophore have their intensities enhanced. Normal modes, which have a large shift in equilibrium geometry upon electronic excitation, produce intense resonance Raman features.

The enhancement in the RR spectrum is typically between 10^3 and 10^4 . The RR effect can be obtained at concentrations of 10^{-4} M•L⁻¹ or less. At these concentrations normal Raman spectra are usually undetectable. Thus, RR provides a means of selectively probing vibrational frequencies of a

chromophore with a sensitivity approaching that of ultraviolet absorption spectroscopy.

Raman, like IR, has great specificity, but differs from IR in two important aspects. Raman is well suited to condensed phase samples and UV-RR has the sensitivity for analyses at the ppb level for some strong Raman scatterers (chromophores) without sample concentration. The vibrational information obtained is complementary to IR because the selection rules are different and may be especially useful for skeletal vibrations and some specific vibrations such as the $\text{-C}\equiv\text{N}$ stretch. The technique is still immature and requires relatively cumbersome equipment such as an excimer laser and Raman shifter or a crystal to frequency-double a tunable visible laser source. The Raman technique offers a large linear dynamic range, and water can be used as a suitable solvent.

Mann and Vickers (1988) applied ultraviolet resonance-enhanced Raman (RR) spectroscopy to hazardous waste analysis both directly and in conjunction with HPLC. Some hazardous pollutants that have been analyzed by Raman include phenols, dimethylsulfone, sulfate and bisulfate.

Asher et al. (1983) found that PAHs, for example, could be studied with excitation far enough in the UV region that fluorescence background was not obtained. The disadvantage from the environmentalist's point of view is that only the chromophore is excited. Most pollutants do not have a suitable chromophore in the visible region, and UV lasers are still expensive and complex to operate under field conditions.

SURFACE-ENHANCED RAMAN SPECTROSCOPY

Surface-enhanced Raman spectroscopy (SERS) appears to be the most promising Raman technique for ultratrace environmental analysis, and consequently it

deserves more detailed discussion. SERS was first observed by Fleischmann et al. (1974) from pyridine molecules adsorbed on silver electrode surfaces that had been roughened electrolytically by oxidation/reduction cycles.

Enhancements in the Raman scattering efficiency have been observed by factors of as much as 10^6 in favorable cases when a compound is adsorbed on or near special metal surfaces (Jeanmaire and Van Duyne, 1977). This enormous enhancement of the normally weak Raman scattering process helps to overcome the relatively low sensitivity of Raman spectroscopy. Its disadvantages are that it is still not well understood; electromagnetic and chemical sorption effects both appear to be involved, and the effect does not occur to the same extent for all analytes.

The electromagnetic effect is associated with large local fields caused by electromagnetic resonances occurring near metal surface structures. A major contributor is surface plasmons associated with collective excitations of surface conduction electrons in metal particles (Chang and Furtak, 1982). These plasmons are excited by the incident radiation (Ritchie, 1957). At the plasmon frequency the metal becomes highly polarizable, resulting in large local surface fields that increase the Raman emission intensity, which is proportional to the square of the applied field at the surface. Other types of electromagnetic enhancement effects include the lightning-rod effect, where electromagnetic field lines near high curvature points on the surface become concentrated, and the image effect, where the surface is polarized by dipole-induced fields in adsorbed molecules.

Electromagnetic enhancement mechanisms are: (1) long range in nature, because the dipole fields in polarizable metal particles vary as the inverse cube of the distance to the center of the particle; (2) generally independent of the adsorbed molecule and dependent on the electronic structure of the substrate and the roughness of the surface.

The chemical sorption effect is associated with the overlap of metal and adsorbate electronic wave functions, which can lead to ground-state and light-induced charge transfer processes. The chemical effect relating to SERS is short range (0.1 to 0.5 nm), depending on the adsorption site, the geometry of bonding, and the energy levels of the adsorbate molecule. Although the contribution of charge-transfer processes to SERS may be large in some cases ($\times 10^{-10}$), the chemical enhancement mechanism is restricted by its specificity.

The SERS effect is similar to normal Raman scattering in that the intensity of the scattered light is linear with that of the incident light and is depolarized. This effect seems to occur only under specific experimental conditions relating to the dielectric constant and morphology of the surfaces. Silver surfaces give the strongest enhancement effects, followed by Cu, Au, Pt, and Ni. The roughening of the surfaces is also critical and depends on the type of surface preparation. Microspheres, posts, metal islands, colloids, and metal-coated cellulose have been used. For spheroidal silver particles, diameters ranging from 10 to 100 nm are optimal. For roughened silver electrodes the surface protrusions are generally between 25-500 nm.

The SERS effect for silver island substrates was found to occur with the first monolayer of adsorbate molecules. SERS spectra of pyrene adsorbed on silver-coated quartz posts were found to show some peak shifts (e.g., 1582 cm^{-1} vs 1597 cm^{-1} for NRS of pyrene in solution). This indicates that these vibrations were affected by adsorption to the metal surface. For large molecules, only chemical groups close to the SERS-active surface may be enhanced.

Vo-Dinh and coworkers (1984) evaluated the SERS technique for environmental applications using practical SERS-active substrate materials based on silver-coated Teflon microspheres deposited on glass and filter

paper. A wide variety of organophosphorus chemicals including methyl parathion, fonofoxon, cyanox, diazinon, formothion, and dimethoate were investigated (Alak and Vo-Dinh, 1987). SERS analyses were reported of several chlorinated pesticides including carbophenothion, bromophos, dichloran, linuron, chlordan and 1-hydroxychlordene (Alak and Vo-Dinh, 1988). The detection limits for these pesticides were measured at nanogram and subnanogram levels. The results achieved with these chemicals are of great analytical interest because these chemicals are difficult to detect by other techniques, such as luminescence spectroscopy, due to the low luminescence quantum yields of these compounds. A mixture of structurally related compounds and a soil sample contaminated with pesticides were analyzed by SERS to illustrate the selectivity of this new technique as a screening tool for environmental applications (Alak and Vo-Dinh, 1987). Vo-Dinh (1989) has demonstrated the SERS spectrum of complex environmental samples (diesel particulate samples from the National Institute for Standards and Technology) containing six PAH compounds as spotted on various SERS-active substrates.

Carrabba et al. (1987) have reported using SERS to analyze for compounds such as hydrazines used for rocket fuels. They currently are developing a prototype field-deployable SERS using utilizing electrochemical roughening of silver electrodes. A fiber-optic system was also recently developed for SERS in situ analysis using a silver-coated, microparticle-based sensing probe (Bello and Vo-Dinh, 1990).

The use of silver colloids for SERS measurements in solutions has been investigated widely (Tran, 1984; Sheng et al., 1986; Laserna et al., 1987; Ahern and Garrell, 1987). Recently, Fateley and coworkers have developed the SERS colloid technique for HPLC detection (Freeman et al., 1988). Measurements of SERS in the near IR region have also recently been investigated (Chase and Parkinson, 1988).

CONCLUSIONS

Raman spectroscopy, because it is a relatively under-utilized technique involving complex instrumentation and laser excitation, is probably the farthest from field deployment. Normal Raman spectroscopy has structural information overlapping with, and complementary to, IR. It has the advantage that water and glass are not interferents and that solid samples and unusual sample shapes and sizes can be accommodated. NRS is also relatively insensitive with detection limits between 20 and 1000 ppm. Techniques with greater sensitivity, rivaling luminescence, are resonance Raman (RR), which requires even more complex instrumentation (excimer lasers or frequency-doubling crystals and Raman shifters) and surface-enhanced Raman.

SERS is a promising technique in terms of its potential sensitivity and specificity. It could also be used with sensor technology. One of its disadvantages is that the intensity of the Raman signal is dependent on the substrate surface and material and also on the specific analytes being studied. Also, SERS is a new technology, not yet fully understood and implemented. Although there is interest in developing a field-deployable instrument, only a few research groups can so far obtain reliable, reproducible, and sensitive SERS results even in the laboratory. Pollutants which have been successfully studied by this technique include pyridine, hydrazine, and other rocket fuels, PAHs, and organochlorine and organophosphate pesticides. Extensive research efforts are currently being undertaken to develop the potential of this relatively new analytical technique.

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SECTION 7

SPECTROSCOPIC IMMUNOASSAY TECHNIQUES

INTRODUCTION

Immunoassay-immunological methods, offering the capability of excellent selectivity and specificity through the process of antibody-antigen recognition, have revolutionized many aspects of chemical and biological sensor technologies down to ultratrace levels. Although radioimmunoassay (RIA), utilizing radioactive labels, has been most widely used, it has disadvantages for field use, such as cost of instrumentation, short shelf life of some radioisotopes and hazards of handling radioactive materials under field conditions. Fluoroimmunoassay (FIA) using fluorescent labels and related assay methods has great potential advantages for field use with a spot test approach and has been discussed elsewhere in great detail (Smith et al., in Wehry Vol. 3, 1981; Karnes et al. in Schulman, 1985).

DISCUSSION

The theory of immunoassay is beyond the scope of this report, but considerable chemistry and biochemistry is involved for the development of each test. Suitable derivatives of the pollutant must be developed that can be complexed to proteins so that specific antibodies can bind to them with high affinities. Conjugates of these derivatives must be prepared with properties to allow rapid bonding to immobilized antibodies and good recovery and stability of enzyme activity.

A survey of all aspects of luminescence immunoassay is given by Karnes et al. (1985). This rapidly moving field was earlier surveyed by Smith et al., in Wehry (1981). Karnes et al. (1985) stated that FIA sensitivities were typically in the 10^{-11} M range. FIA techniques are not yet as sensitive as RIA procedures, although they can be made more sensitive using laser excitation. Currently, commercial instrumentation for FIA is limited to simple analyses not requiring extremely high sensitivities. One approach to improve FIA sensitivity would be to use time-resolved fluorescence or phosphorescence detection. Use of image detectors for spectral or spatial resolution would also reduce sample analysis time.

FIA can also be used with fiber optic chemical sensors. Vo-Dinh et al., (1987) have developed immunochemical fiber optic sensors for specific environmental pollutants such as benzo(a)pyrene.

Colorimetric immunoassay tests are also specific and sensitive although not quite as sensitive as FIA and RIA. Colorimetric portable immunoassay kits for pesticides such as paraoxon were recently discussed by Duquette et al. (1988). In this case the analyte competes with an enzyme-analyte conjugate for a limited number of immobilized antibody sites. This test can detect paraoxon at one microliter in water with positive results indicated by color development in ten minutes. This test is operable in salt water and fresh water and is stable under field conditions for as long as one year. This assay format could be modified to measure other environmental pollutants such as PCBs.

Three other examples of field-portable colorimetric immunoassay (biomarker) procedures were recently reported by White and Van Emon (1989) and are discussed below.

Westinghouse Bioanalytic Systems (Rockville, MD.) has developed a rapid test for the wood preservative pentachlorophenol which is sensitive to 3 ppb and takes only 30 minutes to perform. A pentachlorophenol-enzyme conjugate competes with free pentachlorophenol for binding to the immobilized antibody. The enzyme binds on a colorimetric substrate with absorbances being measured on a battery-operated field portable colorimeter. This method was successfully demonstrated at a Superfund site in New Brighton, MN.

Antox Corporation developed an enzyme-linked immunosorbent assay (ELISA) for toxic light aromatics including benzene, toluene, and xylene (BTX), which is claimed to be sensitive to the ppm level. The BTX screening assay uses a polyclonal antibody-coated tube as the solid phase. This test is still under evaluation; phenols do not appear to be an interferent but the antibody may cross-react with alkylated aromatics.

A third assay described by Brady et al. (1989) for aldicarb, requires minimum sample preparation and analysis time of 2.5 hours. The assay response is linear over the range of 16 to 2000 ng.

