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**DETERMINATION OF AIRBORNE ORGANICS BY
DIRECT SAMPLING MASS SPECTROMETRY**

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Two new state-of-the-art mass spectrometer systems are currently being evaluated for the determination of part-per-billion levels of organics in ambient air. These instruments include an ion trap mass spectrometer (ITMS) and a glow discharge quadrupole mass spectrometer (GDMS). Both of these instruments can be configured for direct air sampling or may be operated in conjunction with thermal desorbers for the analysis of samples preconcentrated on resin traps. Glow discharge ionization is particularly amenable to direct air monitoring; however, the use of a single quadrupole mass analyzer limits the ultimate specificity of this particular system. Important features of the ITMS include the ability to perform selective chemical ionization as well as collision induced dissociation (CID) tandem mass spectrometry (MS/MS) for compound identification. Applications of this technology have included the determination of ambient nicotine in environmental tobacco smoke (ETS), the determination of trace levels of organo-phosphonates in air, and the detection of target volatile organics in indoor atmospheres.

INTRODUCTION

The potential adverse health effects of exposure to indoor air pollution is becoming an increasingly important issue in our society. In order to fully characterize the nature of indoor air pollution as well as to assess exposure levels to hazardous compounds, rapid, sensitive, and reliable analytical methods are needed. A wide variety of analytical devices and methods currently exist for the measurement of air pollutants including Drager tubes, gas chromatography (with and without trap preconcentration), gas chromatography/mass spectrometry, coated piezo-electric crystal oscillators, flame ionization detectors, infrared spectrometers, and atmospheric pressure ionization mass spectrometers, among others. These encompass a wide range of cost, complexity, sensitivity, and versatility. Of the analytical techniques mentioned, mass spectrometry is one of the most sensitive and also provides a very high degree of confidence for the identification of compounds. Although mass spectrometry is widely used as a laboratory-based technique for the analysis of a variety of types of environmental samples, the large size, high cost, and complexity of the instrumentation generally makes it less attractive as a field technique compared with other types of instruments which are commercially available for field monitoring. We report the use of two new state-of-the-art mass spectrometer configurations which are intended for direct monitoring of trace organics in ambient air. Analytical methods for the determination of volatile and semivolatile organics in air are currently being developed and

refined. Although our work is being presently being performed with laboratory-based instrumentation, both of the mass spectrometer configurations are potentially amenable to eventual size reduction and routine mobile operation.

Previously, most direct monitoring mass spectrometry for the determination of air pollutants has been performed with atmospheric pressure ionization (API) triple quadrupole mass spectrometers (1,2). Single stage quadrupole mass spectrometers equipped with capillary restrictor and/or membrane sample inlets have also been used. API mass spectrometers generally have very rapid response times, excellent detection limits, and the ionization sources are somewhat tolerant to abuse. However, a major problem with many API mass spectrometers is that they are highly susceptible to the formation of water cluster ions which have a tendency to complicate the spectral background and also sometimes spread the ion current of the analytes over several different mass peaks, reducing the ultimate detection limits. Single quadrupole mass analyzers equipped with capillary or membrane interfaces to atmosphere frequently have slower response times (due to slow pumping speeds) and since they generally use conventional electron impact (EI) sources, they are often less sensitive than are API mass spectrometers. The glow discharge quadrupole instrumentation described in this paper has many of the desirable features of API instruments without the formation of cluster ions, while the ion trap mass spectrometer has many of the features of a triple quadrupole instrument with the simplicity of a single analyzer and the convenience of a capillary restrictor sampling interface.

