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Monitoring of Toxic Compounds in Air Using a Handheld Rectilinear Ion Trap Mass Spectrometer

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A miniature, handheld mass spectrometer, based on the rectilinear ion trap mass analyzer, has been applied to air monitoring for traces of toxic compounds. The instrument is battery-operated, hand-portable, and rugged. We anticipate its use in public safety, industrial hygiene, and environmental monitoring. Gaseous samples of nine toxic industrial compounds, phosgene, ethylene oxide, sulfur dioxide, acrylonitrile, cyanogen chloride, hydrogen cyanide, acrolein, formaldehyde, and ethyl parathion, were tested. A sorption trap inlet was constructed to serve as the interface between atmosphere and the vacuum chamber of the mass spectrometer. After selective collection of analytes on the sorbent bed, the sorbent tube was evacuated and then heated to desorb analyte into the instrument. Sampling, detection, identification, and quantitation of all compounds were readily achieved in times of less than 2 min, with detection limits ranging from 800 parts per trillion to 3 parts per million depending on the analyte. For all but one analyte, detection limits were well below (3.5–130 times below) permissible exposure limits. A linear dynamic range of 1–2 orders of magnitude was obtained over the concentration ranges studied (subppbv to ppmv) for all analytes.

Recently increased interest in detecting and quantifying toxic vapors has spurred the development of small, portable chemical instrumentation that can operate outside the laboratory. Ideally, such instrumentation should be sensitive, selective, and handheld, operate from batteries, and provide signal with good temporal resolution. Such devices might be employed for public safety purposes, air quality monitoring, and in controlling sensitive processes, e.g., clean room operations.

Many detection techniques could be developed to meet these requirements, although all have limitations. Gas chromatography is generally too slow to meet the emerging 5-s guideline for air analysis. Ion mobility spectrometry^{1–3} is widely deployed and highly sensitive, but has limited chemical specificity, although differential ion mobility spectrometry^{4,5} shows more promise.

Electrochemical sensors⁶ are simple and optimized for detecting particular toxic gases (e.g., carbon monoxide)⁷ and most suitable when the sample contains one or, at most, a few analytes. Additionally, they may have high limits of detection (LODs) or be subject to interference by commonly encountered species.⁶ One-use gas detection tubes are accurate and robust against interferents, although assessing the color change can be difficult near the detection threshold.⁸ Another promising approach is the use of arrays of chemical sensors such as those based on metalloporphyrin dyes; these devices are still in the early stages of development.⁹ Spectroscopic methods are virtually the only choice when stand-off detection is mandated.

Mass spectrometry (MS) provides the necessary chemical selectivity, sensitivity, and adaptability to new threat compounds. Indeed, laboratory methods incorporating mass spectrometry serve as the ultimate confirmation of the identities of many of these compounds,¹⁰ making MS the “gold standard” method in trace organic analysis. Traditionally, samples have been brought back to the laboratory; little on-site analysis has been reported. This should soon begin to change, however, as there has been considerable work over the past decade on the development of portable mass spectrometers. Mass analyzers of all types have been miniaturized,^{11,12} including magnetic sector,¹³ time-of-flight,¹⁴ ion cyclotron resonance,^{15,16} and quadrupole mass filter instruments.^{17–20}

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Of special note are the advances in miniaturizing the cylindrical ion trap (CIT), a simplified geometry version of the three-dimensional quadrupole ion trap (3D Paul trap).^{21,22} These efforts^{23–25} include the CIT-based instrument by Patterson et al.^{26,27} and its later commercialization.²⁸ Parallel arrays of small CITs^{29–31} allow the rf voltage to be decreased without loss of ion trapping capacity. However, simulations suggest that some of the smaller CIT arrays may not be fully practicable, as potential well depths are quite shallow and trapping of ions is difficult.^{29,30}

