DEVELOPMENT OF AN OPTICAL MONITOR
FOR TOXIC ORGANIC COMPOUNDS
IN AIR

by

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DISCLAIMER

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FOREWORD

Measurement and monitoring research efforts are designed to antici-
pate environmental problems, to support regulatory actions by developing
an in-depth understanding of the nature and processes that impact health
and the ecology, to provide innovative means of monitoring compliance
with regulations, and to evaluate the effectiveness of health and
environmental protection efforts through the monitoring of long-term
trends. The Environmental Monitoring Systems Laboratory, Research Tri-
angle Park, North Carolina, has responsibility for: assessment of
environmental monitoring technology and systems for air, implementation
of agency-wide quality assurance programs for air pollution measurement
systems, and supplying technical support to other groups in the Agency
including the Office of Air and Radiation, the Office of Toxic Sub-
stances, and the Office of Solid Waste.

Analysis of organic compounds in the atmosphere is a difficult task
requiring a variety of analytical techniques to ensure that identifica-
tion and quantification are valid. The environmental analyst requires
methods that are precise, accurate and easy to implement. This study is
concerned with the development of a new instrument which utilizes the
information available in the high resolution absorption spectra of
organic compounds in the ultraviolet and visible regions. The use of
this instrument in the analysis of organic compounds may greatly improve
the ability of the analyst to produce valid results.

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ABSTRACT

The objectives of this study were: a) to design, construct, and deliver a prototype atomic line molecular spectrometer (ALMS) benzene monitor and b) to locate matches of atomic lines and sharp molecular absorption features in other toxic organic compounds for possible use with the ALMS or TALMS technique. ALMS and TALMS are newly developed high resolution molecular absorption techniques that are used in the vacuum ultraviolet and ultraviolet regions of the spectrum to detect organic molecules in the gas phase. The dual beam prototype ALMS instrument was designed constructed, tested, and delivered to the Environmental Monitoring Systems Laboratory, U. S. EPA, Research Triangle Park, North Carolina, in December, 1984. It was designed for monitoring benzene and other organics with the 184.9 and 253.7 nm mercury lines. The instrument consisted of three units: The optical unit (weight: 28 lbs, dimensions: 28x10x12"); the electronics unit (weight: 6 lbs, dimensions 19x7x5.25") and a lamp driver (weight: 24 lbs, dimensions 14.5x14x6.5"). The total weight was 58 lbs, which is less than the TALMS benzene monitor previously developed (82 lbs). Tests of the performance of the ALMS benzene monitor showed an approximate detection limit of 250 ppbv at 184.9 nm.

The process of searching for signals in organic compounds has been simplified by the development of a computer accessible data base of atomic line location and relative intensities. This data base was used to select lines for ALMS detection of o- and m-xylenes. Line matches and TALMS signals were found for three new compounds: p-difluorobenzene (Pt: 265.9 nm), m-dichlorobenzene (Ge: 269.1 nm), and p-chlorofluorobenzene (Fe: 275.6 nm). The high resolution absorption spectrum of p-difluorobenzene was determined near the 265.9 nm platinum line.

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SECTION 1

INTRODUCTION

There is a great need for instruments to monitor specific organic pollutants and classes of pollutants in ambient air and near sources such as waste disposal and industrial production sites. Direct monitors are needed for specific chlorinated hydrocarbons and various aromatic hydrocarbons such as benzene, toluene, and other substituted benzenes. Since substituted benzenes and other organic compounds absorb light in the vacuum ultraviolet and the ultraviolet spectral regions, one possible detection method is the use of optical absorption techniques in the gas phase. The use of high resolution absorption methods would increase the selectivity of the technique by exploiting rotational-vibrational fine structure in the absorption spectra of the compounds.

Tunable atomic line molecular spectroscopy (TALMS) is a high resolution, molecular absorption approach to monitoring organic vapors that is different from most present analytical techniques [1] [2]. Whereas present methods depend on some form of chromatographic separation for compound identification, the TALMS technique depends only on ultraviolet absorption properties. There is no separation procedure involved. It is highly specific because it responds only to very sharp rotational-vibrational molecular absorption features. However, TALMS has not been shown to be very sensitive due to difficulties in locating atomic probe lines near high intensity molecular absorption maxima. The lowest detection limit found for benzene is approximately 10 ppmv [3], which is too high for direct ambient air measurement.

A related technique, atomic line molecular spectroscopy (ALMS), resulted from extending the ideas behind the TALMS technique in an attempt to improve the detection limits. Differential absorption at two wavelengths is the basis of both methods. In the TALMS case the wavelength difference is determined by the very small Zeeman splitting of the atomic line chosen for measurement. The small splitting insures that the background correction will eliminate most interferences. In the ALMS case, the wavelength positions are determined by choosing two different atomic lines that are necessarily separated by a much greater distance than in the TALMS technique. The inherent detection limit in both techniques depend upon the differences in intensities in the molecular absorption spectra at the two wavelength positions. Because the wavelength separation is much greater with ALMS, the absorption difference can be much larger yielding a great improvement in detection limits. For example a TALMS detection limit of 10 ppmv has been found for benzene at 253.6 nm [3]. Judging from the much higher extinction coefficients in the vacuum ultraviolet region for benzene, detection limits

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should be at least one thousand times better with the ALMS technique. This would result in detection at 10 ppbv levels, a useful limit for ambient air monitoring.

The major disadvantage of the ALMS technique is the possibility of interferences from compounds other than those sought. The use of multiple analysis lines will reduce this problem. However, the essential assumption for background correction with additional analysis lines is that absorption by interfering compounds is constant over the wavelength interval used. If several different lines are used to monitor the same molecule, the presence of an interferent can be detected because different apparent concentration values will be obtained at different wavelengths. Although this may not provide a background correction, it will alert the analyst to the presence of a problem. With the ALMS technique the use of multiple analysis lines at properly chosen wavelengths in the vacuum ultraviolet and in the ultraviolet regions may also allow the determination of classes of compounds.

Previous studies of TALMS [4] [5] have resulted in construction and evaluation of prototype instruments for general laboratory use and for monitoring benzene. The goals of the present study are to: a) design, construct, and deliver to the Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, an ALMS monitor and b) to determine the spectral location of absorption features and matching atomic lines in toxic compounds other than benzene. An ALMS instrument would be useful in laboratory detection and field monitoring for benzene and other toxic compounds. Determination of spectral locations of molecular absorption maxima is necessary to optimize instrument performance and to extend the technique to other organic compounds.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Design and construction of a prototype ALMS instrument for the detection of benzene and other compounds was completed on schedule and delivered to the Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina, in December 1984. It consisted of three parts: an optical module, an electronics module, and a lamp driver. The optical module weighs 28 lbs, the electronics module 6 lbs, and the lamp driver 24 lbs. An instruction manual and schematic diagrams of the electronics were also supplied. The instrument was constructed to operate in the vacuum ultraviolet and ultraviolet spectral regions and was equipped with a mercury lamp. Benzene and other organic compounds can be detected with the mercury 184.9 and 253.7 nm lines. Tests with benzene at 184.9 nm gave approximate detection limits of 250 ppbv. This is an improvement by a factor of forty over the best TALMS detection limits. Other atomic lamps can be used to obtain different analysis wavelengths as required.

Searches for TALMS signals in other organic compounds were continued. This tedious process was greatly improved by development of a computer search technique using National Bureau of Standards atomic line information. After considerable experimentation with a variety of lamps and medium resolution absorption spectra, TALMS signals were found for p-difluorobenzene (Pt: 265.9 nm) m-dichlorobenzene (Ge: 269.1 nm) and p-chlorofluorobenzene (Fe: 275.6 nm). TALMS signals have now been found for benzene, bromobenzene, chlorobenzene, toluene, p-xylene, aniline, phenol, pyridine, formaldehyde, m-dichlorobenzene, p-chlorofluorobenzene, and p-difluorobenzene. Wavelengths for the ALMS detection of ortho and meta xylenes also were selected. The high resolution absorption spectrum of p-difluorobenzene was determined near the platinum 265.9 nm line.

It was recommended that several modifications be made to improve ALMS instrument performance. An arrangement could be devised to alternately send two different lines from the same light source through the instrument. Electronic subtraction of the signals from these two lines will greatly reduce light source noise and electronic noise with a corresponding increase in sensitivity. For simultaneous detection of several compounds a device that automatically positions different wavelength regions on the exit slit of the monochromator should be constructed. If it is necessary to make measurements in the vacuum ultraviolet region or use weak emission lines, an arrangement for purging the instrument and optical path will be important in order to increase transmission. Addition of commercially available intense lamps of other

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elements is also important. The goal of these modifications is to improve sensitivity, reliability and portability

Since major decreases in detection limits and extension of this technique to other compounds are dependent on the location of proper analysis lines, it is recommended that more studies be carried out to locate such lines for compounds of interest.

SECTION 3

ALMS INSTRUMENT CONSTRUCTION AND TESTING

BENZENE DETECTION BY ALMS

The gain in sensitivity that can be realized by using the ALMS technique can be seen by comparing the extinction coefficients of compounds to be monitored with the extinction coefficients now being used for the TALMS technique. For benzene, at the mercury 253.7 nm line, the extinction coefficient is approximately 100. Figure 1 shows the absorption spectrum of a number of benzene derivatives [6] with the position of several emission lines of iodine and arsenic superimposed. The peak of the benzene absorption in the vacuum ultraviolet region corresponds to an extinction coefficient of 126,000 [7]. This leads to the expectation that a gain in sensitivity of 1000 is possible. Figure 1 indicates that with the proper choice of atomic lines in the vacuum ultraviolet region, comparable gains can be achieved in the detection of other benzene derivatives.

A block diagram of a double beam ALMS instrument is given in Figure 2. Light from an atomic lamp, e. g. mercury, passes through a purgable monochromator to a beam splitter. Part of the light passes through the sample cell to the photomultiplier tube (PMT 1). The remaining light is reflected to another photomultiplier tube (PMT 2) which is used to compensate for lamp fluctuations. The signals from the photomultipliers are processed through amplifiers and filters, and an absorbance signal is produced on a strip chart recorder.

Before design and construction of the ALMS prototype instrument began, tests for benzene detection were carried out on a laboratory instrument. The instrument was like the one shown in Figure 2 with a GCA McPherson Model 218 monochromator. The light path in the monochromator was one meter and was purged with flowing argon during the experiments to prevent absorption by oxygen in the vacuum ultraviolet region. The light path outside the the monochromator was also purged. The 13 cm cell had a volume of 124 mL. With high purity quartz lenses and windows it was possible to extend the usable spectral region to 165 nm by gas purging. In these experiments the wavelengths were selected manually.

