

A FIELD DEPLOYABLE ION TRAP MASS SPECTROMETER FOR THE MEASUREMENT OF TRACE ORGANIC COMPOUNDS IN AIR

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INTRODUCTION

A number of new monitoring techniques for characterizing hazardous air pollutants have arisen in response to the limitations of standard batch methods. Based on mass spectrometry and direct air sampling interfaces, the techniques measure all of the target analytes in a sample simultaneously without prior sample preconcentration or chromatographic separation [1]. Those based on the ion trap mass spectrometer (ITMS) offer a powerful means of developing compact, field-deployable systems with high sensitivity, specificity, and speed for continuous real-time monitoring of volatile organic compounds (VOCs) of environmental interest in air [1-5]. The necessary specificity is provided by tandem mass spectrometry (MS/MS) in which parent ions are isolated selectively before undergoing dissociation to form characteristic product ions.

Although the ion trap is uniquely suited to take advantage of the inherent capabilities of MS/MS [6], its storage capacity is limited by space charge effects. A broadband resonance excitation technique that makes use of filtered noise fields (FNF) has been developed to enhance the trap's storage capacity for analyte ions [7-8]. A commercially-available instrument with full FNF and MS/MS capability is the compact field-deployable Teledyne 3DQ™ Discovery ion trap.

We have attached a direct air sampling (DAS) interface, an air sampling glow discharge ionization (ASGDI) source [2,9], to the 3DQ ion trap. This allows trace organics in air to be ionized externally before they are injected into the trap where they are selectively stored and dissociated using the FNF technique [3,8]. We have explored the potential of the ASGDI/3DQ combination and filtered noise fields for rapid field MS/MS analysis of VOCs at trace levels in air.

EXPERIMENTAL

All experiments were carried out on a Teledyne (Mountain View, CA) 3DQ Discovery ITMS. The 3DQ is a compact, field-deployable ion trap with full FNF capability, and has been described in detail previously [3]. With the FNF method, a flat broadband waveform with a large number of evenly spaced frequency components is applied to the end caps of the trap [7]. The frequency components span the entire trappable mass/charge ratio (m/z) range of the trap, and their amplitudes are set sufficiently large so that initially all ions are resonantly ejected. Then, "notches" that correspond to specific masses are inserted at the appropriate resonance frequencies in the basic FNF waveform, and the notched FNF signal is applied to the end caps. In this way, unwanted ions are ejected and the full storage capacity of the trap is used to accumulate only selected target ions. The isolated ions may be collisionally dissociated (MS/MS mode) by

applying resonance excitation to the end caps using either a single frequency or a frequency bandwidth.

Filtered noise fields are implemented through scan functions, which are generated by constructing a contiguous series of scan descriptor "tables." Each table contains a description of the procedures needed to perform a specific task within the scan function. By allowing a single table to perform several functions, a standard ion isolation step can be defined with only two tables, and an MS/MS experiment with just three tables. Tables can be viewed and edited through an interactive Windows™ edit program. Additional tables may be quickly added to extend the functionality of each scan function.

The ASGDI source has been described in detail elsewhere [2,9]. Briefly, the ionization region is defined by two circular plates mounted parallel to one another on the outside faces of a hollowed-out vacuum flange. Air enters the source, at a pressure of ~0.6-1.0 torr, through a narrow aperture in the outer plate and sustains the discharge which, in the positive ion mode, is established by applying a potential of about 400 V between two half plates mounted in the source region perpendicular to the two outside circular plates [2,9]. Ions formed in the discharge are focused into the trap via a three-element einzel lens. The central element of the lens is electronically pulsed using the standard ITMS circuitry to gate ions into the trap. Helium flows into the vacuum chamber at an uncorrected pressure of 4×10^{-4} torr and serves as the buffer gas as well as the collision gas in the MS/MS dissociation experiments.

RESULTS

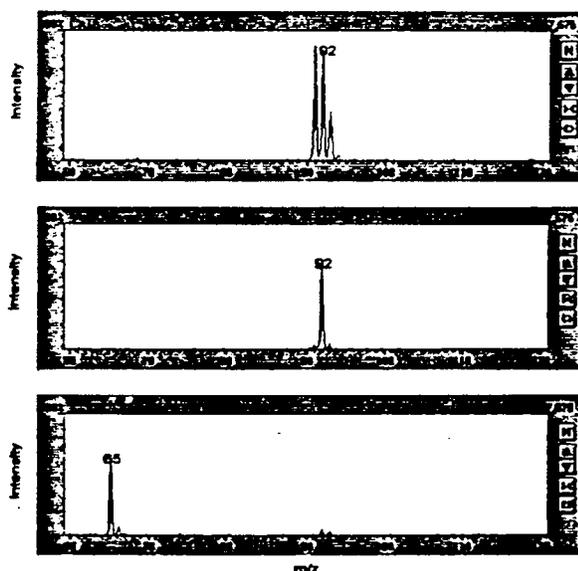


Figure 1. ASGDI/3DQ ion trap mass spectra of toluene: (a) molecular ion region without FNF ion isolation; (b) spectrum with FNF single-notch isolation of m/z 92; (c) MS/MS spectrum resulting from collisional dissociation of m/z 92 to m/z 65.