Work has also proceeded on the miniaturization of two-dimensional (2D or linear) ion traps. These devices resemble quadrupole mass filters, except that additional electrodes affixed at each end are biased to contain the ions axially. Mass analysis occurs in a fashion analogous to a 3D quadrupole trap, with the rf amplitude scanned so that ions are radially ejected through slits cut in the rods. Rectilinear ion traps (RITs)³² are simplified forms of 2D traps. Ion injection efficiency for externally created ions is >80%³³ whereas it is only about 5–10% for CITs and other 3D traps.³⁴ Newer methods of fabrication, including laser-based rapid prototyping polymerization,³⁵ provide an alternative and attractively simple method of fabricating rectilinear ion traps and their arrays.³⁶

Miniaturization efforts should aim at producing fully functioning, general-purpose, miniature mass spectrometers. The entire instrument, including the control and data acquisition electronics and vacuum system, must be miniaturized to render it truly portable. There are six such instruments of which we are aware. Syms and co-workers fabricated a quadrupole mass filter using MEMS techniques, although the rod diameter of 0.5 mm and

inscribed radius of 0.22 mm represent macroscopic dimensions.¹⁸ It forms the heart of a recently commercialized portable (10 kg) mass spectrometer.³⁷ Lauritsen developed a 12-kg mass spectrometer built around a Ferran multipole mass analyzer¹⁷ and featuring a membrane inlet, a mass range up to 300 Th (1 thompson = 1 Da/elementary charge³⁸), and <1 ppmv limits of detection.¹⁹ The toroidal ion trap^{39,40} was recently commercialized, with a mass range of 50–500 Th, a package size of 11 kg, and sample introduction by solid-phase microextraction syringe.⁴¹ Jet Propulsion Laboratory has made a full-sized quadrupole ion trap ($r_0 = 10$ mm) with miniaturized electronics and vacuum pumping. Exclusive of the miniature gas chromatograph and preconcentration unit (which add ~1 kg total), the instrument weighs 5.4 kg and consumes 42 W. The limit of detection is ~50 ppbv for gas-phase species without preconcentration and the mass range is 15–100 Th.⁴² Johns Hopkins Applied Physics Lab reported a miniature TOF system with four parallel mass analyzers in a vacuum chamber footprint of 28×32 cm². The reflectron electrodes are printed on flexible circuit board material to save weight and increase ruggedness.¹⁴ Gao et al. recently constructed a miniature instrument (10 kg)⁴³ based on the RIT.³² The present paper describes the application of this instrument to monitoring air for toxic gases.

Finally, arrays of microfabricated CIT analyzers²⁹ deserve special mention, although not elaborated into a portable instrument. Ramsey and co-workers reported two such arrays that were fabricated using phosphorus-doped polysilicon electrodes and silicon dioxide insulating layers, with either 256 or 2304 individual channels of radius 20 μ m.⁴⁴ Ions are created by internal EI; the traps are operated at 100 MHz (45–90 V). At present, only limited resolution (~5) and mass range (~140 Th) have been achieved.

The requirement of small system size limits the pumping speed of the vacuum pump used in a portable mass spectrometer. Hence, the gas load on the vacuum system must be minimized, which in turn influences the choice of sample introduction system. Trace atmospheric analysis requires either exclusion of the air matrix from the vacuum manifold, enrichment of the analyte, or both. Membrane inlet mass spectrometry (MIMS)^{45,46} is very useful, but the chemical identity of the membrane will limit the range of analytes. Gas chromatography may be employed for analyte preconcentration, but bulky carrier gas cylinders limit portability. Other preconcentration techniques, such as solid-phase microex-

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traction,⁴⁷ provide good matrix exclusion but are somewhat delicate, are not typically automated, thus requiring operator attention, and may be limited in adaptability to emerging threats by the choice of stationary phase used. A newer approach is fitting an atmospheric inlet to a miniature instrument, although the weight and size of the required pumping system is significant.⁴⁸