Specially constructed iodine lamps were used. The iodine lines may be obtained at high intensity by the use of an electrodeless discharge lamp. The iodine lamp used in this experiment was excited using a one quarter wave stub cavity powered by a 200 watt microwave diathermy unit produced by The Burdick Corp., Milton, WI (Model MW/200). The tip of the lamp extended beyond the cavity and was immersed in a beaker of water to lessen the effect of temperature changes on the vapor pressure
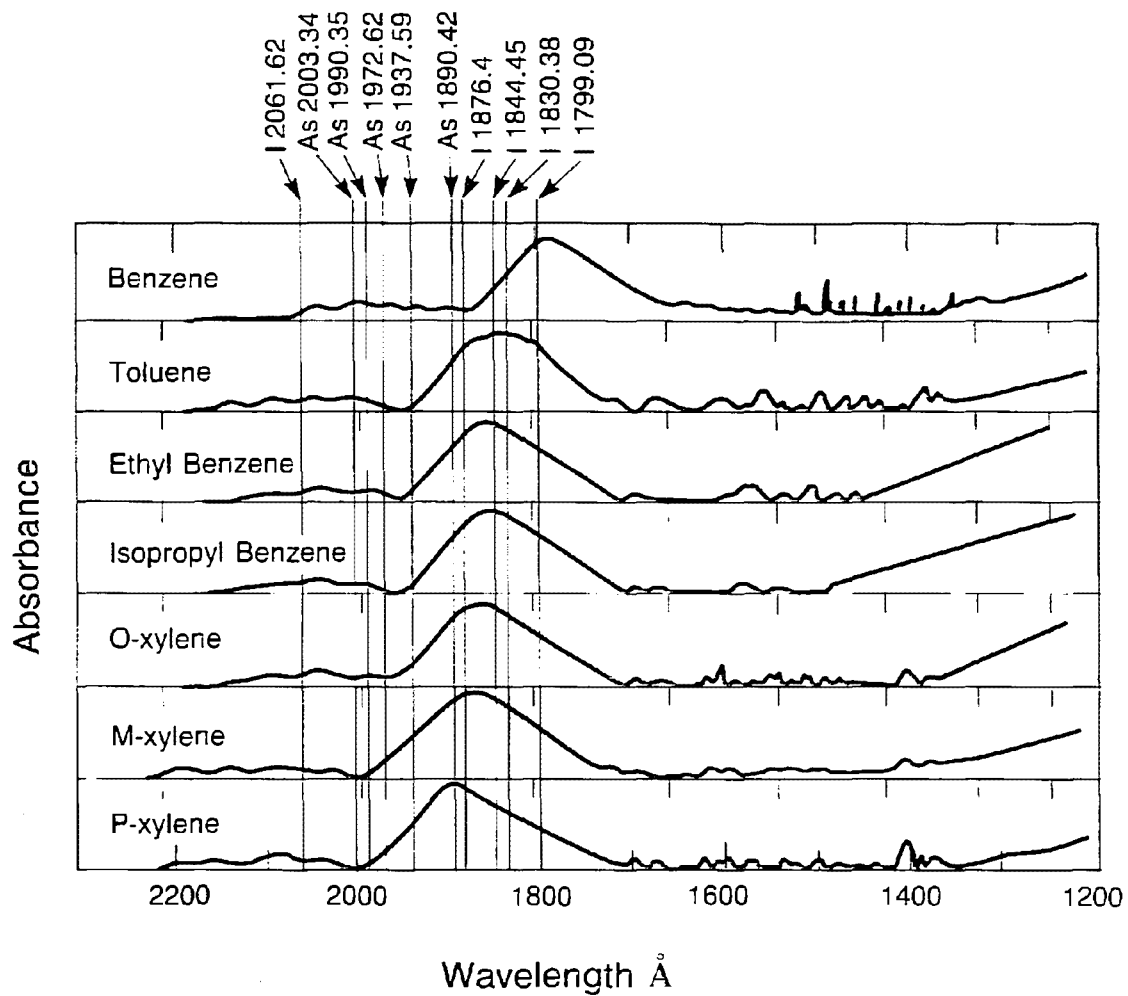
Figure 1. Vacuum ultraviolet absorption spectra of benzene derivatives and superimposed atomic lines [7].

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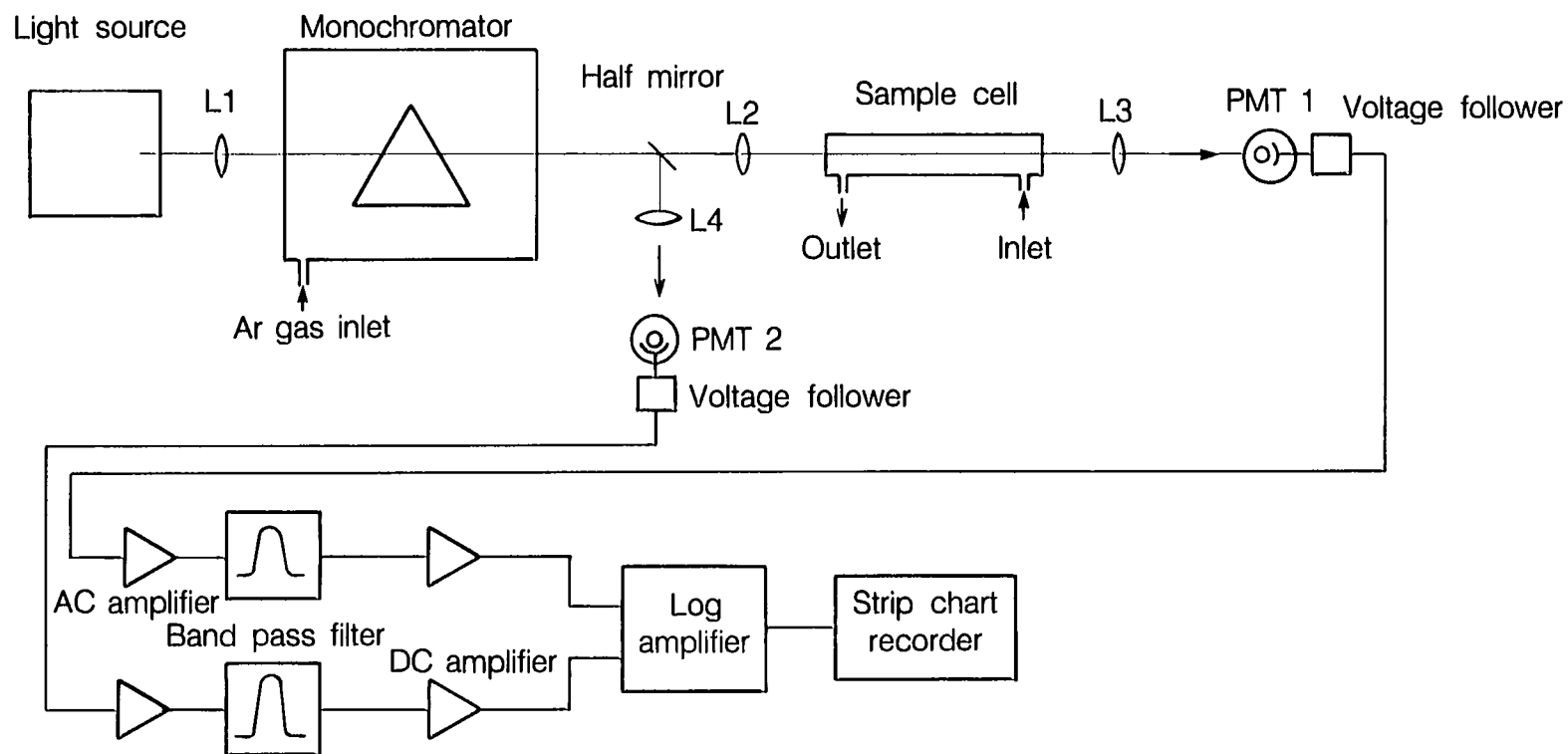
Figure 2. Diagram of ALMS prototype instrument. L designates lens and
PMT photomultiplier tube.

of iodine in the lamp. The tube was operated continuously for a week at 80 % power and produced intense, neutral lines at a low noise level. Because this was a continuous, rather than a pulsed, light source; the ac amplifier and filtering electronics were bypassed in the signal processing circuit.

Molar extinction coefficients for benzene were determined at five iodine wavelengths: 179.91, 183.04, 184.44, 187.64, and 206.16 nm by injecting known amounts of benzene vapor in air into the sample cell. The results are shown in Figure 3. The largest extinction coefficient was approximately 72,000 at 179.91 nm. This is considerably larger than the extinction coefficient at the mercury 253.6 nm line of about 100. The approximate detection limit of benzene at 179.9 nm was found to be 100 ng in a 124 mL cell. This corresponds to a detection limit of 250 ppbv.

PROTOTYPE CONSTRUCTION

A portable TALMS monitor that had been in use at the EPA Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina, was returned to the Lawrence Berkeley Laboratory and converted to an ALMS instrument. This involved removal of the magnet and squeezer assemblies and modification of the electronics. A new mercury light source was installed, and the output was checked to verify that a steady baseline was produced. With new cell windows and lenses the instrument can be operated in the vacuum ultraviolet and ultraviolet regions. Photographs of the optical and electronic units are shown in Figures 4 and 5 respectively.

The prototype ALMS that resulted had a total weight of 58 lbs compared to a weight of 82 lbs for the benzene TALMS monitor developed previously. The optical unit weighed 28 lbs and had dimensions:28" x 10" x 12". The electronics unit weighed 6 lbs and had dimensions of 19" x 7" x 5.25". The lamp driver weighed 24 lbs and had dimensions of 14.5" x 14" x 6.5". Brief descriptions of the design and construction of the instrument are given below. The operating instructions and circuit diagrams for the prototype unit are given in Appendices A and B.

Optical Unit

A photograph of the 28 inch long optical unit is shown in Figure 4. The basic arrangement of the optical unit is shown in Figure 2. A mercury Penray lamp was used with a JY H-10 monochromator for line isolation. A 15 cm sample cell equipped with high quality quartz windows was mounted on the optical bench. Photomultipliers were model R128 from Hamamatsu Photonics.