As summarized by White and Van Emon (1989), immunoassay techniques have important advantages and disadvantages. The advantages include relative sensitivity, specificity, cost-effectiveness, and speed in comparison with more common GC-MS analysis. They can be used as rapid field-portable semiquantitative or quantitative methods, to process large number of samples, to reduce time for sample preparation, and as screening methods.

Disadvantages include the fact that these methods usually can not be used for unknown chemicals or chemical classes or on complex mixtures of unknown compounds. Also, they are subject to interferences and cross-reactivities with compounds other than the target analyte. They are not real time methods; sample preparation and time for reaction is needed. They may have a limited

dynamic range. Also, considerable lead time can be involved in developing immunoassay procedures.

CONCLUSIONS

Fluoroimmunoassay (FIA) and colorimetric immunoassay techniques can be extremely sensitive (especially FIA) and specific (perhaps too specific, they usually cannot be used for class detection). Because of their specificity individual reagents are usually required for each pollutant, when, in many situations, broad classes of pollutants are of interest. Nevertheless, immunoassay can be made field-portable and applicable for pollutant monitoring. These techniques will be most needed where simpler fluorescence, colorimetric, or fluorometric procedures do not apply and when extreme specificity is needed. They also can be used with FOCS, in some cases.

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SECTION 8

FIBER OPTIC CHEMICAL SENSORS

INTRODUCTION

Fiber-optic chemical sensors (FOCS) offer a means of expanding the role of spectroscopy in environmental monitoring. The need for in situ, low-cost, real-time monitoring of organic and inorganic pollutants in ground water and surface waters has been one of the main forces driving the development of fiber optic sensors, particularly FOCS. The toxic pollutants of interest cover a wide range of contaminants from organic chlorides, phenols, and heavy metals from industrial and hazardous waste sites to aromatic hydrocarbons from leaking underground storage tanks to organophosphates from Department of Defense installations.

FOCS can be made very sensitive and specific to satisfy regulatory requirements. Other advantages of FOCS include their small physical size, geometric flexibility, and the possibility of real-time, multiple analyses in situ. Disadvantages include short operational and storage life (due to complex chemistries) and lack of ruggedness. Another disadvantage is the relatively narrow spectral range of inexpensive, commercially available fibers, although better UV and IR fibers are being developed. The present lack of performance and calibration standards for interfiber reproducibility represents another problem to be overcome by developing peer-approved ASTM standards. Recent advances in spectrochemical instrumentation, laser miniaturization, biotechnology, and fiber optics research have provided

opportunities for novel approaches to the development of sensors for the detection of environmental pollution by toxic chemicals.

DISCUSSION

Fiber optic sensors may be divided into two general classes. The first class of sensors uses the waveguide, usually an optical fiber, as a simple lightpipe taking light to and from a sensing device, such as a microcell containing a dye that exhibits changes in absorbance or luminescence with varying concentrations of a substance or a physico-chemical parameter (e.g., CO_2 , O_2 , or pH). For this class of sensors, one important factor involves the light transmission efficiency through the fiber. The second category of sensors involves an intrinsic change in the properties of the optical fiber itself, which serves as the sensing element. This category may be further subdivided into two subcategories: evanescent field sensors and surface plasmon resonance sensors.

Fiber optics sensors can use either bifurcated or single-strand fibers. In a device based on bifurcated design, separated fibers carry the excitation and emission radiation. In the single-fiber device, a dichroic filter or mirror-pinhole assembly is generally used to separate the excitation and emission radiation. When compared to multiple (bifurcated) fiber designs, sensors that utilize a single optical fiber to transmit excitation radiation to the sample, and the emission radiation from the sample to the detector, have the advantages of good signal collection efficiency and small size. The small-diameter attribute is important for environmental applications, since it may be important to fit a number of different sensors down a one or two inch monitoring well. Single-fiber sensors, however, exhibit high optical background levels because a significant amount of excitation radiation, which is reflected at the fiber tip, is not efficiently rejected by spatial filtering. Attempts to minimize this back-scatter radiation problem include

the use of high rejection ratio double monochromators, and grinding fiber faces at angles that minimize the reflected optical background. Disadvantages of these correction techniques include the relatively low throughput of double monochromators and the difficulty of producing small quartz surfaces with precise angles.

Optical fibers utilize total internal reflection (TIR) to achieve propagation length with very low loss, but another complementary feature of TIR can be used in optical sensing for surface sensitivity. Evanescent-field spectroscopy is an extension of the well-known internal reflection method. The evanescent-field technique uses an optical waveguide as the transmitting medium in place of the crystal medium often used in internal reflection spectroscopy. When light is reflected at a dielectric interface, i.e., at the interface between two materials of different refractive indices, the energy associated with the light is not totally confined to the material in which the incident and reflected waves are propagated. There is a drastic decrease of energy away from the reflected point into the second material. This field is known as the evanescent field, because energy cannot be propagated in this direction. It decays within a distance comparable with the wavelength of the light.

Sensors can also be based on the application of the surface plasmon resonance (SPR) principle. It is possible to arrange a dielectric/metal/dielectric sandwich such that, when light impinges on a metal surface, a wave is excited within the plasma formed by the conduction electrons of the metal. A surface plasmon is a surface-charge-density wave at a metal surface. A plasmon resonance is induced in the surface of a metal conductor by the impact of light reflected off the metal surface. The critical angle is naturally very sensitive to the dielectric constant of the medium immediately adjacent to the metal, and this characteristic therefore lends itself to exploitation for analytical sensors. For example, the metal can be deposited as, or on, a

grating; upon illumination with a wide band of frequencies, the absence of reflected light can be observed at the frequencies at which the resonance matching conditions are met.

The most common FOCs reagents are organic chemicals whose reaction products are suitable for colorimetric or fluorometric measurements. A number of such sensors have been developed (Wolfbeis in Schulman, 1988). Angel (1989) recently field-tested a colorimetric sensor for trichloroethylene. Much of the required chemistry for such sensors is discussed in the older chemical literature. Many of the chemical reagents are not reliable under field conditions or are not designed for stability for the time required for an in situ sensor (3 months to 1 year). Recently fluoroimmunoassay FOCs have been tested by Vo-Dinh et al. (1989) using enzyme coatings. Klainer et al. (1988) recently developed a gasoline sensor based on changes in the refractive index of a proprietary cladding material, due to absorption of the light aromatics in the gasoline by the cladding.

The current status of FOCs have been discussed in a number of recent references by Wolfbeis in Schulman (1988), Eccles and Eastwood (1988), Klainer et al. in Wolfbeis (1990), Vo-Dinh et al. in Wolfbeis (1990) and others. Feasibility studies have been performed on many pollutant sensors including chloroform, gasoline, pH, ammonia, benzo(a)pyrene, aluminum, cyanide, actinides, and sulfur dioxide. Only a few of these sensors have proven rugged enough for long-term field testing and commercialization. Progress is needed in the area of remote sensors because of the tremendous need for continuous environmental monitoring and the large potential cost savings provided by remote sensors in contrast to more conventional analytical techniques.

CONCLUSIONS

Although there is no reason FOCS cannot eventually prove satisfactory for environmental monitoring and screening applications, there may be delays because of the many practical and engineering problems that must be solved before FOCS can be rugged, reliable, and inexpensive enough for general field deployment and commercialization. If chemical sensors rather than remote spectroscopy approaches are to be used, a wide variety of reliable chemical sensors must be developed for the major pollutants. The technology requires better UV fibers and sources, or else chemical reactions to move spectral responses into the visible region. Other important areas for research and development include: better instrumentation with miniaturization of all components of the FOCS system; peer-accepted calibration, characterization and performance standards through organizations such as the American Society of Testing and Materials (ASTM); improved reagent immobilization and polymer membrane technology; and improved methods and systems of optical coupling such as improved molded optics or nonimaging optics. Development of satisfactory FOCS requires interdisciplinary research teams, which might include analytical chemists, polymer and dye chemists, molecular spectroscopists, optical physicists, optical and mechanical engineers, material scientists, and hydrologists. Appropriate instrumentation and laboratory support facilities are also required. Currently, few of the research groups developing FOCS have such complete teams.

FOCS can be thought of as light pipes, combined with detection by colorimetric or fluorometric reagents or by measuring changes in some optical property of the fiber or the protective cladding. Although of great potential long-term applicability to ground-water monitoring, some sensors are closer to field testing and commercialization than others. Some FOCS are currently being field tested and evaluated (pH, temperature, conductivity, alkali metals, and gasoline). Other FOCS are still under development and may require

several years of research and development as well as engineering improvements before they can be applied in the field. For some sensors, immobilization of the coatings and reversibility, stability, and specificity of the reagents are still problems to be addressed in the research laboratory. At present, vapor-phase sensors are more developed than true liquid-phase sensors.

The small sizes of fiber optic sensors could allow smaller diameter (1/2") monitoring wells to be drilled at substantial cost savings. Despite the problems which remain to be overcome, remote fiber optic sensors have an important future in continuous environmental monitoring of ground water.

In addition to FOCS, in situ spectroscopy, using fiber optic probes, is a possibility for most of the spectroscopic techniques discussed in this report.

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APPENDIX A

TYPICAL ENVIRONMENTAL POLLUTANT SPECTRA FOR SOME MAJOR SPECTROSCOPIC TECHNIQUES

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A-3 Room-temperature synchronous fluorescence of No. 6 and No. 2 fuel oils.	4
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A-7 Room-temperature phosphorescence spectra of fluoranthene using several heavy-atom agents.	8
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A-19 Surface-enhanced Raman scattering (SERS) spectrum of methyl parathion. The 647.1 nm line of a krypton laser was used for excitation. A silver-coated microsphere substrate was used.	20

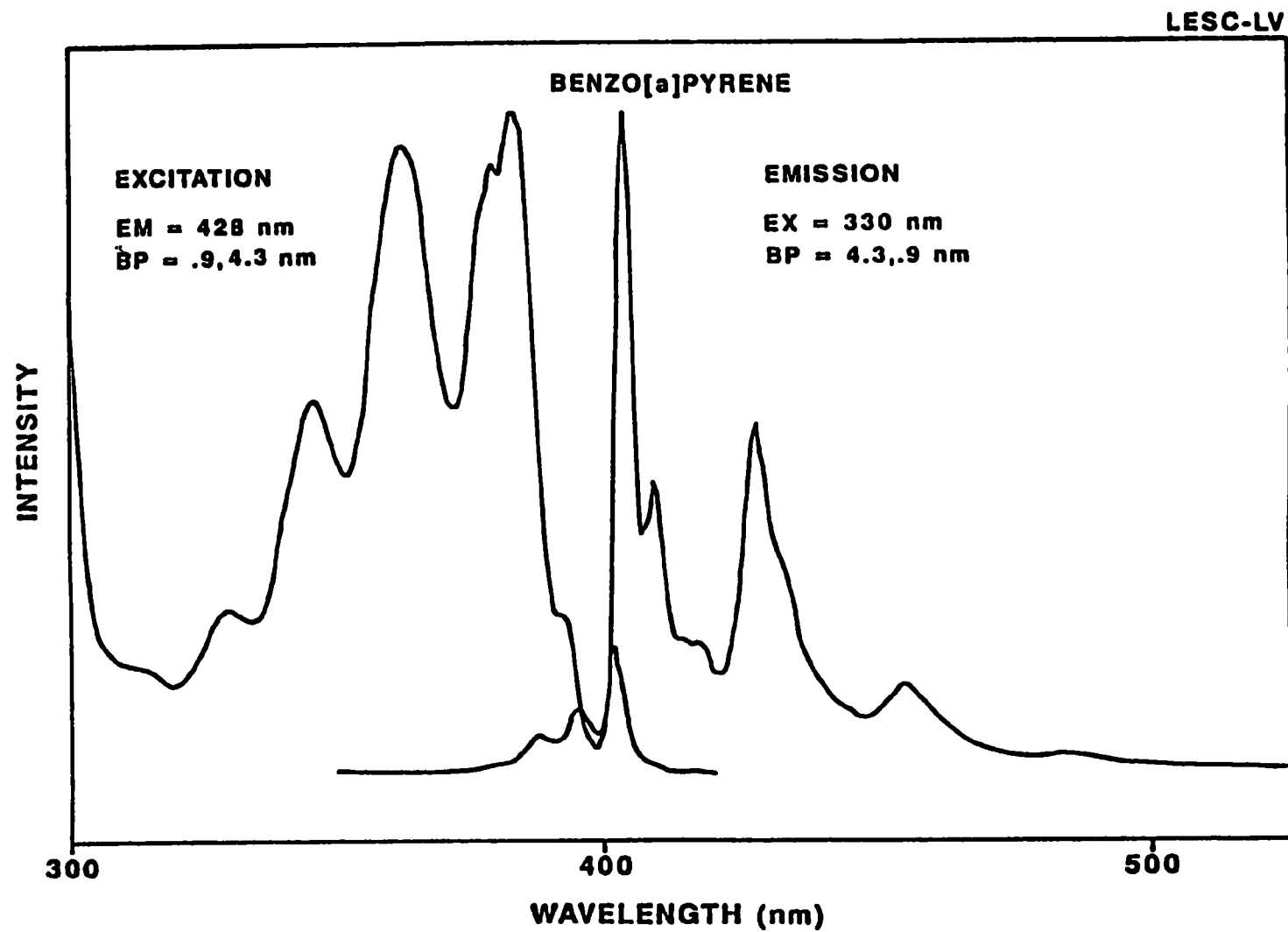


Figure A-1. Excitation and emission fluorescence spectra of benzo(a)pyrene.