In this work, a thermal desorption inlet is used to sample toxic industrial compounds in air. The inlet allows preconcentration of analytes on a bed of solid sorbent material. After sampling, the tube containing the sorbent is evacuated and the adsorbed analyte molecules are introduced into the vacuum chamber of the mass spectrometer by rapid heating. This inlet provides a convenient interface between the vacuum chamber and atmosphere, is simple to construct, can be cycled rapidly, and is easily automated. This method is similar to single-sided membrane inlet mass spectrometry (SS-MIMS);⁴⁹ the main difference is the state of aggregation of the sorbent. A miniature RIT-based instrument, coupled to the thermal desorption inlet, was used in the present study for the detection, identification, and quantitation of the toxic industrial compounds phosgene, ethylene oxide, sulfur dioxide, acrylonitrile, cyanogen chloride, hydrogen cyanide, acrolein, formaldehyde, and ethyl parathion.

EXPERIMENTAL SECTION

Chemicals and Standards. All chemicals were commercially available and used without further purification. Acrolein (Supelco) and acrylonitrile (Aldrich) were obtained with purities of 98.4 and 99+%, respectively. Gaseous standards of ethylene oxide (9.38 ppmv), phosgene (10 ppmv), formaldehyde (29 ppmv), sulfur dioxide (200 ppmv), cyanogen chloride (11 ppmv), hydrogen cyanide (10 ppmv), and arsine (10 ppmv) were obtained in high-pressure cylinders from Scott Specialty Gases (Plumsteadville, PA) using nitrogen as the balance gas.

Sample Preparation. The gas-phase sample generation apparatus was described previously.⁵⁰ The system consists of two mass flow controllers (Teledyne Hastings) fitted with perfluoroalkoxy, Teflon, and stainless steel tubing to control and mix sample and diluent gas flows. The system can generate standards from high parts per trillion (pptv) to high parts per million (ppmv) levels. With pressurized gas standards, dilution of the bulk cylinder gas was accomplished with OSHA grade D breathable air (Inweld, Indianapolis, IN). For compounds available as the neat liquid, saturated headspace vapor was injected, via syringe pump, at a known rate into the diluent flow.

Sample Introduction System. The introduction system, Figure 1a, consists of a prepacked sorbent tube (Chemical Agent Monitoring Supply Co., Houston, TX) containing 10 mg each of Tenax TA and HayeSep C, two solenoid valves (ASCO Scientific), and a sample pump (model NMP015M, KNF Neuberger). Samples were drawn directly from the gas stream (T1) by the sample pump through the sorbent tube at 0.6 L min⁻¹. A three-way solenoid valve (V1) directs the sample into the tube (30 s). Next, solenoid valve V2 is closed and V1 switched to allow desorbed analyte to

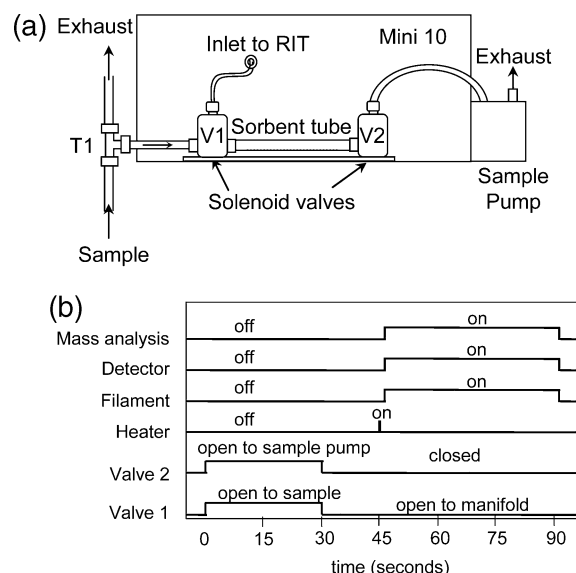


Figure 1. (a) Schematic of automated gas sampling sorbent tube system. (b) Timing diagram for experiment.

flow from the sorbent tube into the manifold. After 15 s to allow residual gas to be pumped away, the tube is heated, desorbing neutral analyte molecules from the sorbent into the RIT for ionization and analysis. The tube is heated by passing a current (2 A at 24 VDC for 3.5 s) through 60 cm of 29-gauge nichrome wire wrapped around it, causing the sorbent to reach ~240 °C within 4 s. Figure 1b shows the timing diagram for one sampling cycle, including the action of valves V1 and V2, the filament, and the detector.