MATERIALS AND METHODS

The mass spectrometer which is used in conjunction with the glow discharge ionization source is comprised of an EXTREL single quadrupole mass filter and its associated control electronics. For maximum ion transmission, 3/4" diameter quadrupole rods are used along with a 1.2 MHz 300 watt power supply. This gives a nominal mass range of 10-500 daltons with unit mass resolution or better possible across the entire range. The quadrupole analyzer assembly is mounted in a custom designed 6" diameter stainless steel vacuum chamber which is pumped to high vacuum by a Varian M-1 oil diffusion pump that is backed by a 110 L/min rotary mechanical pump. The base pressure in the spectrometer is maintained at 1×10^{-7} torr or lower whenever sample is not being admitted into the analyzer region. The entire vacuum chamber is heated with infrared radiant heaters to minimize the adsorption of sample constituents onto the interior surfaces of the spectrometer. For versatility and convenience, the spectrometer is equipped with a standard axial (EI) ionization source in addition to a specially designed and constructed glow discharge ionization source. The axial ionization source remains mounted on the entrance of the quadrupole assembly at all times, even when the spectrometer is operated in the glow discharge ionization mode. This is accomplished by mounting the glow discharge ionization source in a separate differentially pumped vacuum chamber which is itself mounted on the front end of the analyzer vacuum chamber directly in line with the axial EI source. Ions exit from the glow discharge source through a 1.5 mm diameter vacuum conductance limit and directly enter the lens stack of the axial EI source. This configuration enables the lenses of the axial source to be used for focussing ions from the glow discharge source into the quadrupole assembly and also maintains the integrity of the electron impact ionization source for instrument troubleshooting and for the generation of conventional EI spectra.

The glow discharge ionization source was designed and constructed in our laboratory specifically for direct air monitoring purposes. The discharge electrodes consist of a 0.5" diameter x 1" long stainless steel cylindrical electrode with a 1" long 20 gauge stainless steel center electrode arranged in a coaxial orientation. Air flows through a needle valve directly into the discharge region at a flow rate of 1 standard mL/sec. No restrictors or membrane separator is required. Pressure in the discharge source is maintained at 250 mTorr by pumping with a 160 L/min rotary mechanical pump. The voltage on the outer electrode is typically -400 volts and the voltage on the center electrode is typically +100 volts with a total current of 10 mA between the two electrodes. Air is used as the discharge medium and no special gasses are required to sustain a stable discharge plasma. The ions are extracted from the discharge plasma by a series of lenses and focused through the vacuum conductance limit into the lens stack of the axial EI source and the quadrupole mass filter as shown in Figure 1.

An IBM-XT computer is interfaced with the glow discharge mass spectrometer for control of the mass spectrometer, data acquisition, and data manipulation. Software for these tasks was written by the authors.

A Finnigan ITMS was used for all ion trap mass spectrometry work. This system is equipped with a custom designed vacuum chamber that is electro-polished on the inside and pumped with dual 330 L/sec turbomolecular pumps. The high pumping speed and smooth surface were incorporated to minimize absorption of samples on the inside walls of the vacuum chamber which could result in high background signals and unacceptable contamination at low detection levels. Infrared heaters are used internally to maintain the analyzer region at 120°C. All of the electronic accessories needed for selected ion storage and MS/MS were provided with the commercial instrument. The ITMS is interfaced with an IBM-AT compatible computer and is operated with commercial software. Experiment control programs (scan functions) for the detection of specific analytes were written by the authors using the scan function editor provided with the commercial software.

A 1.2 m length of 180 μ m ID uncoated fused silica capillary restrictor serves as the interface between atmospheric pressure and the ITMS analyzer cell. The capillary extends directly into the analyzer cell through a heated stainless steel conduit which is maintained at 200°C. The flow rate of helium gas through the restrictor is approximately 0.5 standard mL/min when it is operated at 200°C. The atmospheric pressure end of the restrictor is either connected to the direct sampling probe or to the outlet of a thermal desorption device.

For real-time air monitoring with the ITMS, a direct sampling probe is used as shown in Figure 2. Air is drawn into the probe by means of a sampling pump and swept across the end of the capillary restrictor by means of a variable splitter arrangement. The pumping speed of the sampling pump can be varied from 0.1-2 L/min. In order to maintain the performance and mass resolution of the ITMS, it is necessary to mix helium buffer gas with the incoming air stream at a ratio of at least 1:1 by volume.