Electronic Components

A photograph of the electronics module is shown in Figure 5. The lamp power supply will differ depending upon the lamp used but might typically provide a discharge that is pulsed at 10 kHz. The photomultiplier tube voltage output is buffered with a voltage follower and amplified. A band pass filter is used to reject noise of frequencies
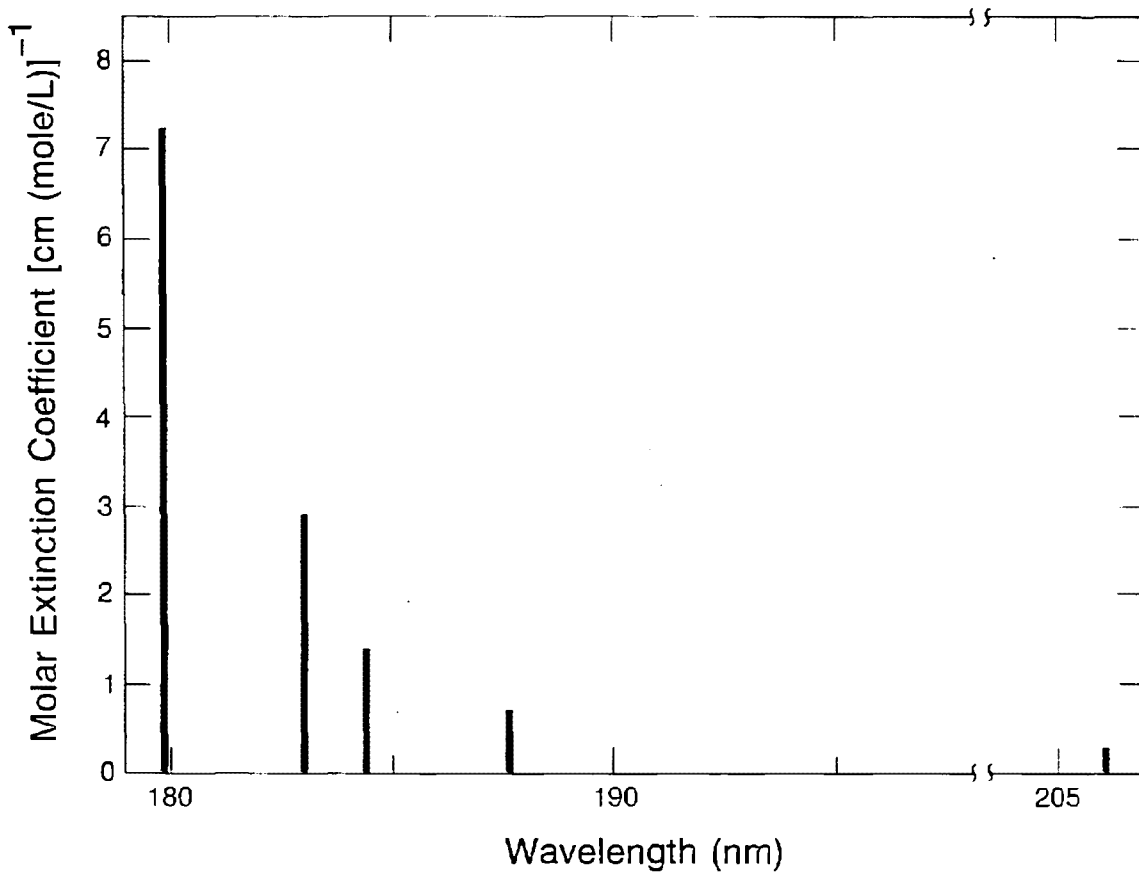
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Figure 3. Extinction coefficients of benzene at various iodine lines.
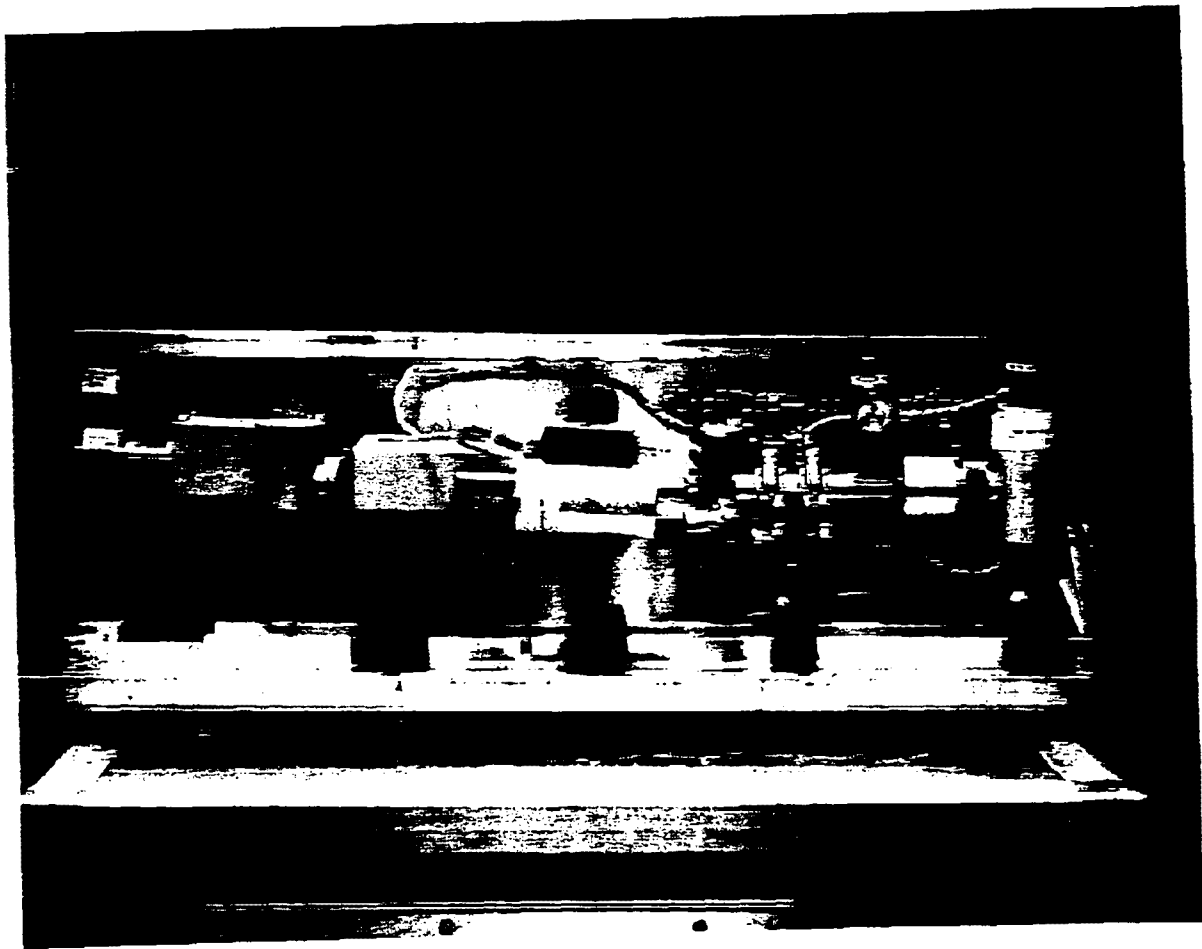
Figure 4. Photograph of prototype ALMS optical unit.

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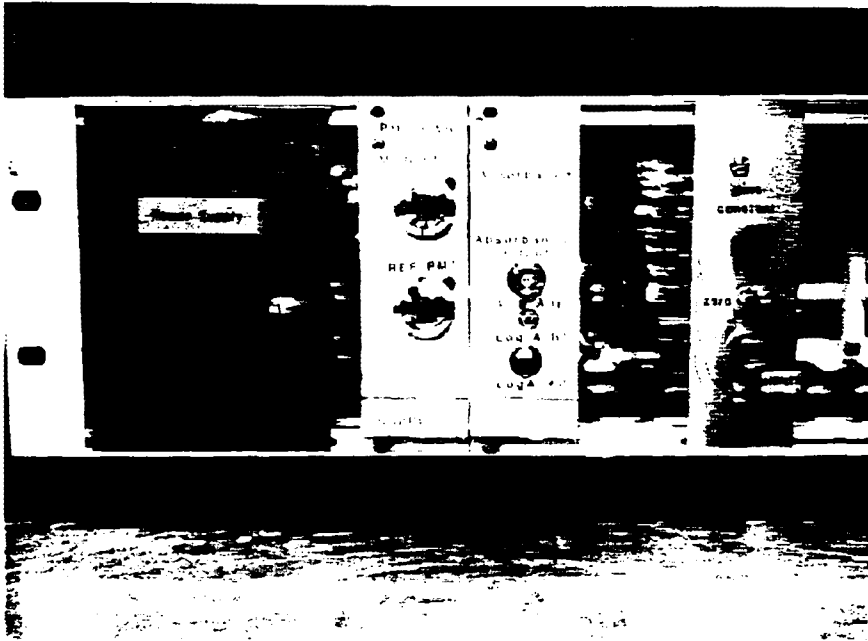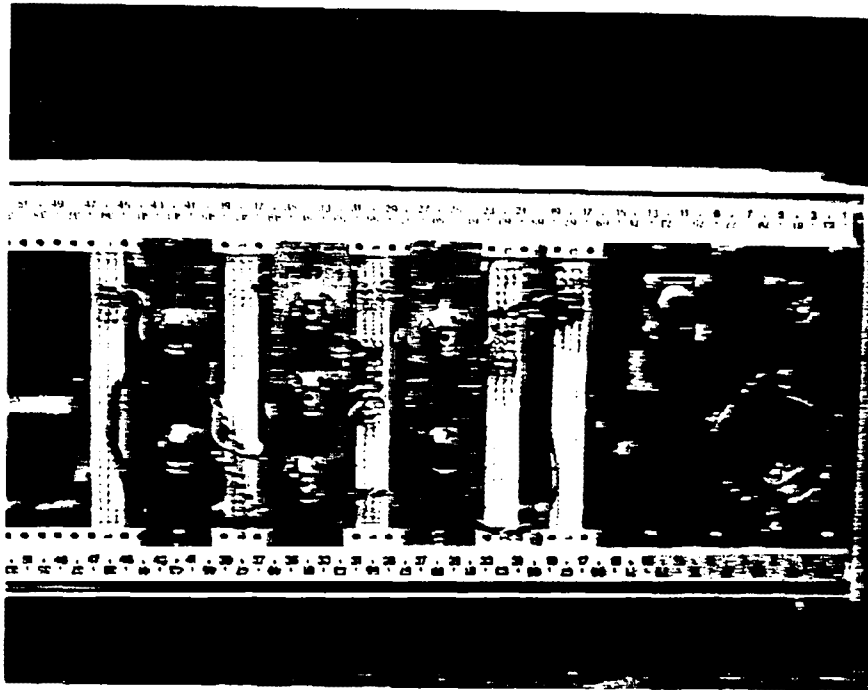
Figure 5.   Photograph of front (top) and back of ALMS electronic module.

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differing from that of the lamp power supply. The filter provides one dB attenuation at 4 kHz and at 20 kHz. The filtered ac signal is then converted to dc, amplified, and fed into a log amplifier (Analog Devices, 755P), whose output is a measure of absorbance. This output (absorbance) is continuously displayed on a strip chart recorder. Schematic diagrams are given in Appendix B.

The prototype instrument was tested for the detection limit of benzene at 184.9 nm before delivery. An approximate detection limit of 250 ppbv was found.

SECTION 4

TALMS AND ALMS DETECTION OF SUBSTITUTED BENZENES

The effectiveness of TALMS or ALMS detection is largely dependent on the atomic lines chosen for monitoring. The goal is to maximize the difference in molecular absorption at two lines while, at the same time, minimizing the wavelength separation between them. If the wavelength separation is small, background correction will be more accurate. Literature searches indicate that many organic molecules possess sharp absorption features. However, data in the literature are incomplete for most compounds, nonexistent for others, and sometimes inaccurate. Atomic line compilations show that lines can be found in any wavelength region, although these lines are often very weak. Finding matches is a tedious process because in many literature citations molecular absorption is not accurately measured, and because quiet, intense light sources that operate in a magnetic field are not easy to produce. However, advances in the application of the ALMS and TALMS techniques to multicomponent determinations at low concentrations depend on the location of additional regions of potential TALMS and ALMS signals. Therefore, searches for TALMS signals in xylenes, m-dichlorobenzene, p-chlorofluorobenzene, and p-difluorobenzene were carried out. A double beam TALMS instrument with a 15 cm cell was used.