Safety Considerations. The concentrations of many of these compounds' premade standards (as well as many dilutions thereof) are well above permissible exposure limits (chronic toxicity thresholds). Researchers wishing to conduct similar experiments are urged to exercise great care in sample handling and to ensure that sample lines, dilution apparatus, and pump exhausts have no leaks and are properly exhausted into appropriate waste air handling systems. It is emphasized that many of these compounds are toxic at levels below which they can be smelled—therefore scrupulous technique should be observed.

Mass Analysis and Data Acquisition. All experiments were performed using a recently developed handheld Mini 10 mass spectrometer (rectilinear ion trap analyzer, dimensions $x_0 = 5.0$ mm, $y_0 = 4.0$ mm, axial length $z_0 = 43.2$ mm, $rf = 970$ kHz, resonant ejection at 345 kHz).^{32,43} Electrons generated by thermionic emission from a rhenium filament (–25 V bias, emission current ~30 μ A) are directed into the trap through a slit in the x -electrode and controlled by an external gate lens. Upon entering the trap, electrons take up additional kinetic energy from the rf field and ionize the neutral gaseous molecules. The resulting gas-phase ions are trapped and mass selected.

The scan function has three periods: ionization (electrons admitted into the trap for 1–10 ms to effect ionization of analyte molecules), cooling (10 ms), and scan out (20 ms). During scan out, the rf amplitude is ramped to effect resonant ion ejection over the mass range of 20–95 Th. Ions are detected using a Channeltron electron multiplier (model 2312, Detector Technology), biased to –1300 V (5×10^7 gain at –2 kV) and operated without a conversion dynode. The instrument was controlled and data were

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Table 1. Toxic Industrial Compound Analysis

| compound | formula | mo wt | ion for quantitation ^a | IDLH ^b ppmv | PEL ^c ppmv | LOD, ppmv | linear dynam range | N ^d | calibration curve parameters | | | | |
|-------------------|--|--------|-----------------------------------|---------------------------|--------------------------|--------------|--------------------|----------------|------------------------------|------------------|----------------|----------------------|--------------------------------|
| | | | | | | | | | slope | std dev of slope | intercept | std dev of intercept | correl coeff (R ²) |
| acrolein | C ₃ H ₄ O | 56.06 | 57 | 2.0 | 0.1 | 0.03 | 61 | 23 | 1,518 | 32 | 62 | 32 | 0.9906 |
| acrylonitrile | C ₃ H _{3.5} N | 53.06 | 53 | 85 | 2 | 0.015 | 200 | 25 | 2,364 | 129 | 164 | 96 | 0.9363 |
| cyanogen chloride | CClN | 61.47 | 61 | 20 | 0.2 | 0.02 | 10 | 20 | 523 | 17 | 0 ^e | e | 0.9810 |
| ethylene oxide | C ₂ H ₄ O | 44.05 | 45 | 799 | 1 | 0.2 | 10 | 20 | 245 | 8 | 0 ^e | e | 0.9776 |
| formaldehyde | HCHO | 30.03 | 31 | 20 | 0.8 | 3 | 100 | 20 | 117 | 4 | 553 | 58 | 0.9798 |
| hydrogen cyanide | HCN | 27.03 | 28 | 50 | 10 | 0.18 | 14 | 7 | 59,951 | 1,838 | 7,654 | 7,698 | 0.9953 |
| ethyl parathion | C ₁₀ H ₁₄ NO ₅ PS | 291.26 | 97 | 0.84 | 0.008 | 0.0008 | 10 | 10 | 288,677 | 13,538 | 232 | 60 | 0.9827 |
| phosgene | COCl ₂ | 98.92 | 63 | 2.0 | 0.1 | 0.012 | 67 | 61 | 2,256 | 53 | 83 | 32 | 0.9685 |
| sulfur dioxide | SO ₂ | 64.1 | 48 | 100 | 5 | 1.2 | 10 | 6 | 5 | 0.32 | 14 | 9 | 0.9834 |