For the analysis of resin traps, a thermal desorber system was specially designed and constructed in our laboratory. It is configured to accept traps which are 3 inches long and 0.25 inches in diameter. A 450 watt heater enables flash heating of trapped components from the resin bed with very high efficiency. Typical heating time is 10 seconds with a

simultaneous helium purge of 25 mL/min. Resin traps may be packed with any suitable sorbent such as Tenax or Chromasorb 106. A septum located in the top of the thermal desorber body provides a convenient means of injecting standards and calibrants into the mass spectrometer under the same conditions as the analytes trapped on the resin tubes. For use in conjunction with the glow discharge mass spectrometer, the effluent from the desorber may be connected directly to the inlet of the ion source without special plumbing. However, for use in conjunction with the ITMS, the desorber effluent is passed through a splitter which is adjusted for a split ratio of approximately 50:1, with most of the effluent directed to the split vent and the remainder to the ITMS through a capillary restrictor interface.

RESULTS AND DISCUSSION

There are several important features of the glow discharge mass spectrometer which are important for air monitoring applications. These include rapid response, excellent detection limits, a wide linear dynamic range, and a very rugged design. Even though the selectivity of the instrument is limited because of the single mass analyzer configuration, the glow discharge mass spectrometer is a convenient instrument for quickly checking ambient air for trace levels of organic compounds. It is capable of detecting volatile and semivolatile compounds virtually instantaneously at part-per-trillion levels. For example, dimethyl-methylphosphonate has been detected and quantified directly at a concentration of 50 ppt in air without preconcentration. Response is linear over a wide range of concentrations as shown in Figure 3 by the response curve for benzene in air from 9 ppb - 1.16 ppm. Further, provided that a sample does not contain a large number of constituents, spectral subtraction routines can often be used to recover both qualitative and quantitative information for up to 10-15 different analytes, even without the use of chromatography or MS/MS.

For field applications, the simplicity and ruggedness of the glow discharge ionization source are important considerations. In particular, since there are no filaments to burn out, the source is highly resilient to oxygen, water, and other contamination. Even when water has been directly aspirated into the ion source, the source and spectrometer have completely recovered within 15 minutes. As an added feature, it is possible to adjust the conditions within the discharge plasma electronically in order to enhance either proton transfer ionization or fragmentation spectra. This allows one to obtain information based on both molecular weight as well as the fragmentation pattern of a compound.

The ion trap mass spectrometer is perhaps one of the most exciting new instruments for air monitoring applications. Not only does this mass spectrometer have the capabilities of selective chemical ionization, selective ion trapping, and CID MS/MS, but the simplicity, small size, and detection limits of the mass analyzer are virtually unmatched by other mass spectrometer configurations. Further, because this type of mass spectrometer is normally operated at pressures of 10^{-4} torr, the performance of the spectrometer is not highly degraded by direct air monitoring through a capillary restrictor. In fact, it is possible to take advantage of the water vapor normally present in air by using it as the chemical ionization reagent for the analytes of interest.

When using a capillary restrictor for direct air monitoring, it is possible to identify and quantify organics at low ppb levels in air as shown by the spectrum of benzene and

toluene in Figure 4. Additionally, because of the ability to perform selective chemical ionization and MS/MS, it is possible to confidently identify and quantify compounds in the presence of wide range of constituents. For instance, full scan CID MS/MS spectra of nicotine have been generated at concentrations as low as 3 ng/L in air and the ultimate detection limit for this compound in air has not yet been established. This suggests that an ITMS could be used as a direct monitor for nicotine at levels which are significant for evaluating exposure to environmental tobacco smoke.