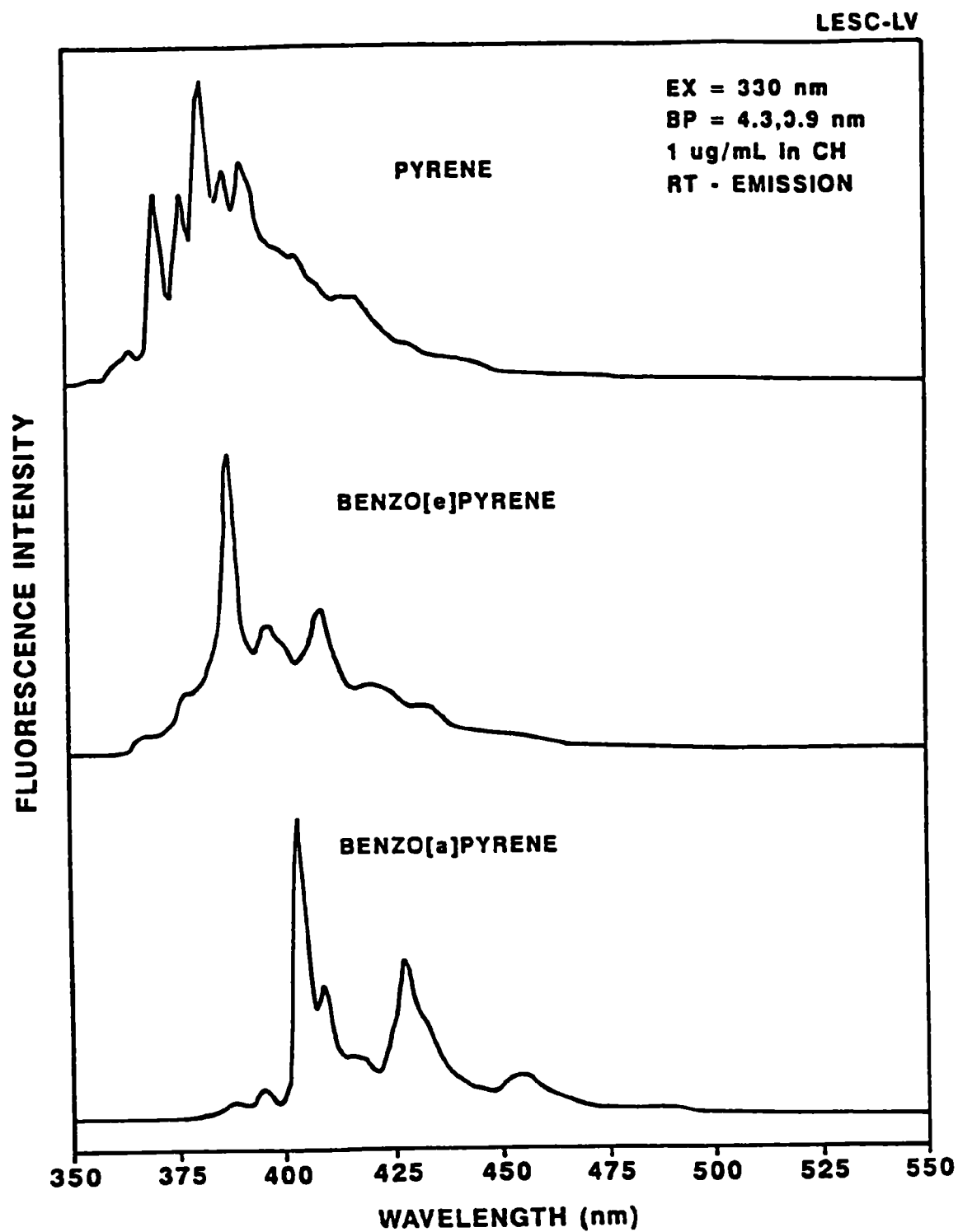


Figure A-2. Room-temperature fluorescence of pyrene, benzo(e)pyrene and benzo(a)pyrene.

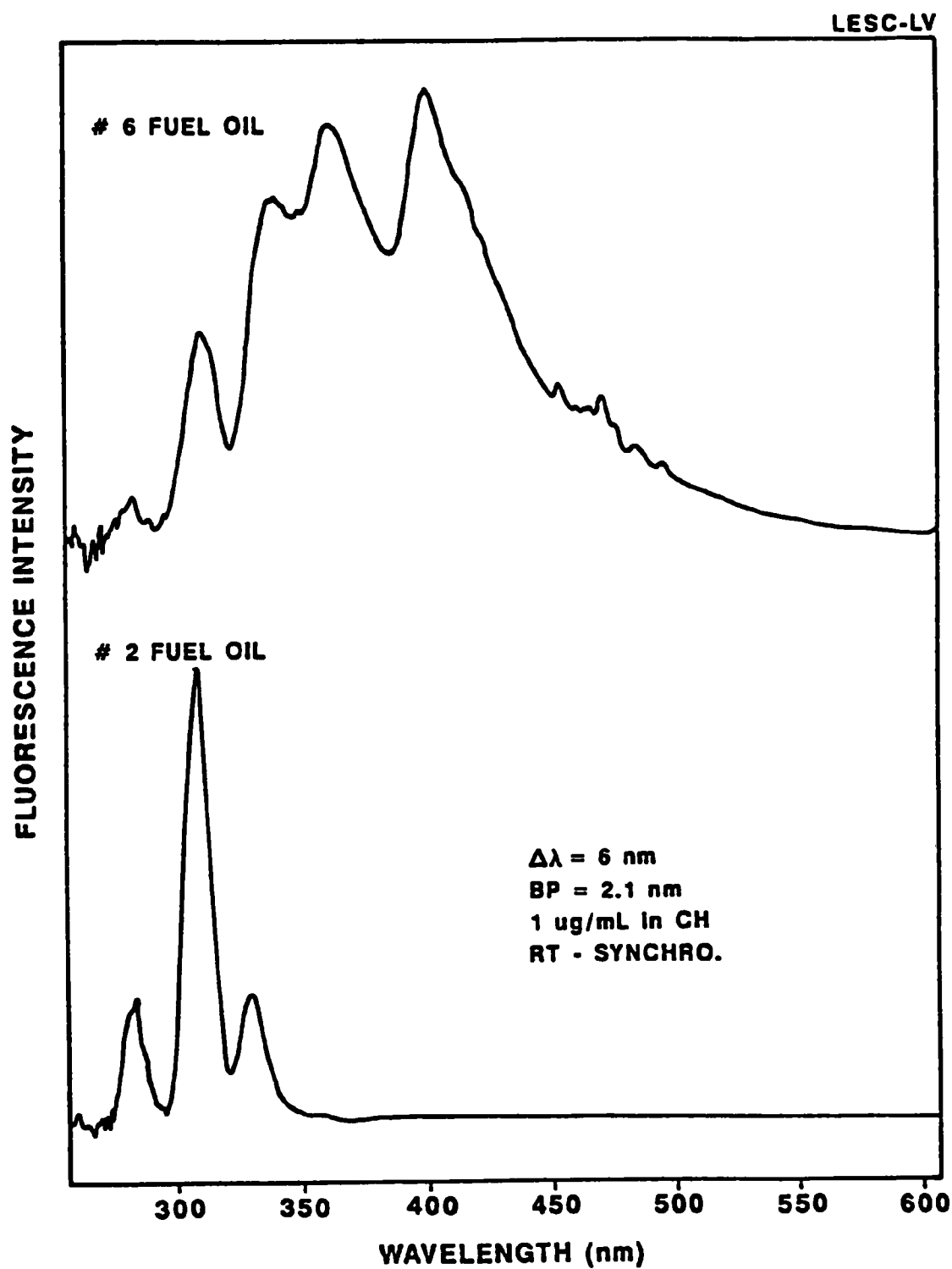


Figure A-3. Room-temperature synchronous fluorescence of No. 6 and No. 2 fuel oils.

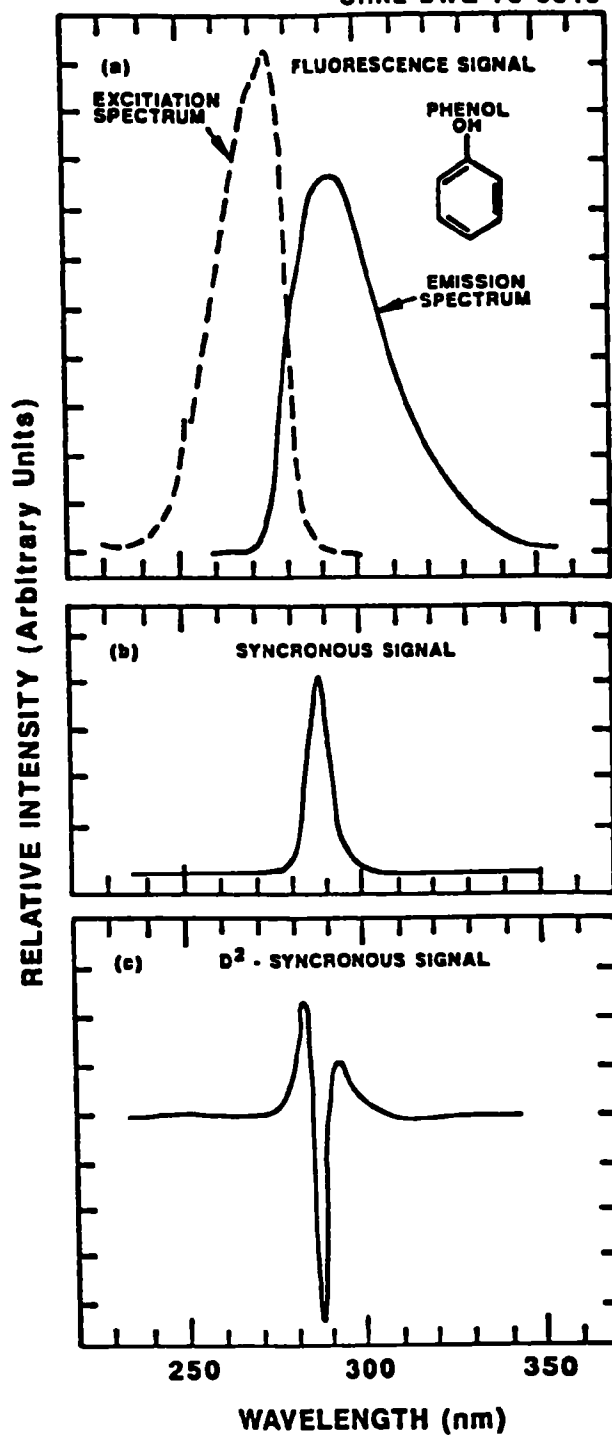


Figure A-4. Fluorescence spectra of phenol
(a) Excitation and emission fluorescence spectra
(b) Synchronous fluorescence spectrum
(c) Second-derivative synchronous fluorescence spectrum