^a m/z of ion peak used for calibration curve. ^b Immediate danger to life and health.⁵² ^c Permissible exposure limit.⁵² ^d Number of points recorded for calibration curve. ^e Intercept set to 0 to fit calibration curve.

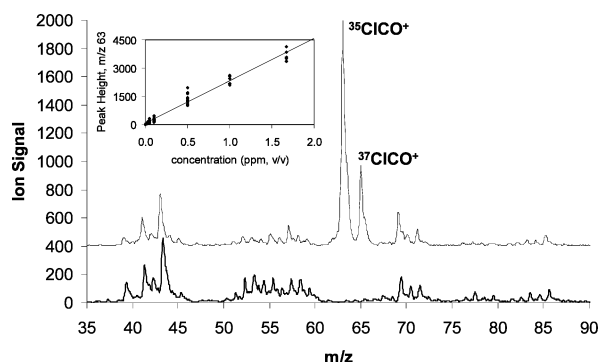


Figure 2. Mass spectrum of 500 ppbv phosgene in air (upper trace, offset for clarity by 400 units) showing peaks corresponding to ClCO^+ (m/z 63 and 65) and blank air sample (lower trace). Inset: calibration curve based on the height of the m/z 63 peak for phosgene in air.

processed using software (Version 1.7) from Griffin Analytical Technologies (West Lafayette, IN). Scans were acquired for at least 15 s during the height of analyte desorption from the sorbent trap. Every 10 scans were averaged and stored as one spectrum. For quantitative analysis, the peak height of the single most abundant ion was used, except for HCN, where the peak area was used. The peak location (m/z) used for each analyte is recorded in Table 1. Vacuum was provided by a miniature turbopump (600 L min^{-1} , Pfeiffer TPD 011) backed by a diaphragm pump (5 L min^{-1} , KNF Neuberger model 1091-N84.0-8.99). The instrument operates on battery power as previously demonstrated, although for convenience, these experiments used 120 VAC power.

RESULTS AND DISCUSSION

Phosgene. Phosgene, Cl_2CO , an important industrial reagent in manufacturing polymers, pesticides, and acid chlorides, is a carcinogen even at low gas-phase concentrations. Like many reactive chlorides, it reacts with water in the respiratory tract to form carbon dioxide and hydrochloric acid.⁵¹ The U.S. National Institute for Occupational Safety and Health (NIOSH) recommends a permissible exposure limit (PEL) of 0.1 ppmv and a concentration immediately dangerous to life and health (IDLH)

of 2 ppmv.⁵² Figure 2 shows a representative mass spectrum for 500 ppbv phosgene in air. The abundant ion signal at 63 and 65 Th corresponds to $^{35}\text{ClCO}^+$ and $^{37}\text{ClCO}^+$. No signal is observed for the molecular ion, Cl_2CO^+ , likely because of relatively facile fragmentation. The NIST quadrupole mass filter spectrum does possess a peak corresponding to Cl_2CO^+ but at only 7% of the intensity of the ClCO^+ peak (also the base peak in the NIST spectrum).⁵³

In our instrument, ionization takes place inside the RIT, and thus, relative ion abundances represent the relative ion abundances produced by electron impact convolved with the simultaneous relative trapping efficiencies of the ions of various mass-to-charge ratios. By necessity, some mass-to-charge ratios will be better trapped than others at a given rf amplitude. In choosing a fairly low mass cutoff, m/z 20, trapping at higher masses is slightly compromised.⁵⁴ We draw attention, throughout this study, to significant differences in our spectra and those in the NIST database that are attributable to differences in mass analyzers and operating conditions, especially the number of collisions suffered by the ions. A detailed comparison of ion abundances observed for spectra in this study and the NIST mass spectra is presented in Table S.1 in the Supporting Information.