ATOMIC LINE DATA BASE

One year ago a magnetic tape was received from the National Bureau of Standards (NBS) containing information on atomic emission lines listed in the CRC Handbook of Chemistry and Physics. This information consists of wavelengths and intensities corresponding to a specified element in a certain ionization state. Sometimes a code referring to some descriptive feature of the emission line also is included. This element, wavelength, intensity information is very useful in attempts to find line matches for both ALMS and TALMS techniques. If these tables could be entered into a computer data base, rapid searches could be made for emission lines within designated wavelength intervals. Unwanted elements and low intensity lines could be screened out in the process. There is also the possibility of obtaining useful information about the statistical distribution of emission lines over particular wavelength regions that would be helpful in deciding what light sources to build.

The NBS data were stored in one hundred files on eight 5.25 inch floppy discs. In general there was only one element per file. Irrelevant material was eliminated, and the remainder of the data were processed on an HP 9826 computer with a storage capacity of 4.886 Mbytes using an HP 9135A Winchester hard disc drive. Only wavelengths in the

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region from 180 to 500 nm were retained.

Sorting the complete data base in numerical order by wavelength was accomplished with internal sorting routines written in the extended HP BASIC language (MAT SORT and MAT REORDER). The radioactive elements were omitted from the data base since lamp production with these elements would be difficult.

After the NBS atomic line information had been transferred and arranged, a search was made for nonrandom wavelength distributions of atomic lines. To conduct this search, a program was written to count the number of lines over a specified wavelength interval with a greater than specified intensity. After a trial and error process, it was found that between wavelengths of 180 and 500 nm an interval of 0.5 nm and a minimum intensity of 500 would most clearly reveal any tendency for atomic lines to cluster in particular regions. However, such clustering of lines was not found. The number of lines available for matching did seem to decrease between 410 and 500 nm and between 205 and 180 nm.

ALMS DETECTION OF XYLENES

TALMS detection of p-xylene at the cobalt 252.9 nm line was successful in previous studies [5]. However, attempts to detect o-xylene and m-xylene were not. Hence, methods of using the ALMS technique to detect these latter components were considered. Our approach to this problem is to use two wavelengths that are close together (separated by 0.2 or 0.3 nm) and assume that differences in absorption caused by substances other than the analyte are negligible over this wavelength range. The ideal situation would be to have two close wavelengths from a single element whose spectrum is easy to excite.

Spectral data obtained from our medium resolution spectrograph indicate that o-xylene has a number of intense absorption features between 267.9 and 269.5 nm, but there are few usable atomic lines in this region. However, germanium (265.16 and 265.12 nm), lead (261.42 and 261.37 nm), or manganese (257.61 and 257.55 nm) lamps could be used for this compound.

Absorption spectra of o-xylene reported by Humby et al. [8] also indicate that platinum (270.24 and 270.59 nm) or iron (271.90 and 272.09 nm) lamps might be used.

The m-xylene absorption features are much broader than those of o- and p-xylene. In fact, it may be impossible to monitor this molecule with the TALMS technique. The best possibility for ALMS detection is to use a platinum lamp which has lines at 270.59 and 270.24 nm.

TALMS DETECTION OF m-DICHLOROBENZENE

Meenakshi and Ghosh have recently published a paper on the high resolution spectrum of m-dichlorobenzene [9]. The wavelengths of absorption features are reported, and absorption intensities are divided into seven categories that range from "very very strong" to "very weak". Data from this publication were converted to wavelengths in air, and wavelengths of features with intensities that were "moderately strong"

or greater were compared with those of atomic emission lines. This was done using the computer program that contained atomic line information from the NBS magnetic tapes. The results indicated that molecular absorption-atomic line matches might occur at the platinum (273.396, 262.803 nm); iron (275.014, 273.358, 271.902 nm); iridium (266.479 nm); or germanium (265.117 nm) lines. Less probable matches were indicated for the ruthenium (273.572 nm); zirconium (271.026 nm); or rhenium (271.547 nm) lines.

Meenakshi and Ghosh determined the intensities of the absorption features from photographic plates using absorption cells that varied in path length from 0.5 to 3 meters. This information was of little value in predicting the change in intensity that would be obtained when this compound was placed in the cell of the TALMS instrument. In fact, when the iron and platinum lamps were used, it was found that only a very small change in intensity resulted from absorption features that were reported as "moderately strong". For this reason the effort was devoted to lines listed as "very very strong", "very strong", and "strong".

Platinum, iron, lead, and iridium light sources were constructed, but no TALMS signals for m-dichlorobenzene were found with them. A germanium lamp was assembled, and a definite signal was obtained at 269.134 nm with a 15 kG (1.5 T) magnetic field in the perpendicular Zeeman direction. Under the same operating conditions no TALMS signals were observed for benzene, p-xylene, toluene, or bromobenzene. Figure 6 displays the TALMS signal obtained with a 15 cm cell.

TALMS DETECTION OF p-CHLOROFLUOROBENZENE

The high resolution spectrum of p-chlorofluorobenzene has been reported by Cvitas and Hollas [10]. The wavelengths of sharp absorption features from this work were compared with those of atomic emission lines. The comparison indicated a TALMS signal might be obtained with the iron 275.573 nm line and this was confirmed experimentally. Converting this wavelength to wavenumbers in vacuum yields the value 36,277.36 cm^{-1}. A representation of the high resolution absorption spectrum of p-chlorofluorobenzene is presented in Figure 7 with the iron line superimposed.

The TALMS signal was obtained using a McPherson 0.3 m spectrograph with a 150 μm slit to isolate the iron line. The TALMS instrument was used in the dual channel mode with automatic gain control. The TALMS signal is displayed in Figure 8. It was obtained in the perpendicular Zeeman direction with a field strength of 15 kG (1.5 T); the intensity of the signal increased with increasing magnetic field up to 17 kG (1.7 T). The experimental arrangement was tested by inserting an ultraviolet neutral density filter (~50 % transmission) into the optical path. No TALMS signal occurred. Five mL of pyridine vapor at room temperature were injected into the cell. Again no TALMS signal occurred although this vapor resulted in 50 % absorption.

Vapor pressure data for chlorobenzene were used to estimate that of p-chlorofluorobenzene [11]. This will only be approximate, but vapor pressure data are not available for the chlorofluorobenzenes. The vapor

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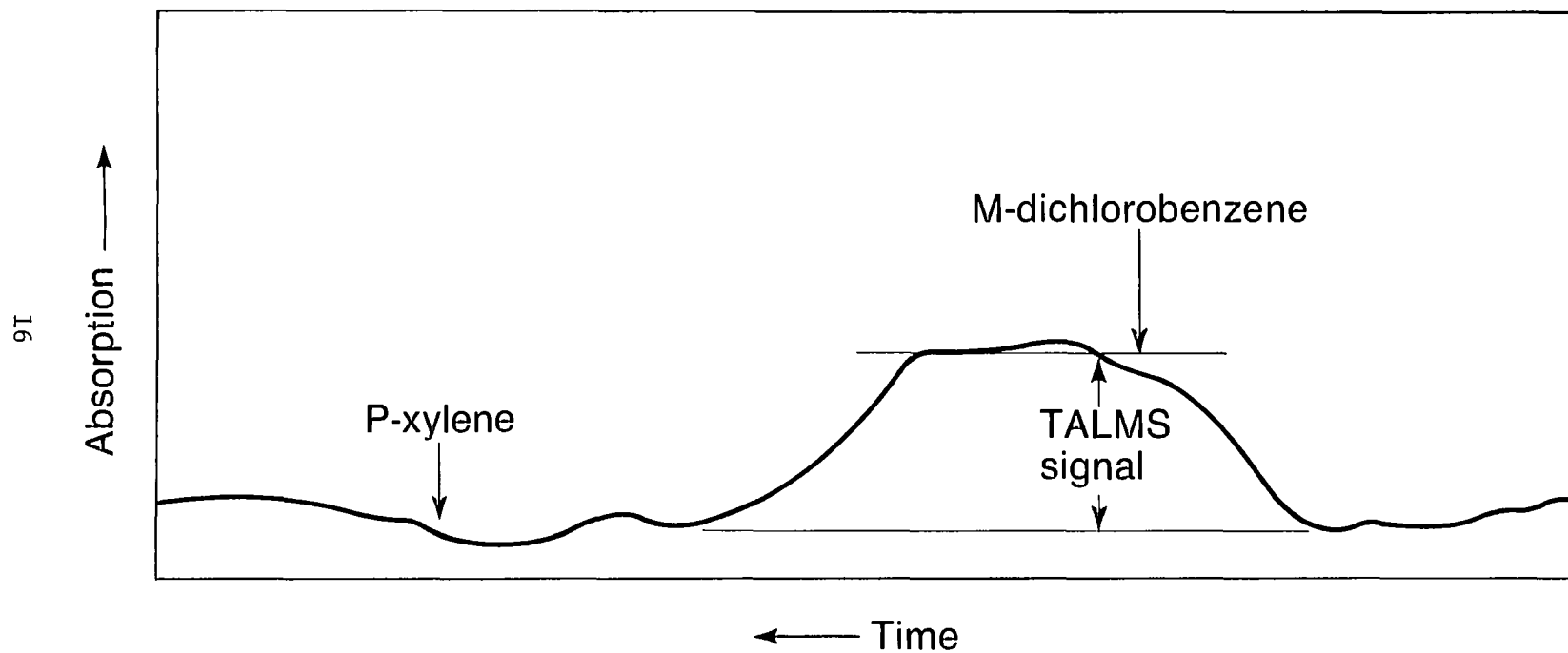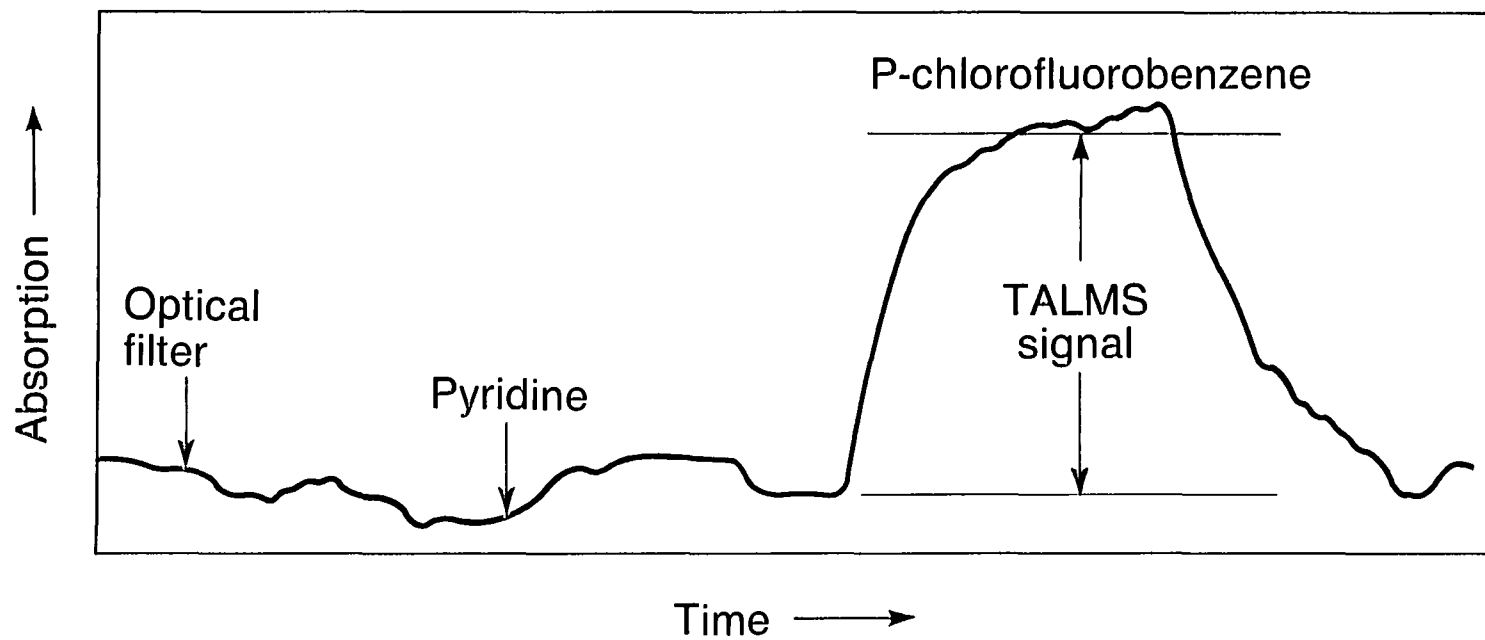
Figure 6.   TALMS signal for m-dichlorobenzene at the Ge 269.134 nm line.
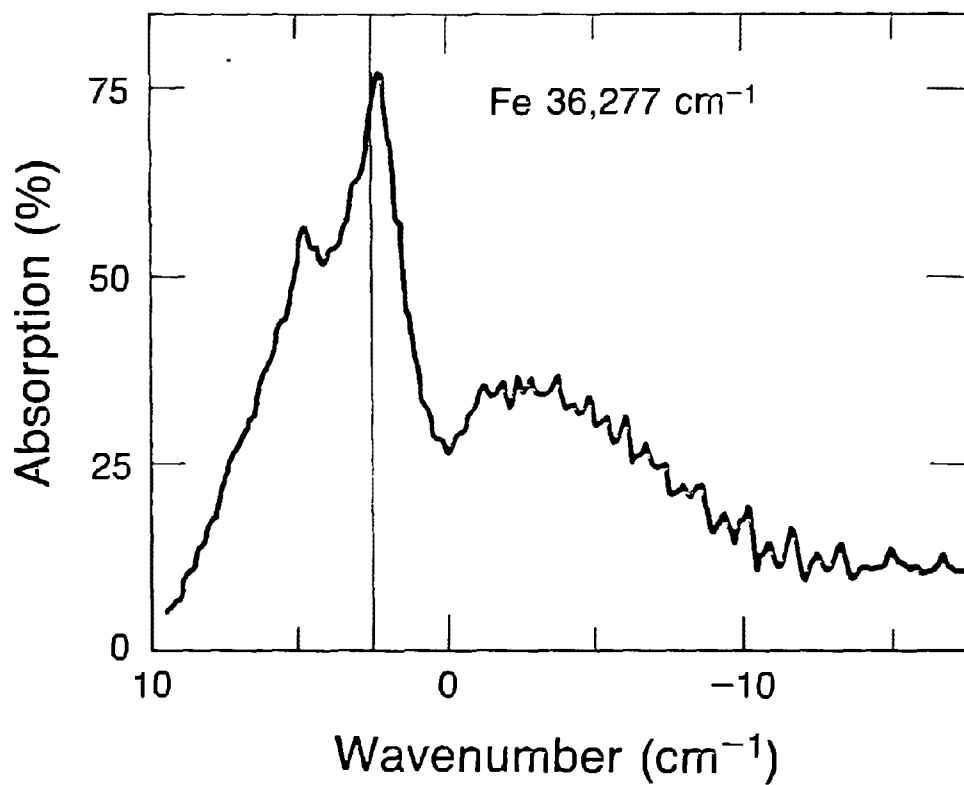
XBL 855-11119