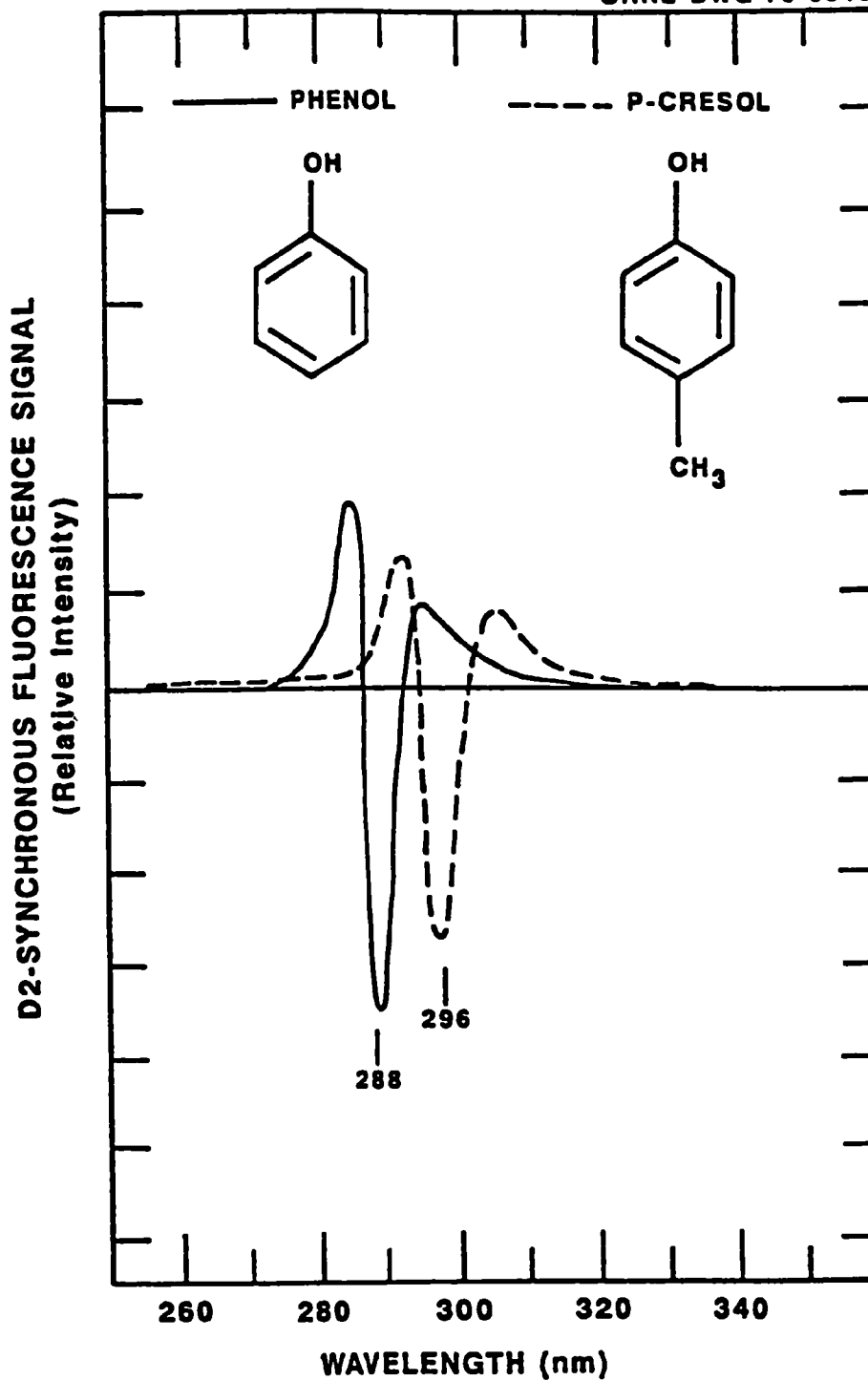


Figure A-5. Second-derivative synchronous fluorescence spectrum of phenol and p-cresol ($\Delta\lambda=3$ nm)

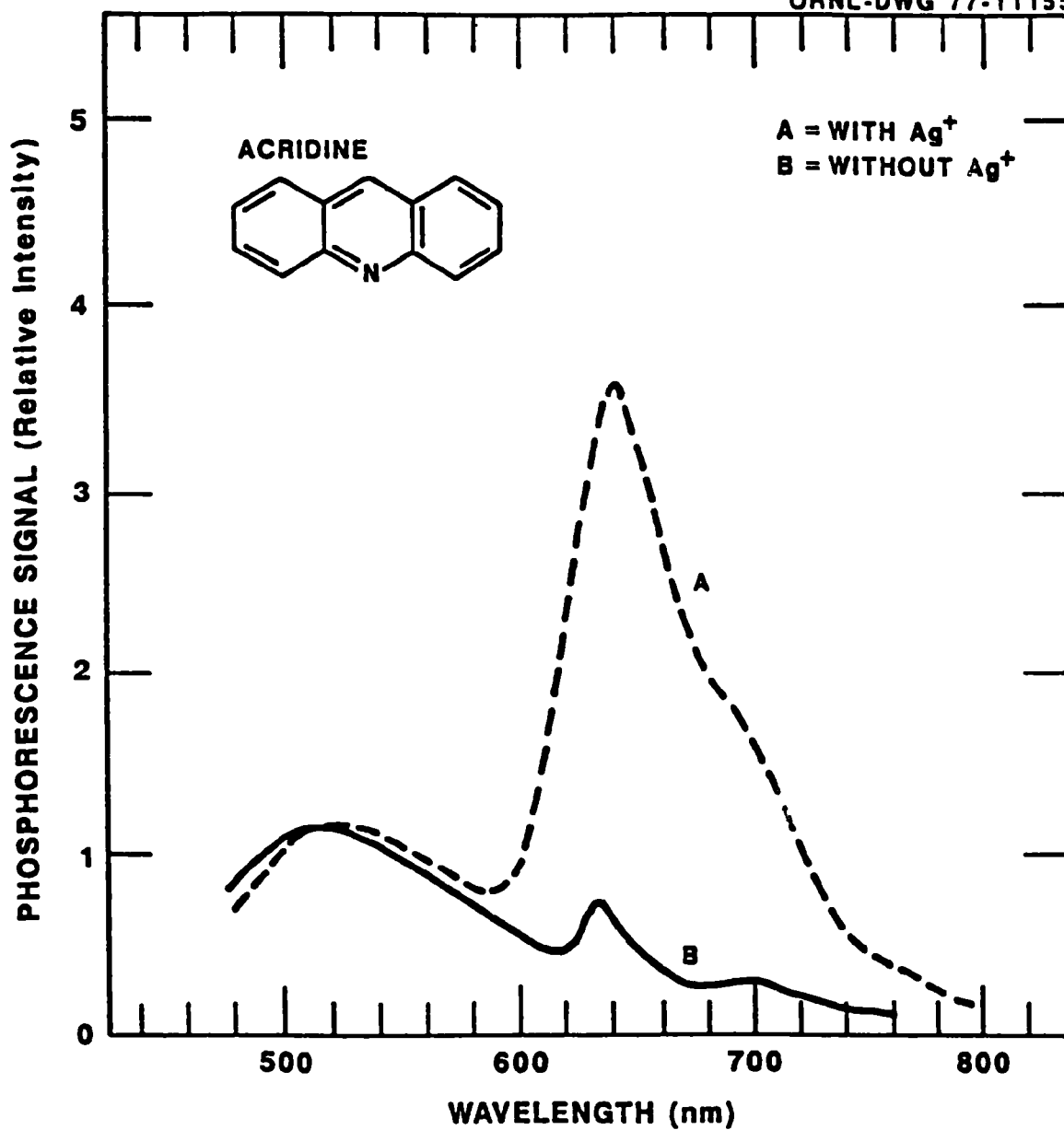


Figure A-6. Room-temperature phosphorescence spectra of acridine with and without silver nitrate as a heavy-atom perturber.

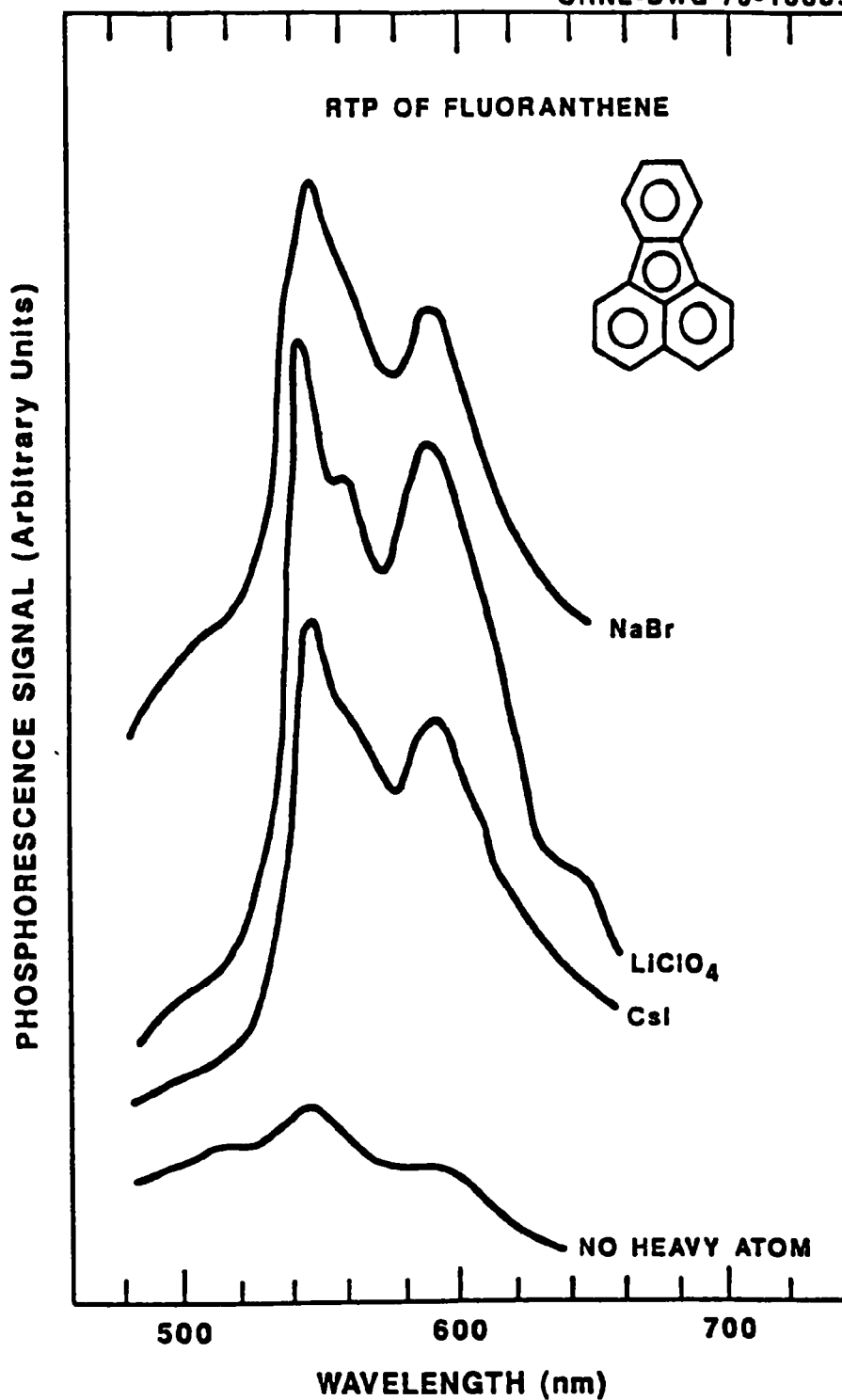


Figure A-7. Room-temperature phosphorescence spectra of fluoranthene using several heavy-atom agents.