A mass spectrum recorded for a blank air sample is also shown in Figure 2. Peaks resulting from slight pyrolysis of the sorbent are also present in all mass spectra. They constitute a significant fraction of total ion signal at low analyte concentrations but do not interfere with most of the characteristic analyte ion peaks. Such background peaks can be removed from consideration when matching a newly acquired mass spectrum with a mass spectral library. Differences between mass spectra acquired with this instrument and those in the NIST library can cause misidentification by a spectral matching algorithm. Thus, the best spectral identification will be obtained using a library of mass spectra generated on this instrument under the relevant conditions.

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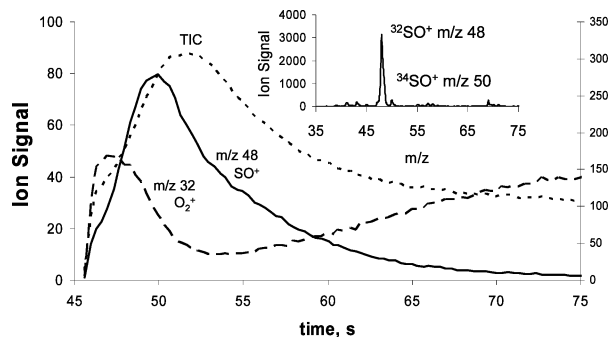


Figure 3. Ion signal vs time for the commercially available premade standard of 50 ppmv SO_2 in N_2 . Signal is plotted for m/z 48, SO^+ , (solid line, left axis); O_2^+ (m/z 32, dashed line, left axis); and total ion signal (signal at all ion masses, dotted line). Inset: mass spectrum observed at 49.9 s during the desorption profile.

A calibration curve is shown as an inset in Figure 2. The peak height at m/z 63 is linear versus concentration from 25 parts per billion (ppbv) to 1.67 ppmv, corresponding to a linear dynamic range of at least 67; greater concentrations were not tested. The statistically based estimate of the LOD⁵⁵ for phosgene is 12 ppbv, with false positive and false negative rates specified at 5%. Details of calibration curves, as well as statistically estimated LODs are presented in Table 1. Our LOD compares favorably with that of 250 ppbv observed by Bocos-Bintintan et al. using a membrane inlet IMS with a ^{63}Ni ionization source.⁵⁶ Some caution should be exercised in comparing LODs between studies, as various researchers may use different definitions of the detection limit.⁵⁷

Sulfur Dioxide. SO_2 is directly emitted into the atmosphere by both fossil fuel combustion and natural sources (e.g., forest fires and volcanoes). It is the source of atmospheric sulfuric acid and an important nucleation species for particulates and droplets with significant implications for global climate. Figure 3 shows ion chronograms for m/z 48 (SO^+), 32 (O_2^+) and the total ion signal for the commercial premade standard of 50 ppmv SO_2 in nitrogen. The time indicated on the x -axis is referenced to the beginning of the experiment, when air sampling first begins. The increase in SO^+ signal upon heating the sorbent (from $t = 45$ s to $t = 48.5$ s) indicates that SO_2 is retained by the HayeSep C/Tenax TA sorbent combination. The signal at m/z 32 results from background O_2 in the vacuum manifold; it decreases as the signal for all other ions increases. Although the total ion current includes a contribution from SO^+ , it is composed mostly of sorbent peaks, especially immediately after heating. Total ion signal, including that for SO^+ and O_2^+ , increases rapidly at $t = 45$ s, when instrument components were turned on.