Resin traps provide a simple and generally unobtrusive means of collecting air samples for analysis at remote sites or wherever it is inconvenient or impossible to perform direct monitoring experiments. Further, by sampling for long periods of time, it is possible to preconcentrate trace constituents sufficiently to enable detection and quantification of volatile and semivolatile organics at very low pptr levels. For example, by using preconcentration followed by thermal desorption into the ITMS, di-isopropylmethylphosphonate has been determined at concentrations of 1-10 pptr in air. A response curve for DIMP generated by thermal desorption chemical ionization, MS/MS is shown in Figure 5. The linear dynamic range is generally 10^3 and reproducibility of response is typically $\pm 15\%$ for replicate samples without the use of an internal standard. Resin trap sampling has also been applied to the determination of ambient nicotine in environmental tobacco smoke with excellent results obtained over a range of concentrations ranging from less than 1 ng/L to over 300 ng/L. Sampling times were typically 1-5 minutes and sample volumes were typically less than 1 L. The analysis time per sample was less than 5 minutes.

CONCLUSIONS AND RECOMMENDATIONS

Both GDMS and ITMS have been demonstrated to be useful for air monitoring applications. Important features of both techniques include excellent sensitivity, rapid response, ease of operation, and relatively simple designs. ITMS is particularly powerful with the added capability of selective ion trapping and MS/MS. Work is progressing on the development and refinement of analytical methods for air monitoring and designs are being considered for down-sized, mobile instruments.

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2. Ketkar SN, Dulak JG, Fite WL, Buchner JD, Dheandhanoo S (1989) Atmospheric Pressure Ionization Tandem Mass Spectrometric System for Real-Time Detection of Low-Level Pollutants in Air. Anal. Chem. 61:260-264.

FIGURES

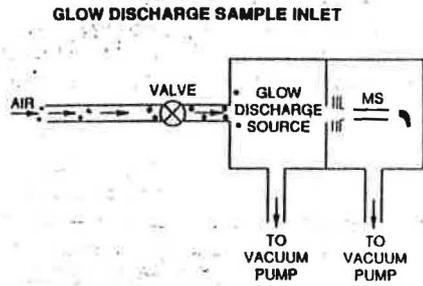


Figure 1. Glow Discharge Mass Spectrometer.

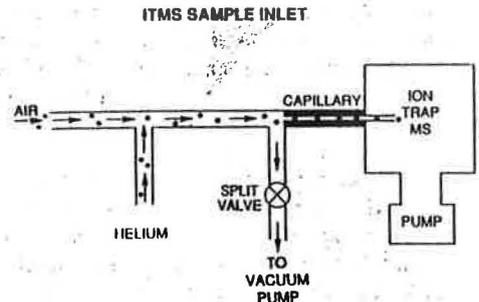


Figure 2. Direct Air Sampling ITMS.

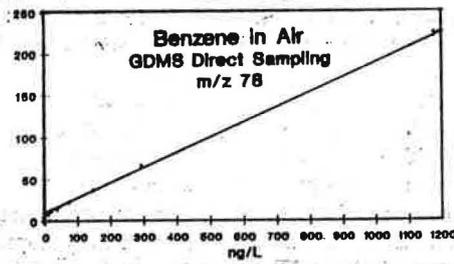


Figure 3. GDMS Response Curve for Benzene in Air.

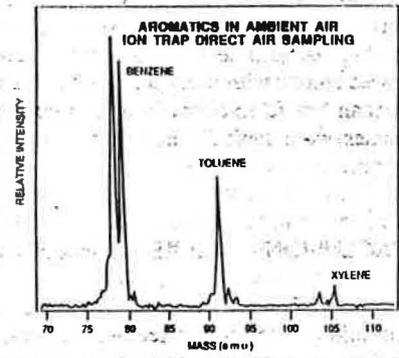


Figure 4. ITMS Mass Spectrum of Aromatics in Air.

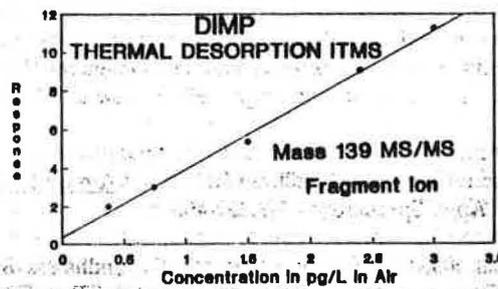


Figure 5. Response Curve for DIMP in Air using Thermal Desorption with ITMS.