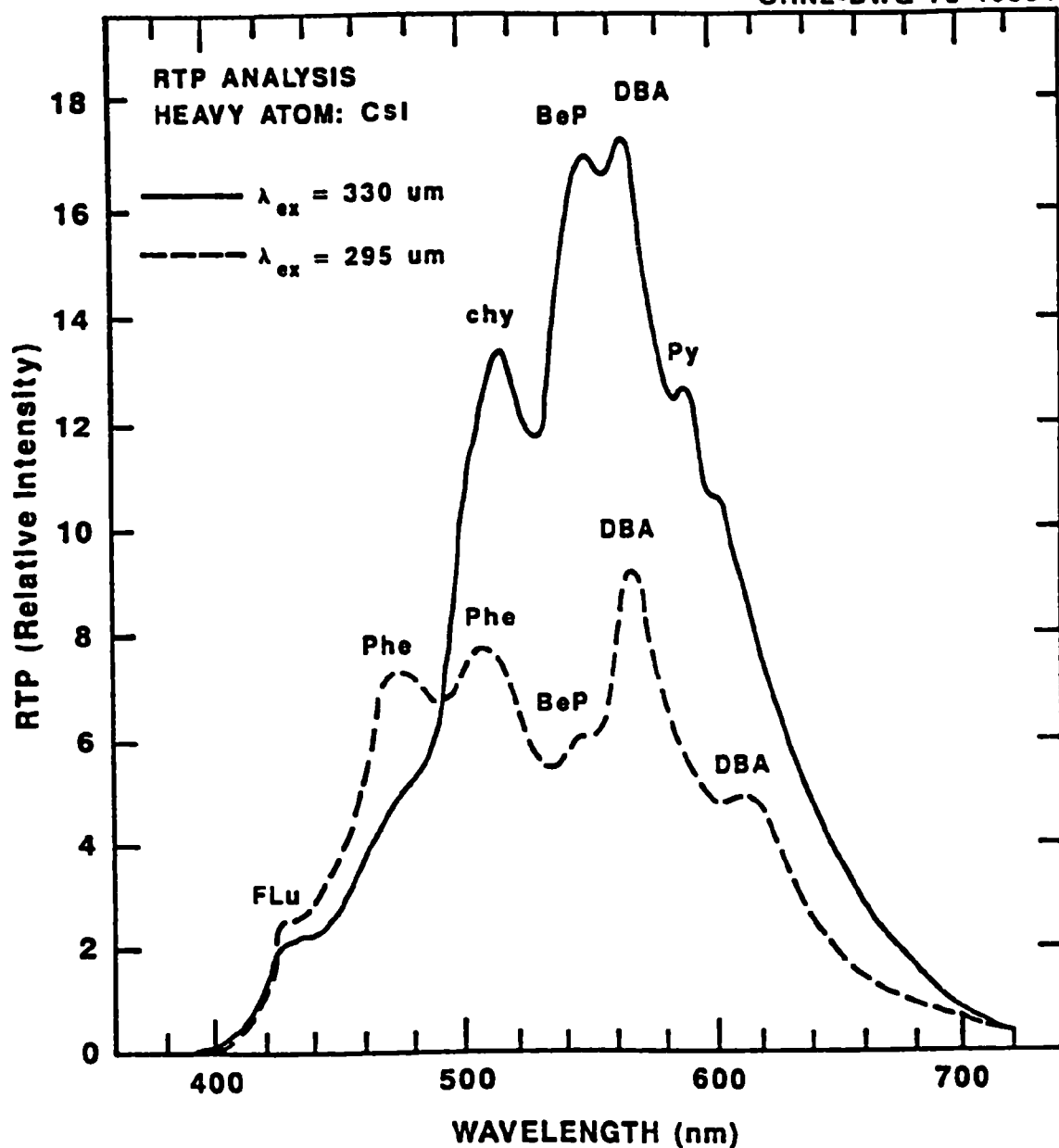


Figure A-8. Room-temperature phosphorescence spectra of a multicomponent mixture of fluorene (FLu), phenanthrene (Phe), chrysene (chy), Benzo(e)pyrene (BeP), Dibenzoanthracene (DBA) and pyrene (Py), using excitation at 295 nm and 300 nm.

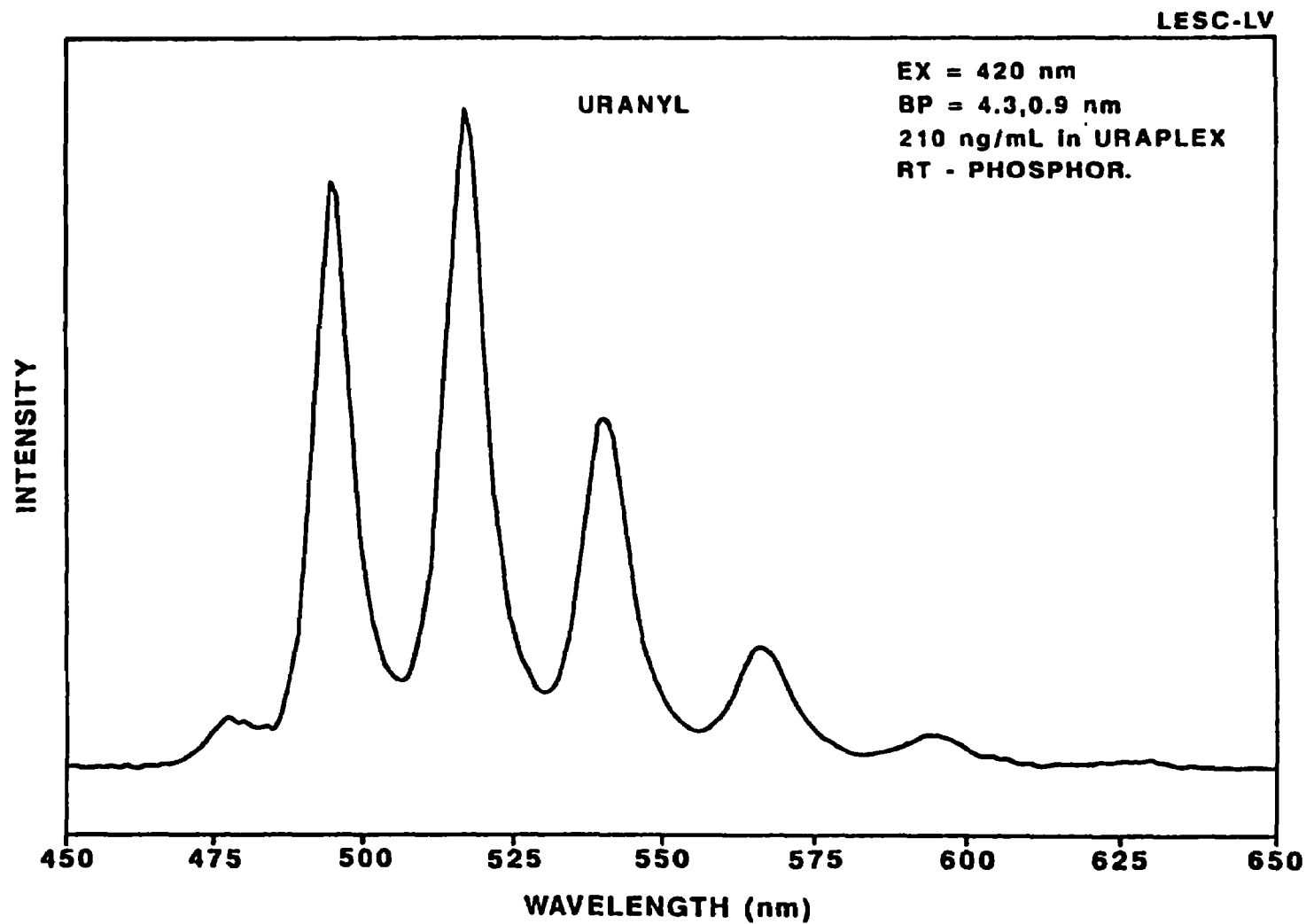


Figure A-9. Room-temperature phosphorescence of uranyl ion complexed with a proprietary complex (Urplex).

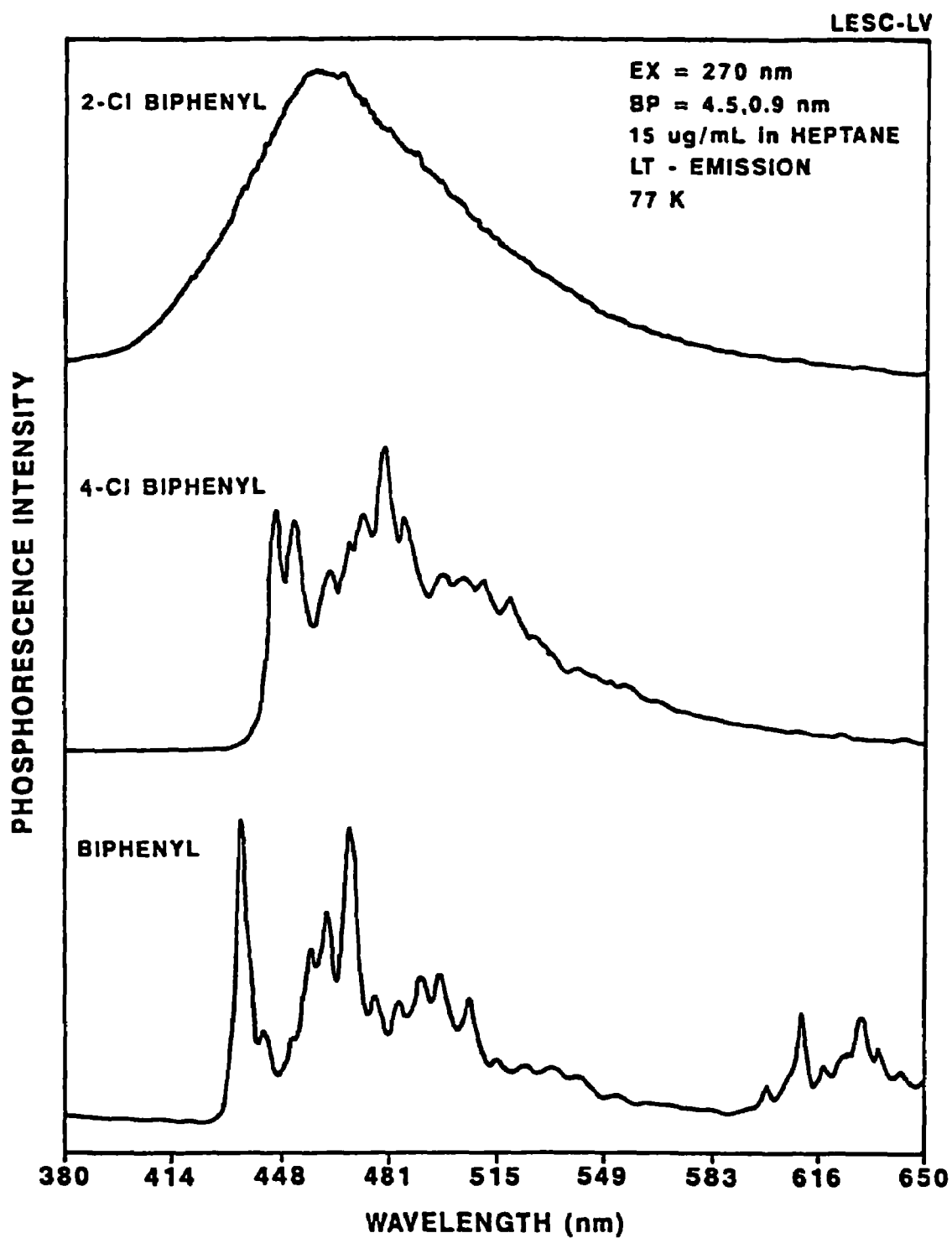


Figure A-10. Low-temperature (77 K) phosphorescence of 2-chlorobiphenyl, 4-chloro-biphenyl and biphenyl (note 2nd order LT-fluorescence of biphenyl).