Figure 7. Iron emission line superimposed on the p-chlorofluorobenzene absorption maximum at 36,277 cm^{-1} [10].

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Figure 8. TALMS signal from p-chlorofluorobenzene at the Fe 275.6 nm line.

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pressure of chlorobenzene as a function of temperature was fit by least squares to the relationship:

$$1/T = A + B \ln P$$

where $A = 3.8596 \times 10^{-3}$ and $B = 2.0695 \times 10^{-4}$ if T is expressed in degrees K and P is in torr. At 25 °C, 0.1 mL of a p-chlorofluorobenzene air mixture produced a signal equal to two times the noise level. This corresponds to an approximate detection limit of 30 ppmv.

TALMS DETECTION OF p-DIFLUOROBENZENE

A TALMS signal was found for p-difluorobenzene at the platinum 265.945 nm emission line. Aside from the boiling point, no vapor pressure information for this compound could be found in the literature. In order to construct an analytical curve and to determine the lower limit of detection, the vapor pressure must be known. Therefore, the experiments described below were carried out to determine a relationship between vapor pressure and temperature.

The p-difluorobenzene was purchased from the Aldrich Chemical Co. and was represented as being 99+% pure with a boiling point range of 88 − 89 C. The vapor pressure-temperature relationship was determined by placing the material in a glass tube capable of being evacuated while at liquid nitrogen temperature. After evacuation, the liquid nitrogen bath was replaced with an ice bath, and the pressure was measured using a Balzers pressure gauge that read directly to 0.1 millibar and could be estimated to 0.05 millibar. The sample was immersed in a liquid nitrogen bath, and evacuation started after the first signs of crystallization (pressure = 20 millibars). This was repeated four times to insure that all of the oxygen and other gases were pumped out of the system before a vapor pressure measurement was made. The following pressures were measured at the listed temperatures:

Temperature (C)	Pressure mbar	(torr)
0	19.5	(14.6)
24.6	59.75	(44.81)
89		(760)

The 89 C point was taken from the literature [12]. These data fit the relationship:

$$\log P = a + b \, (1/T)$$

where P = pressure (mm of Hg), T = temperature (K), a = 8.185 and b = −1928.4, with the square of the coefficient of determination = 0.996.

Data for an analytical curve were obtained by drawing off known volumes of an air and vapor mixture in equilibrium at 0 °C. A glass syringe was used because previous experiments had shown that plastic syringes could be a source of contamination. The signal and background

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levels were averaged for 90 seconds at each point. A ten second time constant was used. The platinum 265.945 nm line was used in the parallel Zeeman direction with magnetic fields of 12.2 kG (1.22 T) and 16.4 kG (1.64 T). The results are plotted in Figure 9.

When as much as two mL (200 µg) of the vapor were injected into the cell; there was almost no transmitted light and the signals were dominated by shot noise. The analytical curve was linear up to injections of about one mL. From the baseline noise of 0.04 v and the analytical curve, two times the noise level corresponds to a detection limit of 4 µg or 50 ppmv.

To measure the extinction coefficient of p-difluorobenzene the ratio of the transmitted light intensity to the incident intensity was determined using the 265.945 nm platinum line. Defining the extinction coefficient (ϵ) by the relationship:

I(transmitted) = I(incident) x $10^{-\epsilon}$ x concentration x pathlength

the value of ϵ was found to be 2200 $[cm(mole/L)]^{-1}$ at this wavelength.

LINE SHAPE MEASUREMENT OF p-DIFLUOROBENZENE

High resolution line shape measurements of molecular features responsible for TALMS signals have several important applications. Because these shapes are characteristic of the molecule, they can be used to avoid interferences. If the molecular line shape is known, the optimum field strength and field direction for maximum sensitivity can be readily chosen. In addition, line shape measurements reveal a fundamental property of the molecule that may have future uses that are not readily predictable.

In previous studies [1] line shape measurements have been made of benzene and chlorobenzene absorption features. These measurements were made in the 253.7 nm region using a relatively noise-free mercury discharge light source. However, line shape measurements made with the magnetically confined lamps of this study are more difficult because such discharges tend to be associated with a higher level of noise. Measurement of the line shape of p-difluorobenzene reported here is more difficult because the platinum 265.9 nm line must be used and it can only be generated with magnetically confined lamps.

When transmission of the σ^+ and σ^- components of the 265.9 nm line was compared, the absorption difference was found to be less than two percent. This provides sufficient information for a TALMS signal because the automatic gain control can be used to smooth out noise from the light source. However, when line shapes are determined, the time elapsed between measurement of the two components precludes use of the automatic gain control.

A measurement system was devised that circumvents this type of noise. It takes advantage of the fact that the difference in absorbance of the σ^+ and σ^- components is greater the higher the concentration in the cell. This larger absorbance difference more than compensates for the fact that a percentage difference of a lower total light intensity

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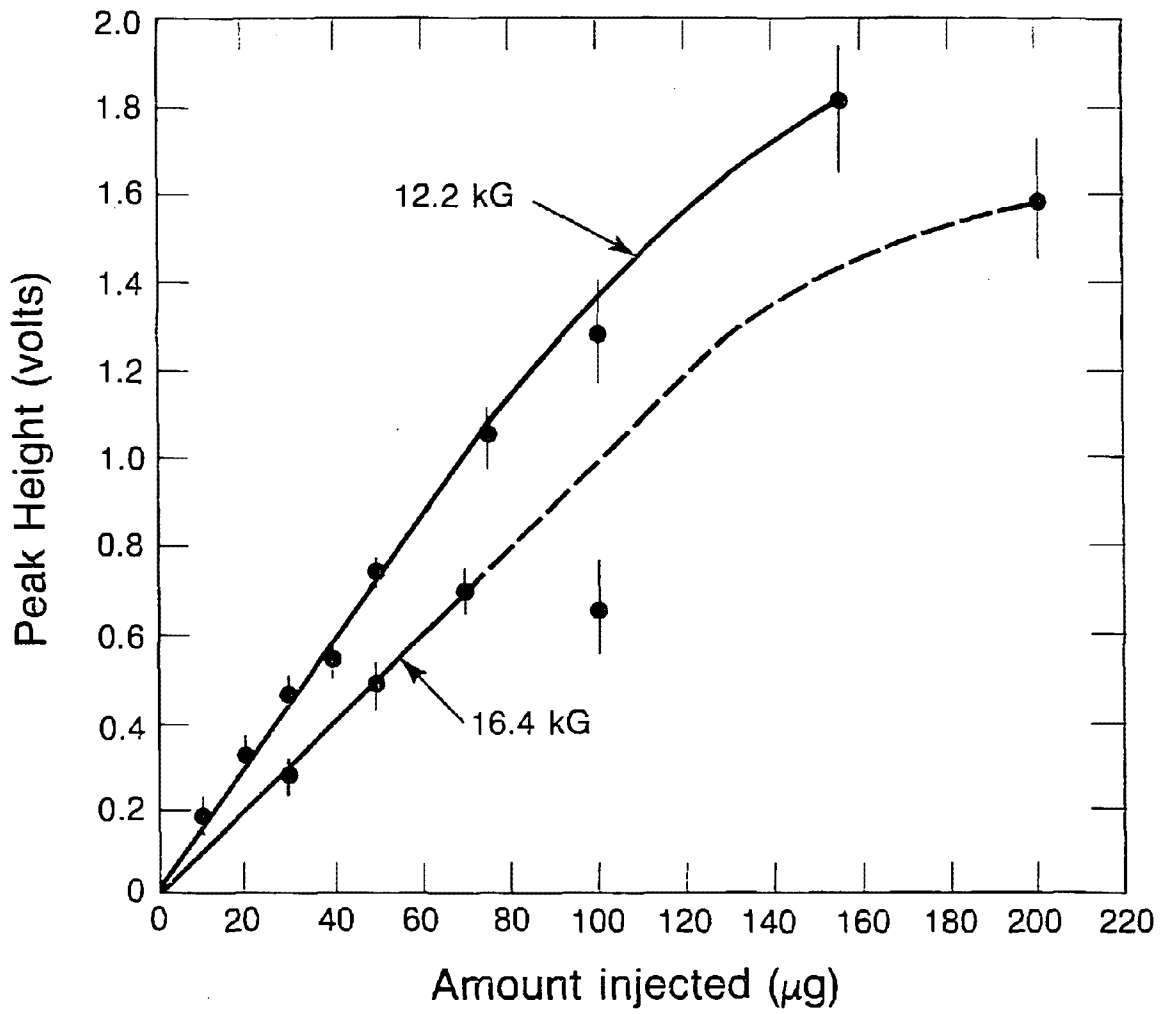
XBL 855-11115

Figure 9. TALMS analytical curves for p-difluorobenzene with the Pt
265.945 nm line.

