



## Project Summary

# Development of an Optical Monitor for Toxic Organic Compounds in Air

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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-ultraviolet 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, USEPA, Research Triangle Park, NC, in December 1984. It was designed for monitoring benzene with the 184.9 and 253.7 nm mercury lines using the ALMS technique. The instrument consisted of three units: the optical unit (weight: 28 lbs, dimensions: 28 x 10 x 12"); the electronics unit (weight: 6 lbs, dimensions: 19 x 7 x 5.25"); and a lamp driver (weight: 24 lbs, dimensions: 14.5 x 14 x 6.5"). 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.

The process of searching for TALMS signals in organic compounds was simplified by the development of a computer accessible data base of atomic line locations 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 platinum 265.9 nm line.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

There is a great need for instruments to detect and 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 including benzene, toluene and other substituted benzenes. Since substituted benzenes and other organic compounds absorb light in the vacuum ultraviolet and ultraviolet regions, one possible detection method is the use of optical absorption techniques in the gas phase. The use of high resolution absorption methods should increase the selectivity of the technique by exploiting the rotational-vibrational fine structure in the absorption spectra of the compounds.

Tunable atomic line molecular spectroscopy (TALMS) is a newly developed high

resolution, molecular absorption approach to monitoring organic vapors that is different from most present analytical techniques. Whereas present methods depend on some form of chromatographic separation for compound identification, the TALMS technique depends only on ultraviolet-visible 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 with the TALMS technique is 10 ppmv, which is too high for direct ambient air measurements.

A related technique, atomic line molecular spectroscopy (ALMS), resulted from extending the ideas behind the TALMS technique in an attempt to improve the detection limit. Differential absorption at two different wavelengths is the basis of both methods. In the TALMS case the two wavelength positions are determined by the very small Zeeman splitting of the atomic line chosen for measurement. The small splitting ensures 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 limits of both techniques depend upon the difference in intensities of the molecular absorption spectrum 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 where the molecular extinction coefficient is approximately 100. Judging from the much higher extinction coefficients in the vacuum ultraviolet region for benzene, detection limits 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, for accurate background correction with ad-

ditional analysis lines, the absorption by interfering compounds must be constant over the wavelength interval used. If several different lines are used to monitor the concentration of the same molecule, the presence of an interference can be detected because different apparent concentration values will be obtained at different wavelengths. Although this measurement may not provide an accurate 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 ultraviolet region may also allow the determination of classes of organic compounds.

Previous studies with the TALMS techniques 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, NC, an ALMS monitor and (b) to determine the spectral location of absorption features and matching atomic lines in toxic organic 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.

## Conclusions and Recommendations

Design and construction of a prototype ALMS instrument for the detection of benzene and other compounds was completed on schedule; and the prototype was delivered to the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, in December 1984. It consisted of three modules: an optical module; an electronics module; and a lamp driver. The sensing module weighs 28 lbs, the electronics module, 6 lbs, and the lamp driver, 24 lbs. An instruction manual and schematics of the electronics were also supplied. It 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 40 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 molecules were continued. This tedious process was greatly improved by the 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-xylene 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 the prototype to improve ALMS instrument performance. An arrangement should be devised to alternately send two different lines from the same light source through the sample. Electronic subtraction of the signals from the 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 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 upon the location of proper analysis lines, it is recommended that more studies be carried out to locate new analysis lines for compounds of interest.

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*The complete report, entitled "Development of an Optical Monitor for Toxic Organic Compounds in Air," (Order No. PB 85-225 027/AS; Cost: \$8.50, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Environmental Monitoring Systems Laboratory*

*U.S. Environmental Protection Agency*

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