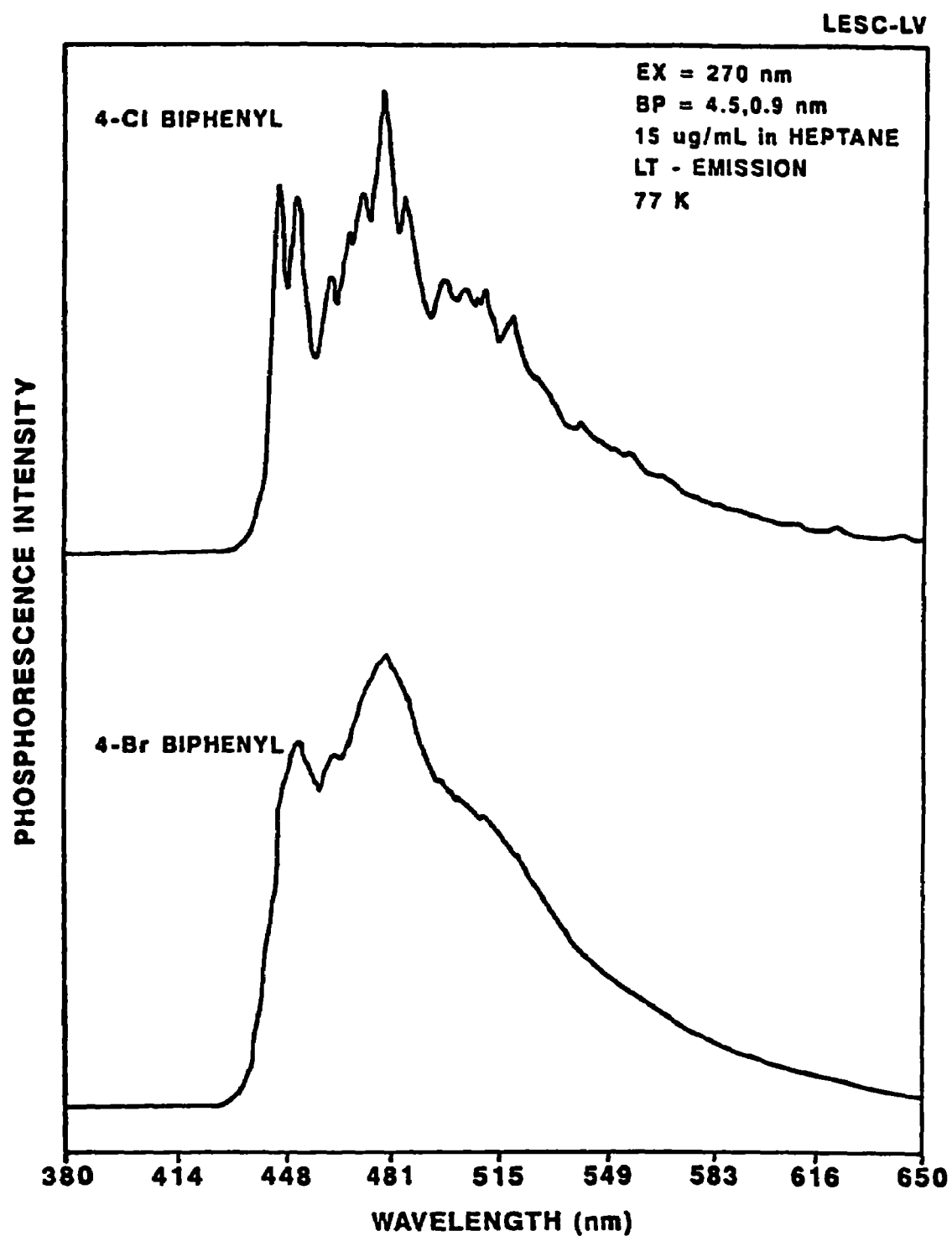


Figure A-11. Low-temperature (77 K) phosphorescence of 4-chlorobiphenyl and 4-bromobiphenyl.

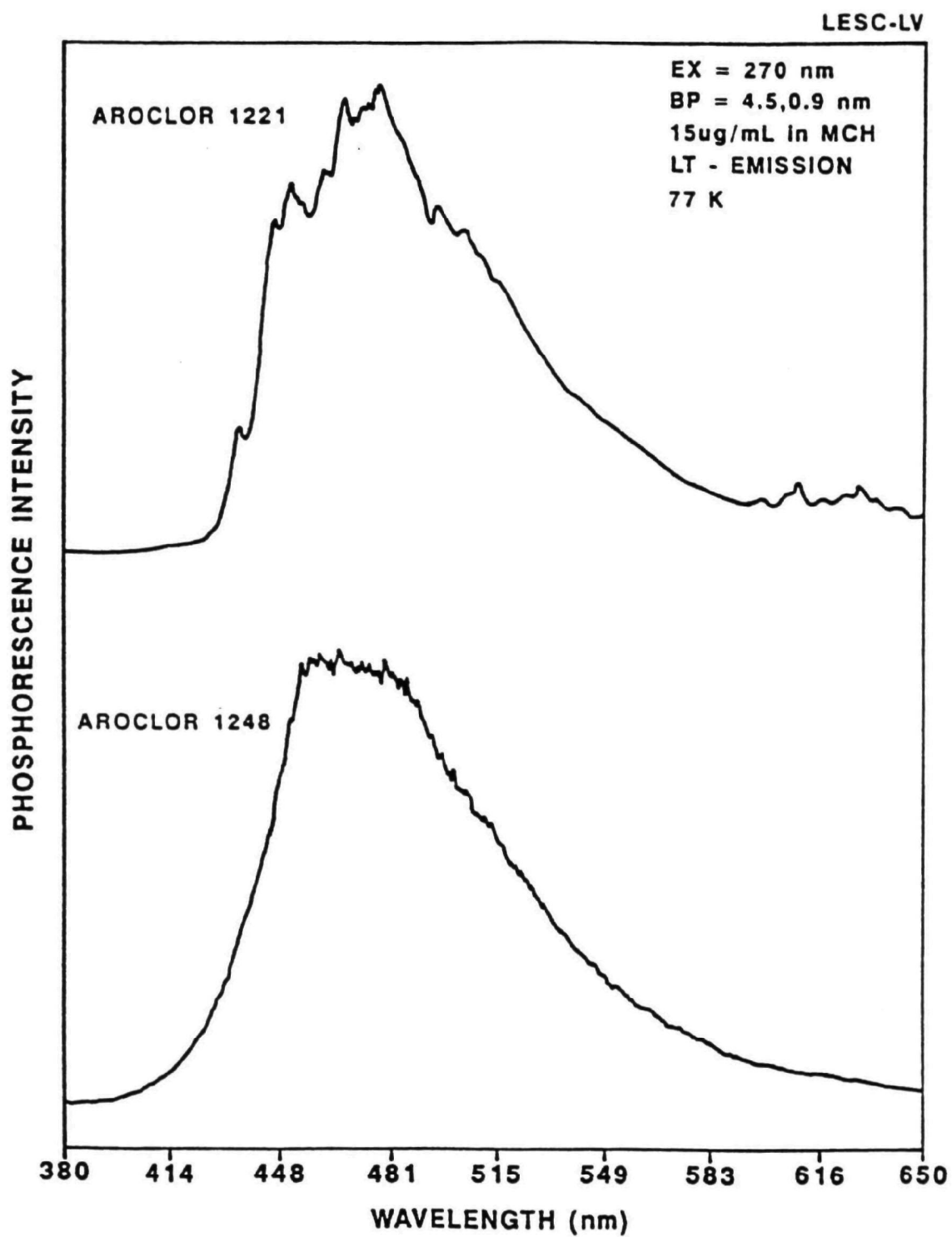


Figure A-12. Low-temperature (77 K) phosphorescence of Aroclor 1221 and Aroclor 1248.

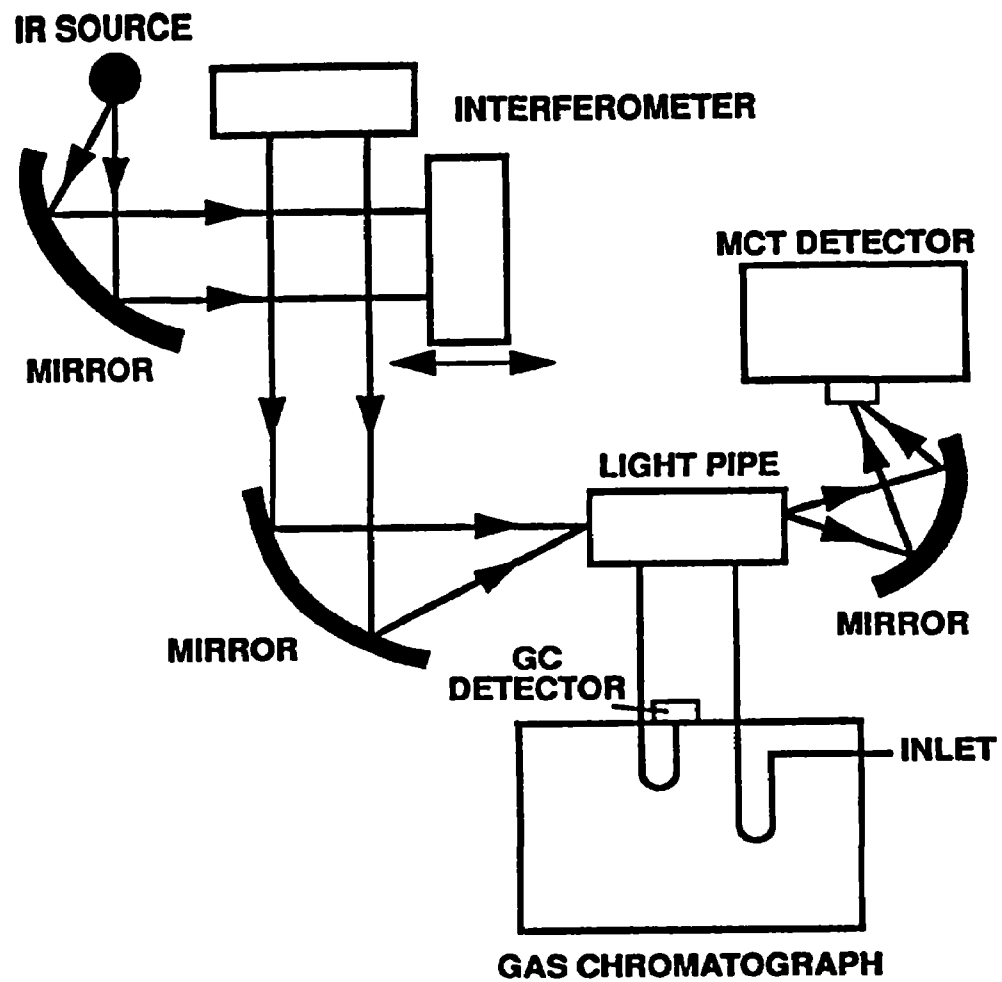


Figure A-13. Schematic of GC-FTIR instrumentation.