Ion Isolation with Unit Mass Resolution.

Figure 1a presents the mass spectrum of the molecular ion region from toluene obtained with the ASGDI/3DQ combination in the absence of a filtered noise field. Application of the single notch FNF broadband signal has a filtering effect on the signal since it removes all of the unwanted ions from the spectrum except those of the selected mass, m/z 92, as shown in Figure 1b.

As a result, the ion gate can be opened for extended periods, significantly increasing the intensity of the mass of interest. The specificity and sensitivity required to analyze complex mixtures is obtained by using resonance excitation to bring about MS/MS dissociation of the isolated ion, which produces only those fragment ions that are formed directly from the parent. Figure 1c shows the collisional dissociation of the isolated molecular ion of toluene to form the

Table 1. Product Ion (MS/MS-Mode) Detection Limits (DL) for Selected Nonpolar and Polar VOCs in Humidified Air Using the ASGDI/3DQ Ion Trap MS System.

Compound	Parent Ion	→ Product Ion	DL (ppbv)	Conversion Efficiency (%) ^a
Benzene	78	51 ^b	0.3	36
1,1,1-Trichloroethane	97	61	0.8	77
o-Dichlorobenzene	146	111 ^b	13	24
Acetone	59	31 ^b	1.0	34
Methyl ethyl ketone	73	55	0.1	81

^a Ratio of product ion signal intensity to isolated (parent) ion signal intensity.

^b More than one product ion observed. Sum of product ions yields conversion efficiency $\geq 75\%$.

product ion at m/z 65, which takes place with a conversion efficiency (i.e., the ratio of the fragment ion signal intensity to the initial parent ion signal intensity) of about 90%. This high conversion efficiency is typical of many positive ion MS/MS dissociations in the ion trap.

Wide Linear Dynamic Range and Low-ppb Detection. MS/MS detection limits obtained for product ions from a representative set of VOCs in humidified air are listed in Table 1. Two of the compounds, 1,1,1-trichloroethane and methyl ethyl ketone, form only one fragment ion each, and the resulting detection limits are in the sub-ppbv range with dissociation efficiencies of ~80%. However, the parent m/z 146 ion from o-dichlorobenzene dissociates to form several fragment ions. Although the conversion efficiency is high for the sum of these fragment ions, it is no more than 24% for the m/z 111 fragment and the associated detection limit is only 13 ppbv. Benzene, on the other hand, is detected with high sensitivity, despite the fact that it also yields several product ions upon MS/MS dissociation.

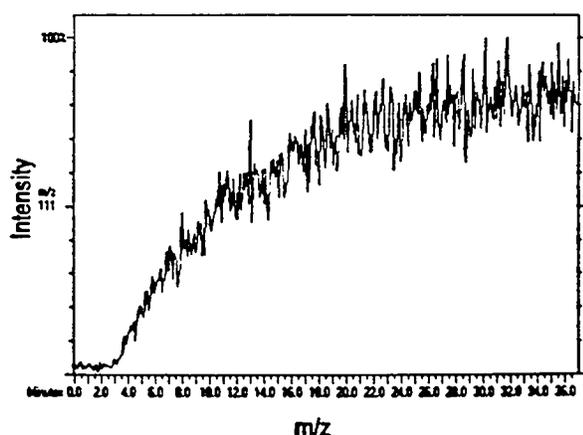


Figure 2. Increase in air concentration of p-dichlorobenzene, measured continuously in real time in the MS/MS mode, as a result of exposure of two "moth cakes" in a small storage room.

Continuous Analyte Monitoring. Figure 2 shows the "step change" in p-dichlorobenzene concentration that results when two "moth cakes" are unwrapped and placed on shelves in a small storage room. The compound was measured in the MS/MS mode by monitoring the intensity of the m/z 111 fragment ion.

Although only a single compound was monitored in this test and the increase in concentration occurred over a relatively long period of time, the system is capable of measuring several selected VOCs simultaneously in the MS/MS mode. Furthermore, the fact that measurements were made at 5-second intervals indicates that the technique can track changes in concentration that occur rapidly and at trace levels.

CONCLUSIONS

Monitoring trace levels of specific VOCs in air in the field can be effectively accomplished using the 3DQ Discovery ion trap mass spectrometer with filtered noise fields and an air sampling glow discharge ionization source as a DAS interface. The instrument provides continuous real-time measurement capability with detection limits for selected nonpolar and polar VOCs in the low- to sub-ppbv range. Although the system described here is still in the developmental stage, it has the potential for direct application in a variety of important real-world applications.

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