The inset in Figure 3 shows the mass spectrum recorded at $t = 47$ s. The SO^+ peak is at 48 Th with the ^{34}S isotope peak visible at 50 Th. No molecular ion signal (SO_2^+) at 64 Th was observed, whereas the NIST spectrum shows a peak for SO_2^+ that is twice the size of the SO^+ peak.⁵³

Using the $^{32}\text{SO}^+$ peak as the basis of quantitation, response was measured at 5 and 50 ppmv; on this limited basis, it appears to scale proportionally. A LOD of 1.2 ppmv is estimated. In

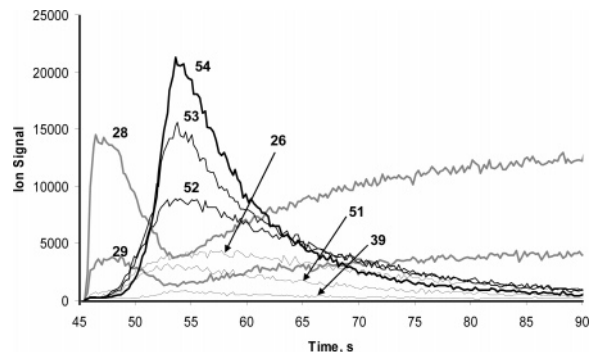


Figure 4. Temporal profiles for several ions observed for 500 ppbv acrylonitrile in air. The signal from m/z 53 corresponds to the molecular ion for acrylonitrile. Ions at m/z 26, 39, 51, 52, and 54 all exhibit temporal profiles consistent with the desorption, ionization, and subsequent fragmentation or protonation of acrylonitrile. The signals for ions at m/z 28 and 29 exhibit no such correlation with m/z 53 and, therefore, do not result from the ionization of acrylonitrile. The sorbent bed heating took place from 45 to 48.5 s; ionization commenced at 45 s.

comparison, using a laboratory-scale instrument, Cotte-Rodriguez et al. reported an LOD of 150 ppbv using negative ion APCI,⁵⁰ Thornton achieved a detection limit of ~ 1 part per trillion with APCI.⁵⁸ Such disparity is not unexpected, given the generality of our method and that the sorbent system, both in temperature and in chemical identity, is far from optimal for SO_2 collection.

Cyanogens: Acrylonitrile, HCN, and C₂H₂. *Acrylonitrile.* Acrylonitrile is a water-soluble synthetic compound, used in the production of plastics and acrylic fibers. U.S. annual production was 1.3×10^6 metric tons in 2005.⁵⁹ Gas-phase concentrations above the PEL of 1 ppmv may irritate the eyes; the IDLH is 85 ppmv.⁵² Figure 4 shows temporal profiles for three forms of molecular ions, at m/z 54, 53, and 52, corresponding to MH^+ , M^+ , and $[\text{M} - \text{H}]^+$. All exhibit time dependences consistent with molecular desorption from the sorbent. Ions at m/z 51 ($[\text{M} - 2\text{H}]^+$), 39, and 26 (CN^+), although less abundant, have similar temporal profiles. Ion signals at m/z 28 and 29 exhibit anticorrelated temporal profiles and thus are identified as chemical noise from the sorbent and not analyte fragment ions. As in Figure 2, the increase in signal immediately at 45.5 s is the result of filament turn-on. As may be discerned by inspection of Figure 4, signal resulting from analyte desorption maximizes at ~ 55 s. Signal was very intense and recorded using only 1-ms ionization time. Under these conditions, detector saturation occurred at 2 ppmv concentration.

This experiment shows the utility of temporal profiles in assigning the identity of fragment ion peaks, at least when only analyte and background peaks are present. Chronograms have been presented in this paper to illustrate typical preconcentration/desorption behavior. An area of future endeavor might be the adjustment of sorbent selectivity, heating program, and other parameters to exploit different temporal desorption behaviors to aid in analyte identification.