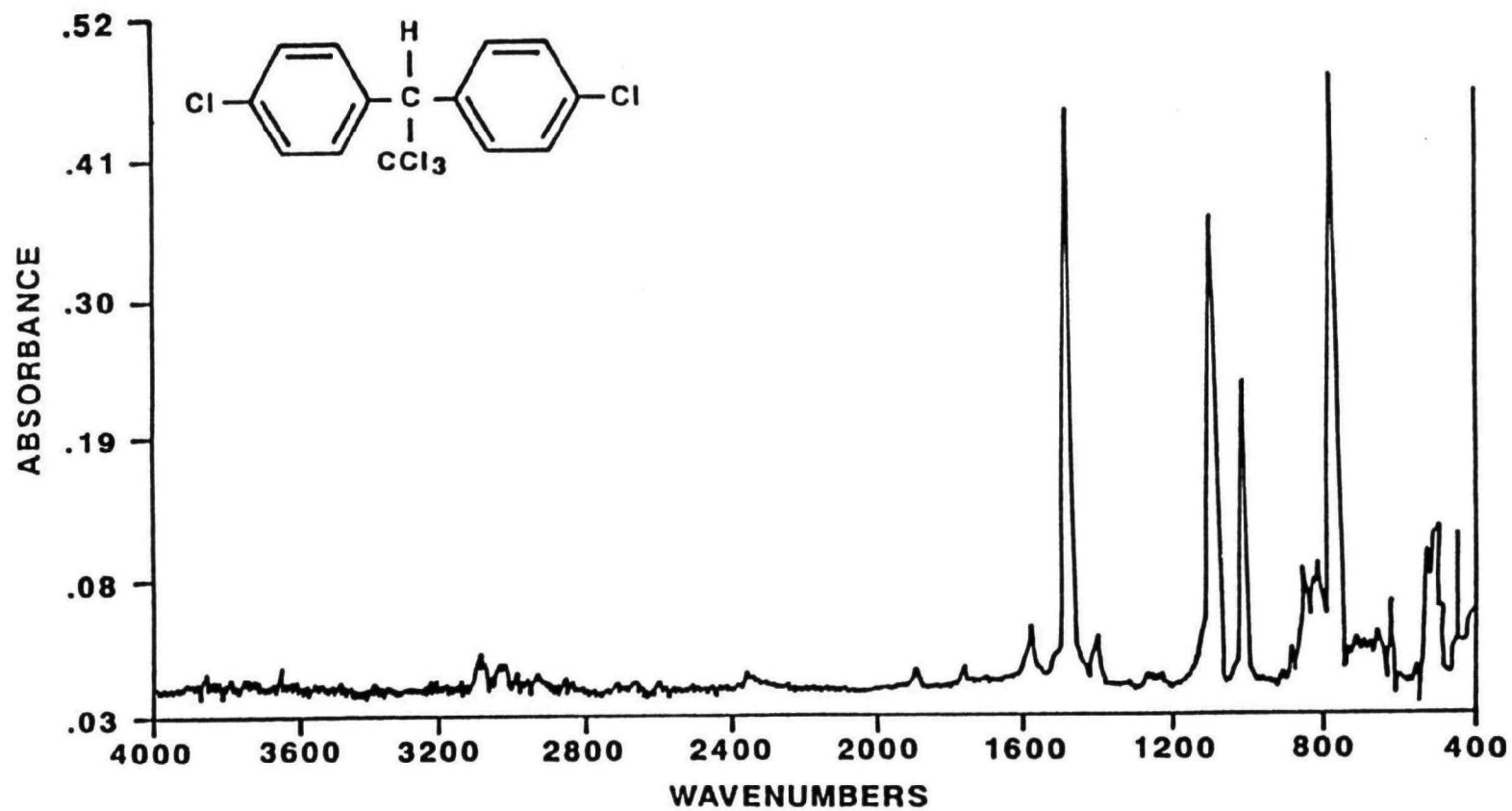


Figure A-14. FTIR vapor phase absorbance spectra of DDT (dichlorodiphenyltrichloroethane).
(D. Gurka, EPA-EMSL-LV)

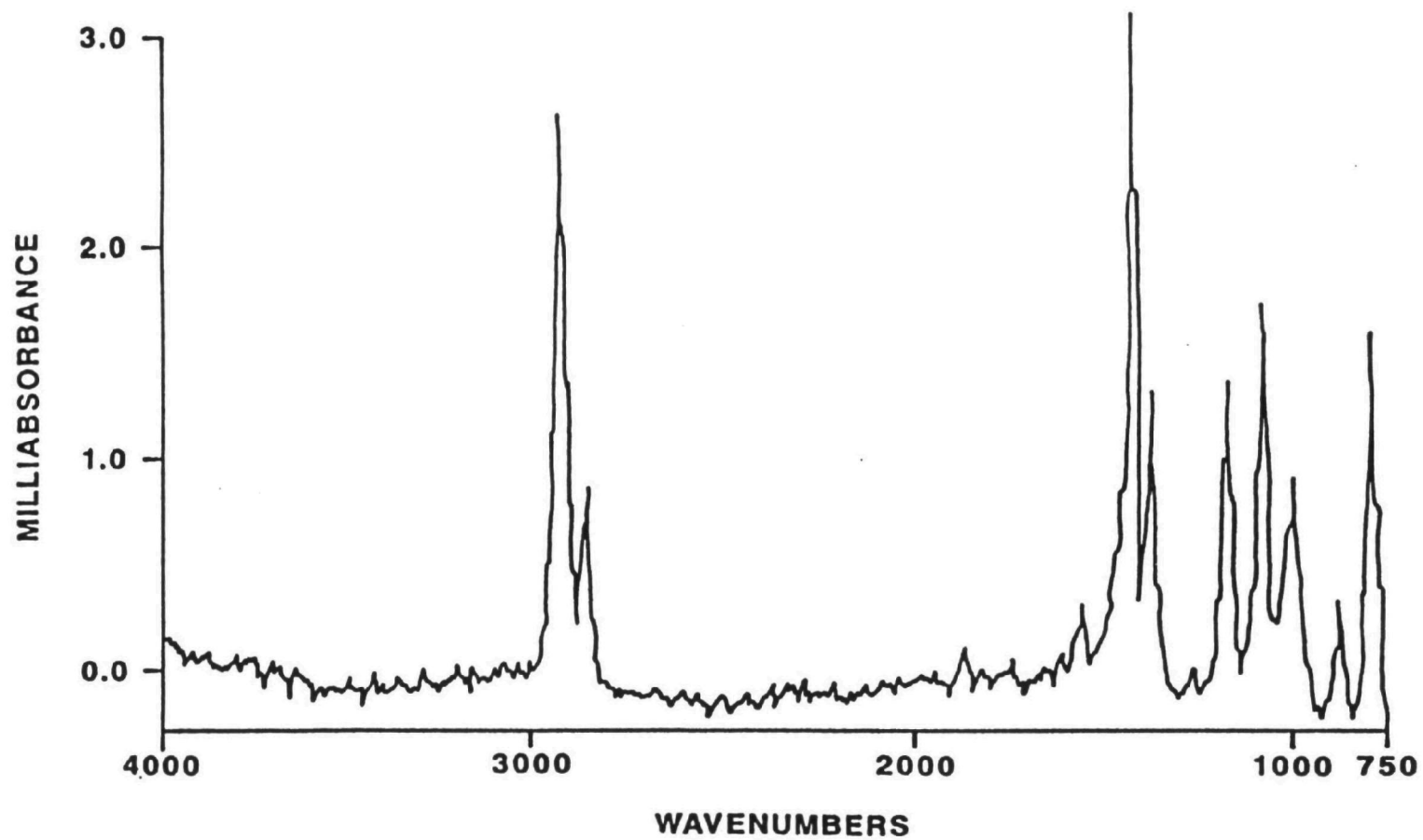


Figure A-15. GC-FTIR vapor spectra for 2,3,6-trichlorotoluene. (D. Gurka, EPA-EMSL-LV)

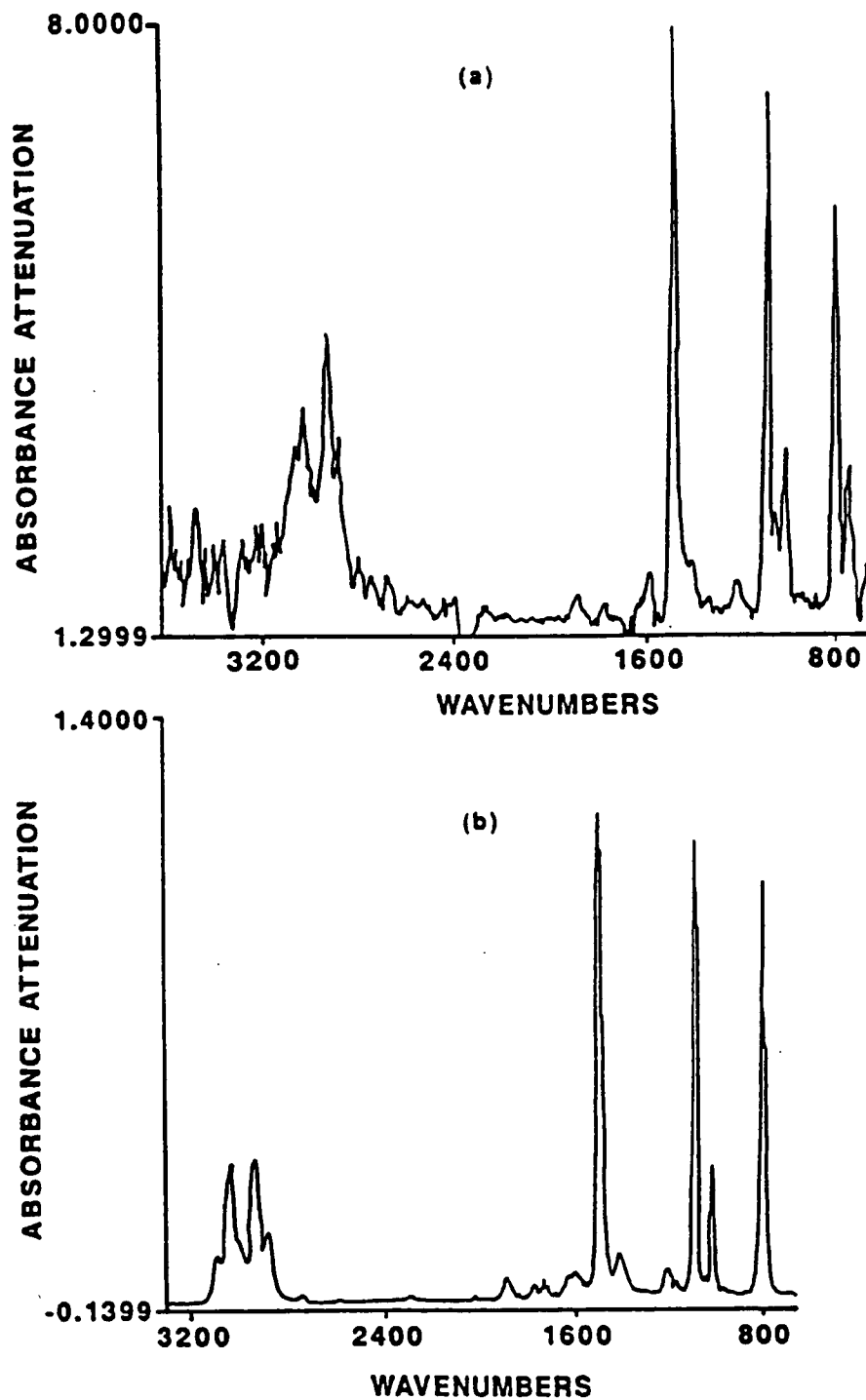


Figure A-16. GC-FTIR spectra search comparison (D. Gurka, EPA-EMSL-LV)
(a) Soil extract identified as p-chlorotoluene
(b) Authentic vapor phase IR spectrum of p-chlorotoluene.