(70 - 80% absorbed) must be determined.

A double beam arrangement was used that monitored intensity before and after passing through the cell. Signals from the photomultiplier tube responding to the reference signal and the one responding to the sample signal were fed into a log ratio module. Ratio recording at high absorbance values greatly reduces the influence of light source noise.

The log ratio module includes two integrated circuits, AD 755N and AD 755P, which according to the manufacturer's specifications are accurate within 1% when they are used for voltage logging between 10 mv and 10 v. The error was found to be much greater than this. The ICs were checked by imposing known voltages from an Analogic voltage source. It was found that in the range below 100 mv the 755P was in error by 1 - 1.5% and the 755N was in error by as much as 8%. The 755N was within specifications in the 0.1 - 1.0 v range. The sample signals were expected to be less than 100 mv, so they were processed using the circuit containing 755P. The reference signals were expected to be greater than 100 mv so they were processed by the circuit containing 755N.

A combination of two linear polarizers on either side of a retardation plate was used to isolate the σ^+ and the σ^- beams. The plate was adjusted to retard wavelengths of 265.9 nm by one-quarter wave as follows:

a.   The linear polarizers were adjusted parallel to each other by maximizing light transmission. The polarization direction was approximately perpendicular to the magnetic field direction.

b.   The quartz retardation plate was mounted between the polarizers so that stress could be applied at 45° relative to the direction of the linear polarizers.

c.   Pressure was then applied to the quartz plate until the transmission was reduced by one half.

d.   The retardation plate was rotated to determine if the transmission was the same in either direction.

Procedure d revealed a difference in the absorbance output between the two orientations, so this value was subtracted from all subsequent peak height measurements. The stress direction was noted for each measurement since the orientation of the retardation plate determines the Zeeman components that pass through the optical system.

Seventy eight µg of p-difluorobenzene were injected into a 7.6 cm cell for the measurements. A single injection was used for all σ^+, σ^- measurements made at each magnetic field value to minimize the influence of injection technique. A new injection was made for different magnetic field values. Voltage measurements were recorded on a strip chart and stored in a HP-85 computer.

In order to define the optimum magnetic field strength for p-difluorobenzene detection, a plot was made of the difference between the σ^+ and σ^- absorbance values divided by the average absorbance at six different magnetic field strengths. (See Figure 10.) These data

indicate the optimum current is 4.0 amperes (14.4 kG). A plot of the extinction coefficient versus magnet current for the σ^+ and σ^- beams is presented in Figure 11. It was not possible to obtain data for field currents less than one ampere because of problems with the light source at this field strength. The shape of this curve depends upon the electronic-rotational-vibrational transitions that occur in this particular molecule and can be used to verify the presence of p-difluorobenzene in unknown samples.

SUMMARY OF TALMS SIGNALS

In this and previous studies, TALMS signals have been found for the molecules listed below using the atomic emission lines contained in the table. (Wavelengths in nm.)

	Ag	Bi	Co	Fe	Ge	Hg	Pt	Sb	Si
Aniline		293.8							
Benzene			252.9			253.7		252.9	252.8
Bromobenzene				266.5			270.2		
Chlorobenzene						253.7			
m-Dichlorobenzene					269.1				
p-Chlorofluorobenzene				275.6					
p-Difluorobenzene							265.9		
Formaldehyde	338.3								
Phenol				275.0					
Pyridine						253.7			
Toluene						253.7			
p-Xylene			252.9				248.7	252.9	
							273.4		252.8
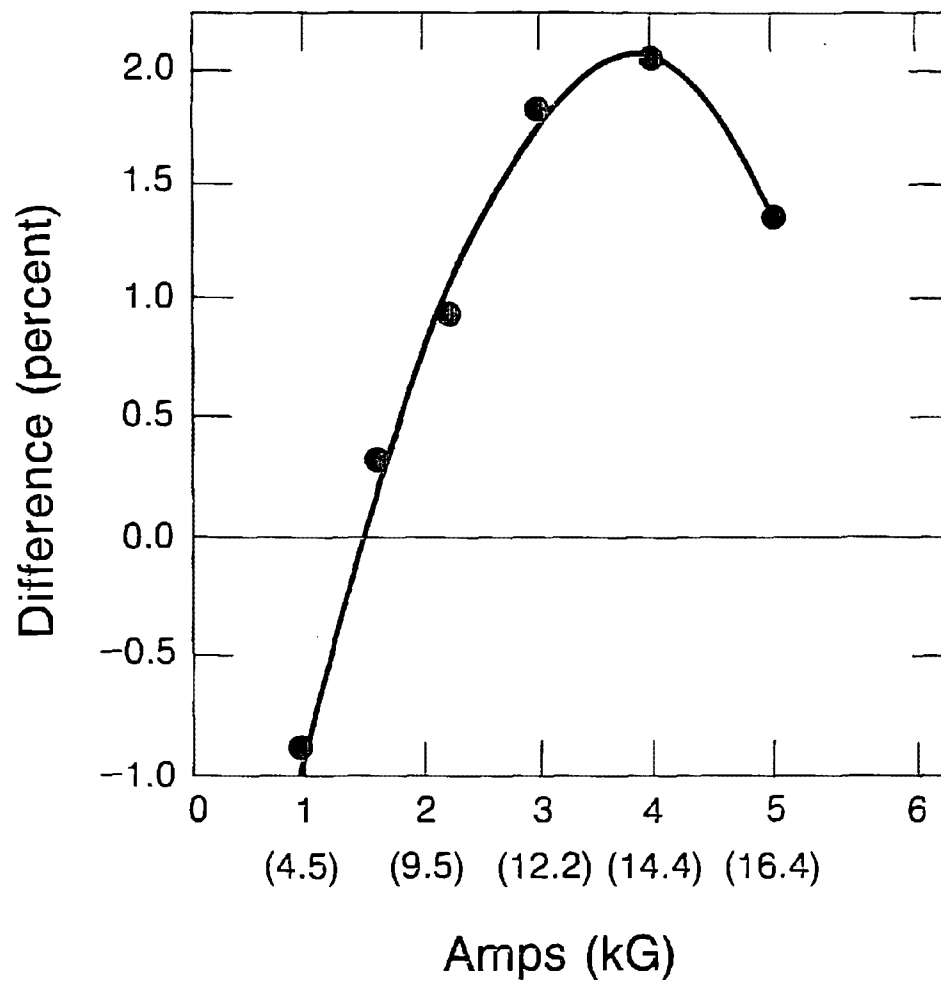
Figure 10. Percentage difference between σ^+ and σ^- absorbance of p-difluorobenzene at Pt 265.9 nm vs. magnetic field current.
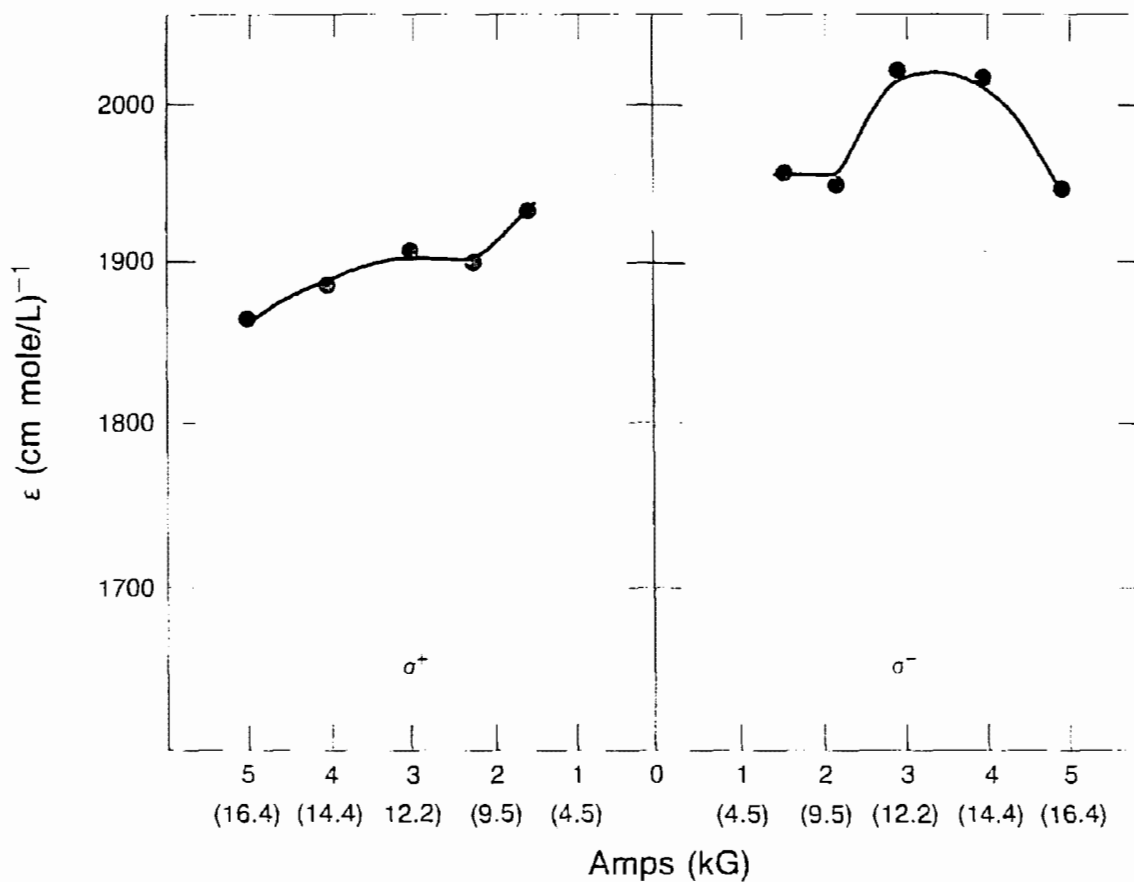
XBL 855-11118

Figure 11. Molar extinction coefficient of p-difluorobenzene vs. magnetic field strength for the σ^+ and σ^- Zeeman components at 265.9 nm.

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APPENDIX A

ALMS INSTRUCTION MANUAL

ASSEMBLY INSTRUCTIONS

1. Mount the monochromator on the optical bench. Remove the tape holding the 0.25 mm slits in the monochromator. The 0.05 mm slits are in a plastic bag with this manual. Slits for the H-20 will also fit in this monochromator.

2. The mercury Pen-ray lamp is taped to the optical bench. Remove the tape.

3. Insert the mercury lamp into the Cajon fitting in the lamp housing. Push it in as far as it will go. Mount the lamp on the monochromator at the end labeled "lamp". The top of the lamp housing screws off so the lamp can be oriented properly.

4. Remove the tape from PMT1. Do not lose the O-ring.

5. Mount the beam splitter, the sample cell, and the PMT1 housing to the optical bench as shown.

6. Connect the beam splitter to the monochromator.

7. Slide the sample cell into the beam splitter and the PMT1 housing over the other end of the sample cell. Slide them together as far as possible. Light leaks can occur at these connections.

8. Remove the tape from PMT2. Do not lose the O-ring.

9. Mount the PMT2 housing on the beam splitter.

10. There are five wires from each PMT tube buffer. The wires from PMT2 are numbered 1, 2, 3, 4, and 5. The wires from PMT1 are numbered 6, 7, 8, 9, and 0. Attach these wires to the corresponding numbers on the bus bar mounted on the wall of the optical bench.

The optical bench is now assembled.

ELECTRONICS MODULE

Each card of the electronics module must be inserted into the proper slot. The connectors at the back of the bin are not the same. Look to see where each card is plugged into the bin before removing it.

To remove the power supply the screws on the front and back must be removed. This module does not slide out freely. (The wires must be

disconnected before the module will completely slide out of the bin.) The other three modules, (the PMT power, signal processing, and time constant modules) will slide out of the bin freely. An extender card has also been provided to assist in repairs of the modules if needed.

OPERATING MANUAL FOR ALMS

The prototype ALMS instrument consists of an optical bench, a lamp driver, and an electronics unit. The electronics unit contains a DC power supply, photomultiplier tube power supply, signal processing module, and a time constant module. Circuit diagrams for all four of these modules are provided in Appendix B.

1. Power to the ALMS instrument unit is turned on by plugging the unit into a wall socket. This power module runs the electronics unit and the output buffer amplifiers on the phototubes on the optical bench. Power is supplied from the electronics unit to the phototube output buffers through the gray three conductor cable that is provided with the instrument. This cable plugs into the back of the DC power supply in the electronics unit and into the three pin connector on the optical bench.

2. The PMT power supply module supplies power to the photomultiplier tubes. The outputs are at the back of the electronics unit. Channel 1 and channel 2 refer to PMT 1 (signal) and PMT 2 (reference) and are marked on the module and the optical bench. Connect channel 1 and channel 2 on the electronics unit to the optical bench using the two BNC cables provided. The PMT power supply signal is a 0 - 7.4 volt DC voltage. The high voltage DC to DC converter is on the phototubes on the optical bench so there is no high voltage on the two PMT power supply cables.

3. The signal processing module takes the PMT output buffer signals from both phototubes and puts them into a log ratio amplifier to get an absorbance signal. The outputs from the PMT buffer amplifiers on the optical bench should be connected to the PMT 1 and PMT 2 inputs on the back panel of the signal processing module using the two BNC cables provided. The absorbance signal can be monitored on the log output on the rear of the signal processing module or the absorbance output on the front panel of the module. The phototube signals can be monitored at the PMT 1 and PMT 2 output connectors at the rear of the electronics unit.

   When the front panel switch on the signal processing module is in the up position,the absorbance output is the log ratio of the channel 1 and channel 2 inputs.

   When the front panel switch is in the down position the input from channel 2 is cut off and replaced by a one volt internal reference signal. The ALMS instrument should be operated with the front panel switch in the up position.

   There is a log adjust screw on the front panel of the signal processing module. This is used to set an offset in the log ratio amplifier. Normally this should not be touched. The proper way to

set the log adjust is to put the same signal into the PMT 1 and PMT 2 inputs. The absorbance output should be zero. If it is not zero, then turn the log adjust screw until the absorbance output is zero.

4. The lamp for the prototype ALMS is a standard mercury pen ray lamp. It is mounted in the housing at the front of the monochromator. There is access to the lamp at the top of the housing for visually orienting the lamp for proper operation. Connect the separate lamp driver into the blue Pomona box mounted on the optical bench using the high voltage BNC cable provided.

5. The ALMS signal is simply an absorbance measurement from the two photomultiplier tubes. With no sample in the cell, set both PMT outputs to the same value so that there is a zero absorbance output. Set the photomultiplier tube outputs to the 1 – 2 volt range.

6. The output of the signal processing module is the input to the time constant module. Turn the knob on the front panel of the time constant module counterclockwise to its final position. The output now has a one second time constant. The next positions, in a clockwise direction, are 10, 20, 30, and 50 second time constants. The zero button zeros the output by discharging the capacitors in the time constant amplifier.

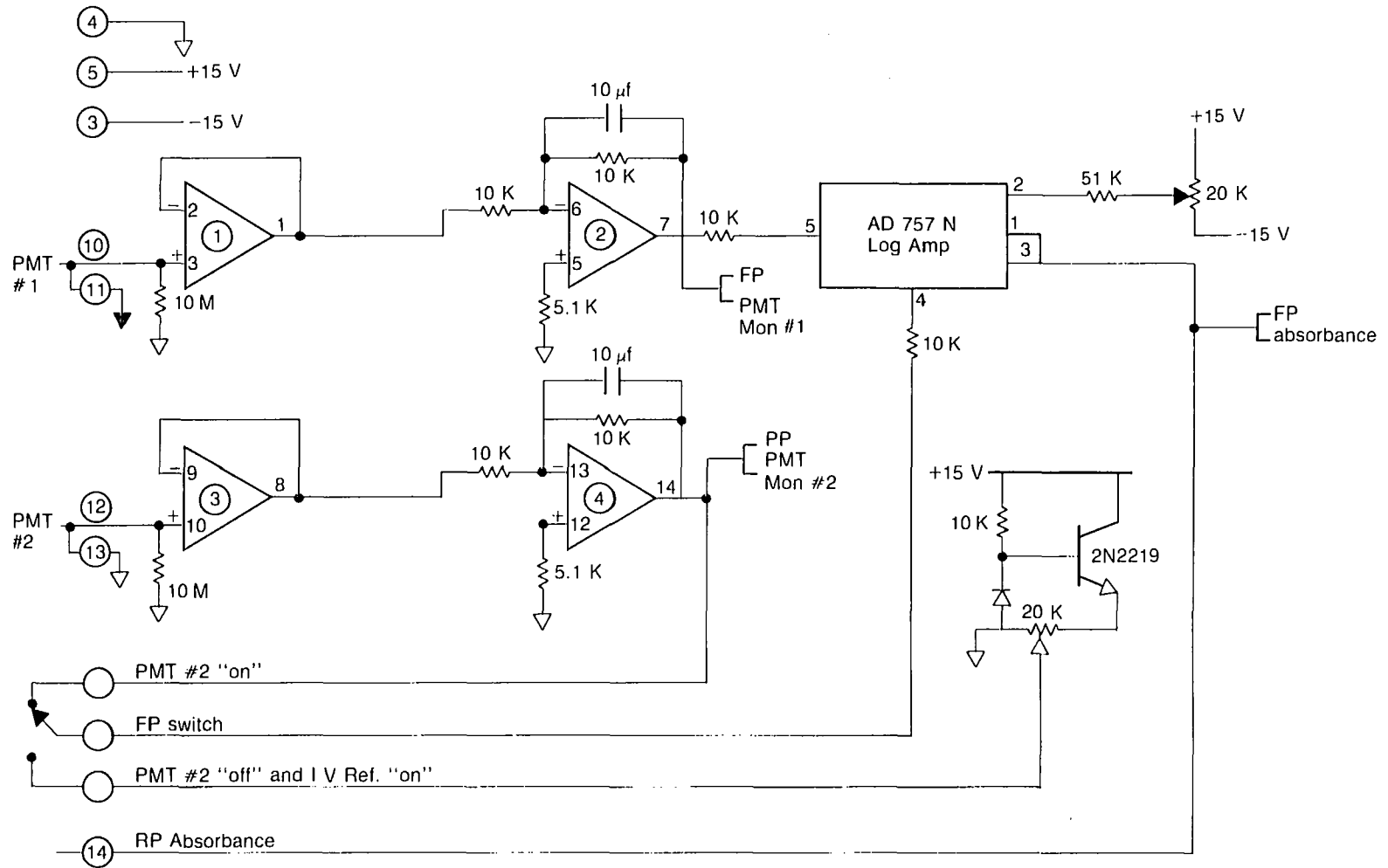The ALMS instrument is now ready to operate.