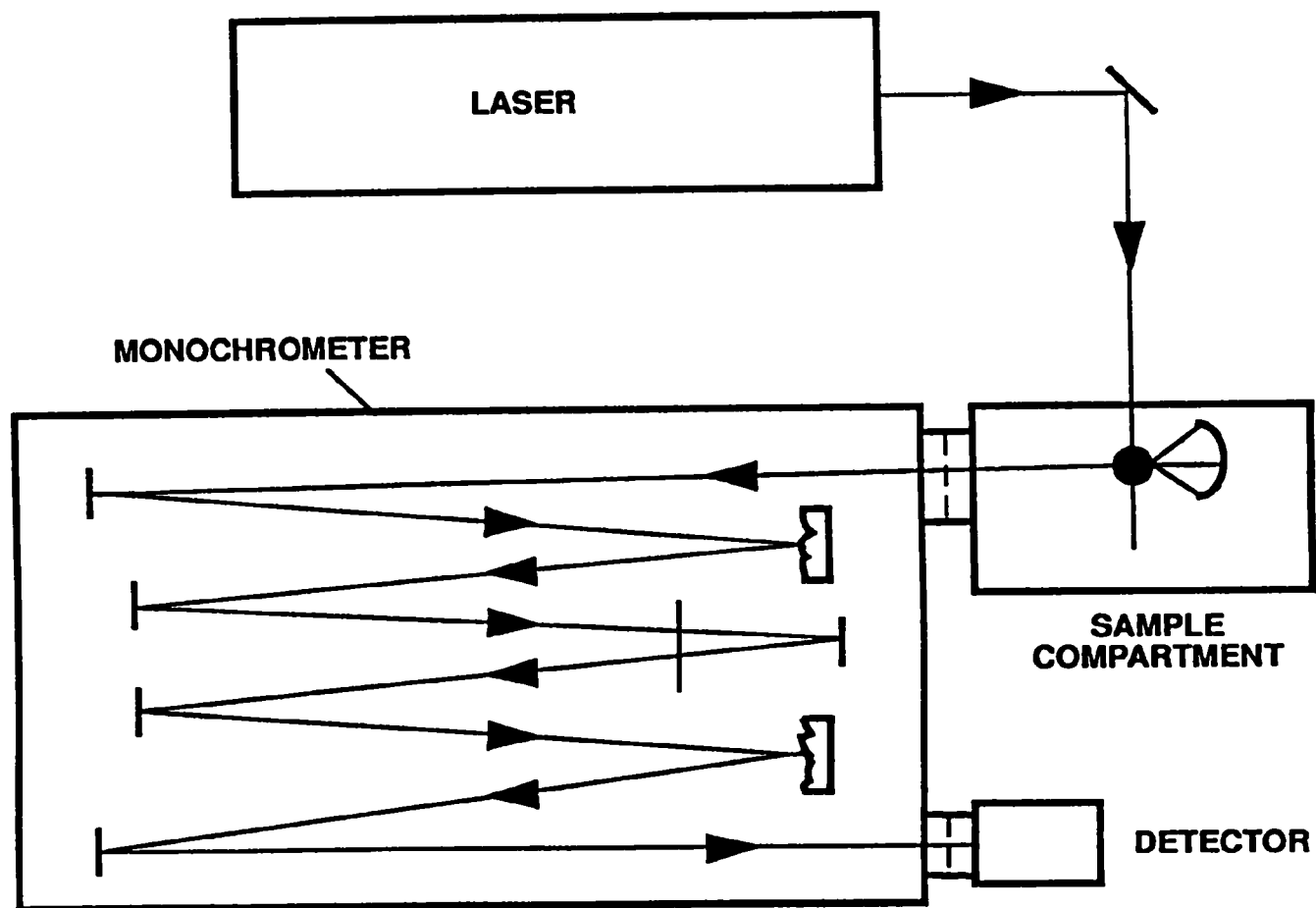


Figure A-17. Schematic of laser-Raman spectrophotometer.

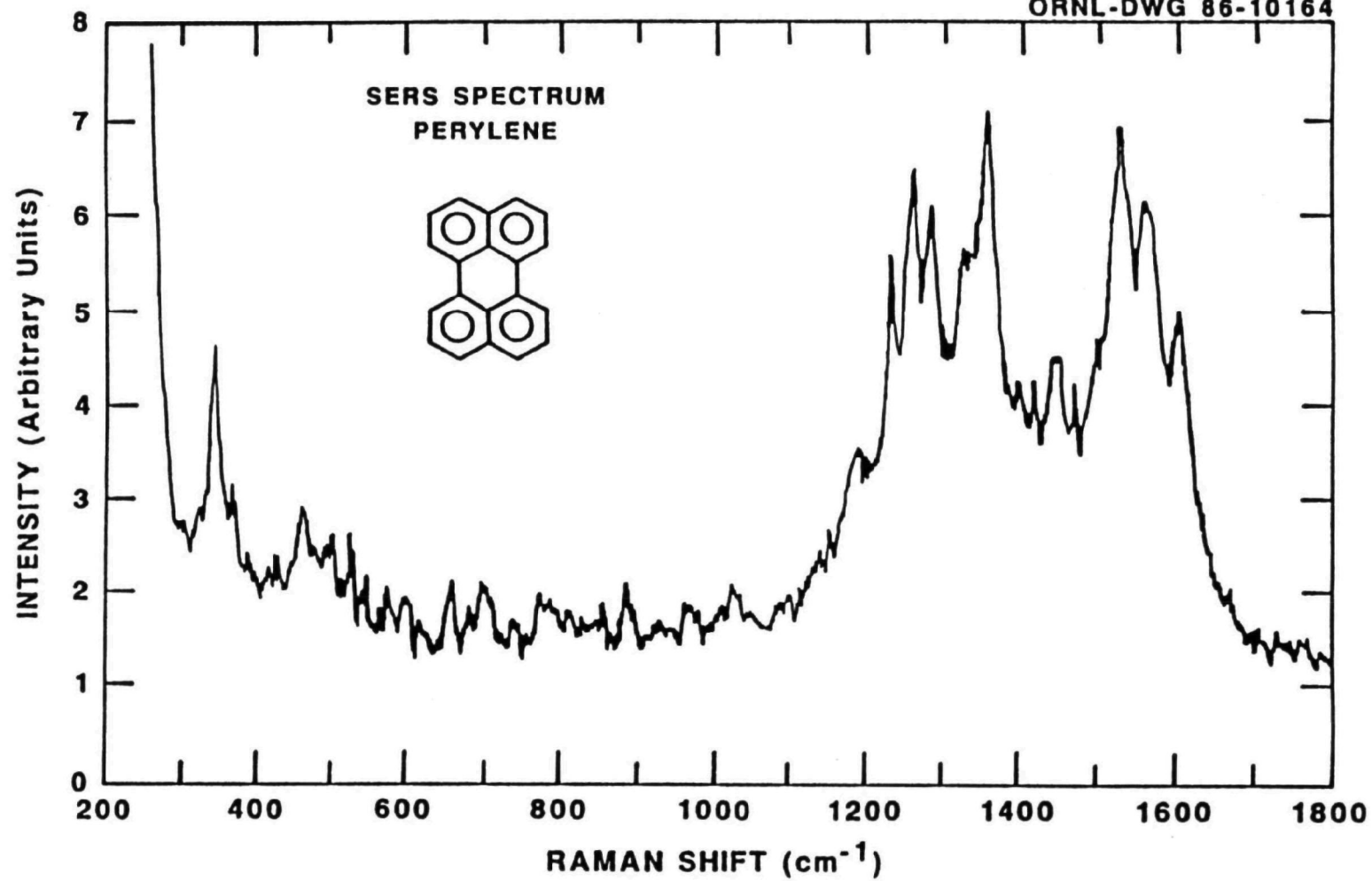


Figure A-18. Surface-enhanced Raman scattering (SERS) spectrum of perylene.

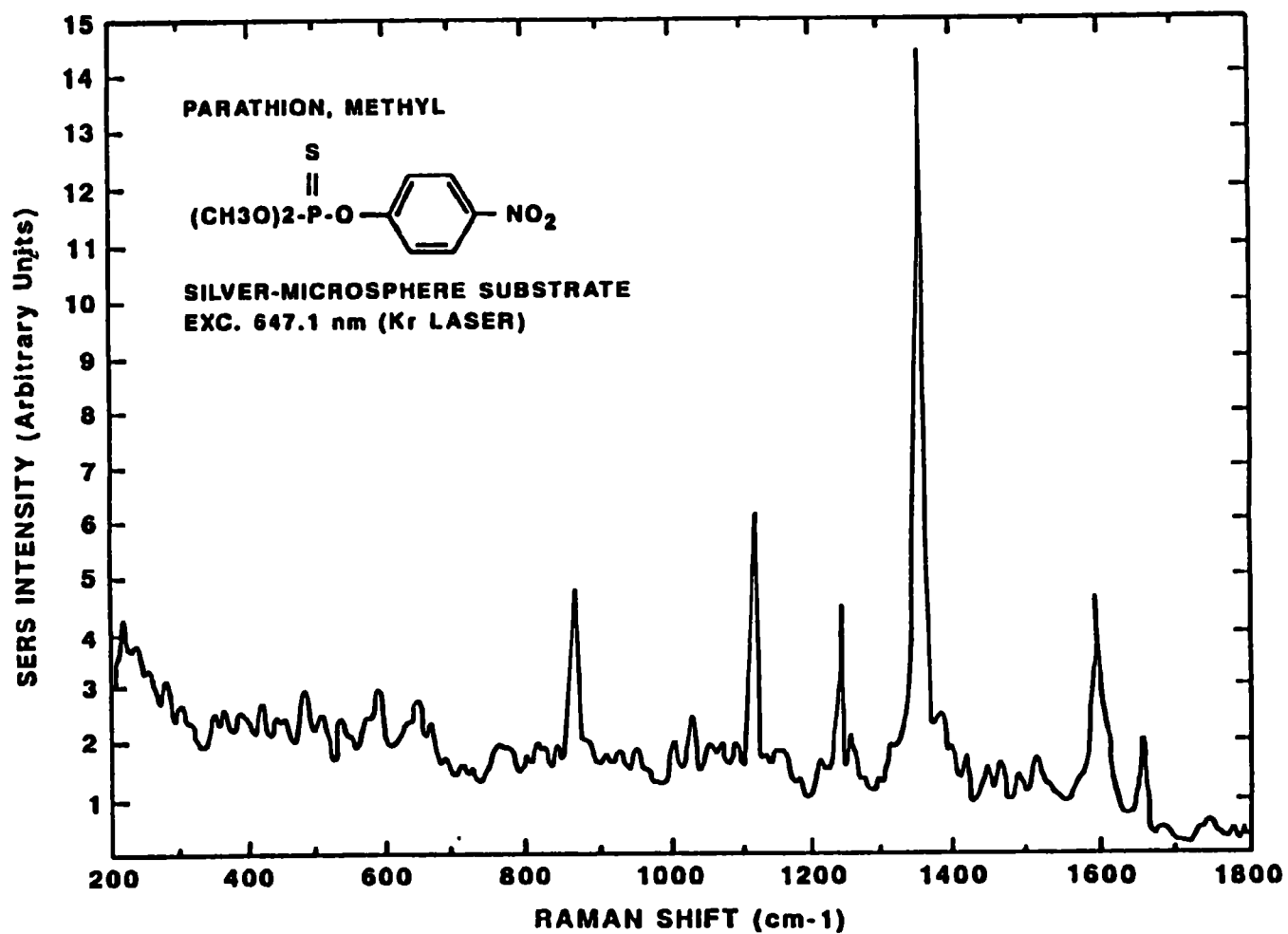


Figure A-19. Surface-enhanced Raman scattering (SERS) spectrum of methyl parathion. The 647.1 nm line of a krypton laser was used for excitation. A silver-coated microsphere substrate was used.