APPENDIX B

ELECTRONIC SCHEMATICS

This appendix contains schematics of the ALMS electronic modules that were sent to the U. S. Environmental Protection Agency at Research Triangle Park, NC, during the month of December, 1984.
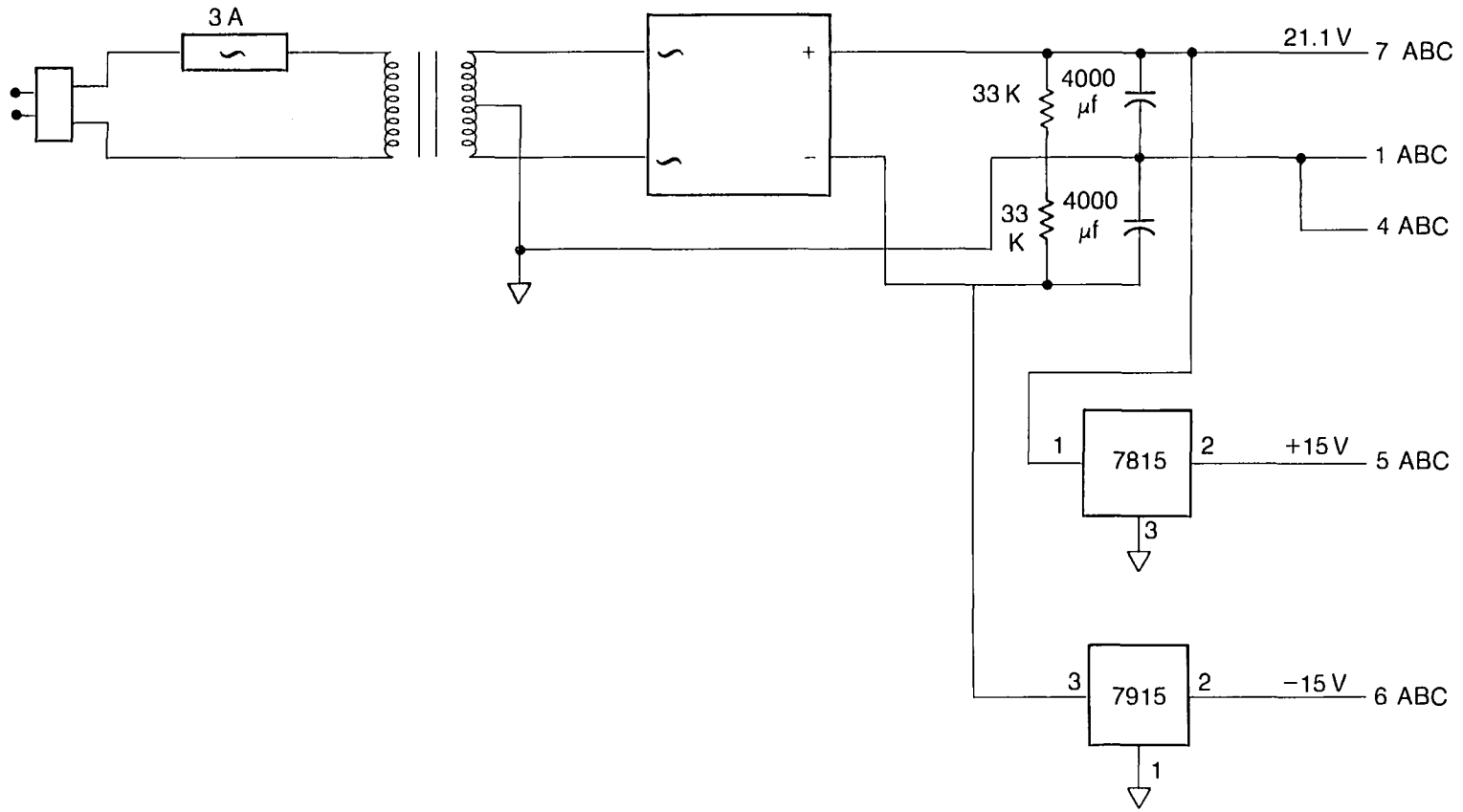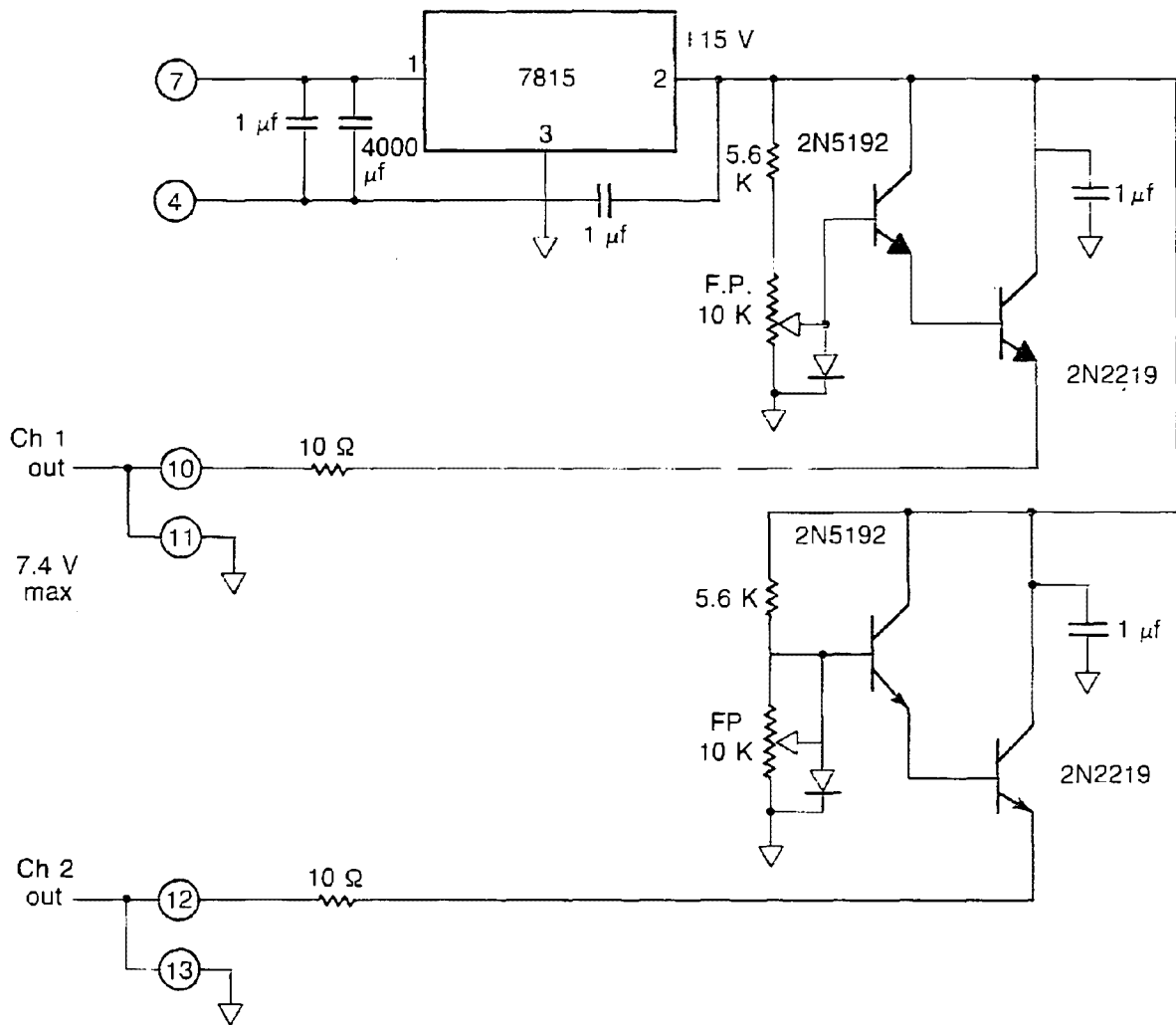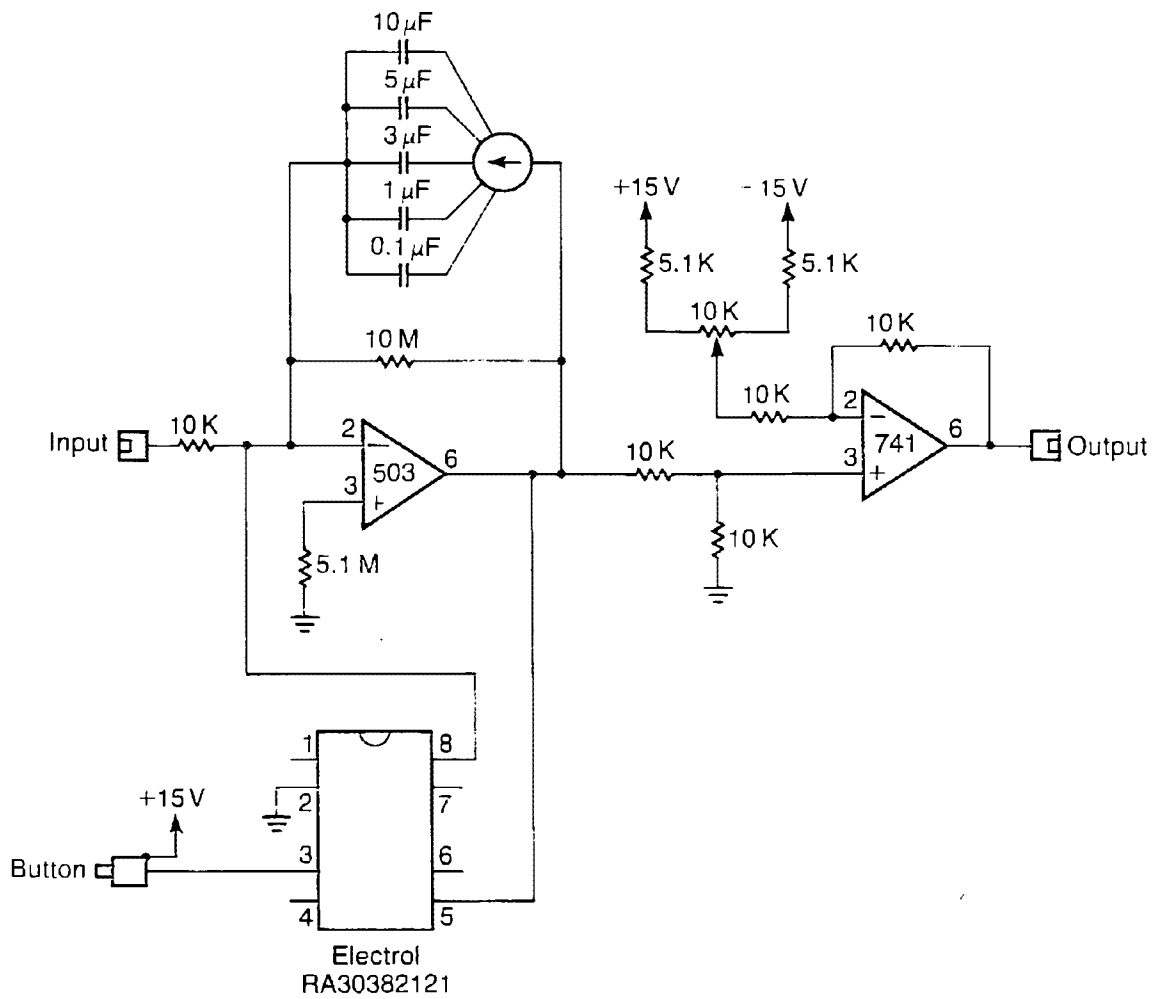
XBL 855-11126

Figure 12.   ALMS power supply.

Figure 13. ALMS logarithmic amplifier.

XBL 855-11127

XBL 855 11121

Figure 14. ALMS photomultiplier tube power supply.

Figure 15. ALMS time constant module.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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7. AUTHOR(S) T. Hadeishi, M. Pollard, R. McLaughlin, M. Koga	8. PERFORMING ORGANIZATION REPORT NO.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The objectives of this study were: a) to design, construct, and deliver a prototype atomic line molecular spectrometer (ALMS) benzene monitor and b) to locate matches of atomic lines and sharp molecular absorption features in other toxic organic compounds for possible use in ALMS or TALMS techniques. ALMS and TALMS are newly developed, high resolution molecular absorption techniques which are used in the vacuum untraviolet and ultraviolet regions of the optical spectrum to detect organic molecules in the gas phase. The dual beam prototype ALMS instrument was designed, constructed, tested and delivered to the Environmental Monitoring Systems Laboratory, U. S. EPA, Research Triangle Park, North Carolina, in December, 1984. It was designed for monitoring benzene and other organic compounds with the 184.9 and 253.7 nm mercury lines. The instrument consisted of three units: the optical unit (weight: 28 lbs, dimensions: 28x10x12"); the electronics unit (weight: 6 lbs, dimensions: 19x7x5.25"); and a lamp driver (weight: 24 lbs, dimensions: 14.5x14x6.5"). The total weight was 58 lbs, which is less than that of the TALMS benzene monitor previously developed (82 lbs). Tests of the performance of the benzene monitor showed an approximate detection limit of 250 ppbv at 184.9 nm. Line matches and TALMS signals were found for three new compounds: p-difluorobenzene (Pt:265.9 nm); m-dichlorobenzene (Ge: 269.1 nm) and p-chlorofluorobenzene (Fe:275.6 nm).

17.	KEY WORDS AND DOCUMENT ANALYSIS	
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