The NIST mass spectrum has strong peaks at m/z 53 (base peak), 52 (72% intensity relative to base peak), 51 (28%), and 26

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(85%); the only substantial difference is the appearance of MH^+ at 54 Th in the present experiment. This is ascribed to protonation of neutral acrylonitrile (proton affinity of 785 kJ/mol⁶⁰) by H_3O^+ ($\text{PA}[\text{H}_2\text{O}] = 691 \text{ kJ/mol}$),⁶⁰ exothermic by 94 kJ/mol. The diluent gas contains as much as 9% relative humidity;⁶¹ no measures were taken to exclude water vapor from the experiment, and ion trap experiments can favor ion/molecule reactions.⁶² Self-chemical ionization, “self-CI” cannot be ruled out in this instance.

Hydrogen Cyanide. HCN vapors can be generated easily by adding acid to aqueous solutions of alkali metal cyanides. (Safety note: do not attempt this experiment without adequate ventilation.) HCN is a colorless gas or liquid (boiling point 25.6 °C)⁵¹ with a bitter, almond-like odor.⁵² IDLH is 50 ppm;⁵² exposure to 300 ppm may result in human death in as little as a few minutes.⁵¹ The mass spectrum (not shown) recorded using the miniature instrument shows only the protonated species H_2CN^+ at 28 Th. The protonated molecule is observed under all experimental conditions, including the highest HCN concentration, where the premixed HCN standard (11 ppmv, balance N_2) is directed into the instrument without dilution. LOD is estimated at 180 ppbv. By comparison, Smith and co-workers could quantitate between 800 ppbv and 52 ppmv HCN, using a carboxen/PDMS SPME fiber and GC/NPD or GC/MS.⁶³ Meanwhile, the NIST mass spectrum shows a very intense signal for HCN^+ at 27 Th, with only minimal signal at 28 Th, attributable to the ^{13}C isotopomer.⁵³ Protonation of HCN to yield H_2CN^+ by H_3O^+ is thermodynamically favorable being exothermic by 22 kJ/mol. Self-CI, involving the formation of HCN^+ by EI, followed by its protonation of a second HCN molecule ($\text{PA} = 712.9 \text{ kJ/mol}$)⁶⁰ to form H_2CN^+ is another possible mechanism for the production of H_2CN^+ . This reaction is exothermic by 184 kJ/mol.^{64,65}

Cyanogen Chloride. ClCN closely resembles HCN in its toxicity, method of toxic action, and use as a toxic agent. As a reaction intermediate, cyanogen chloride is used in manufacturing pesticides, pharmaceuticals, and fertilizers.⁵¹ Figure 5 shows mass spectra for two samples, the commercially available premade standard of 10.9 ppmv ClCN in N_2 (lower trace) and also containing 1% synthetic second-hand smoke mixture (Scott Specialty Gases, upper trace). Ion signals at m/z 61 and 63, corresponding to $^{35}\text{ClCN}^+$ and $^{37}\text{ClCN}^+$, occur in both spectra. The NIST spectrum also contains peaks at m/z 26 and 35/37, CN^+ and Cl^+ , respectively, both $\sim 10\%$ relative to $^{35}\text{ClCN}^+$. However, we observe no significant signal for Cl^+ and that for m/z 26 is $< 4\%$ of that for ClCN^+ . It is interesting to note that the proton affinity of ClCN, 722 kJ/mol,⁶⁰ is higher than that of HCN (713 kJ/mol), for which we see exclusively the protonated molecule. A possible explanation for the absence of HClCN^+ is that protonation of HCN occurs mainly by self-CI, which is precluded in the case of ClCN by the lack of a hydrogen atom.

Figure 5 demonstrates that, at this concentration, the ClCN analyte peaks are readily discernible from chemical noise peaks

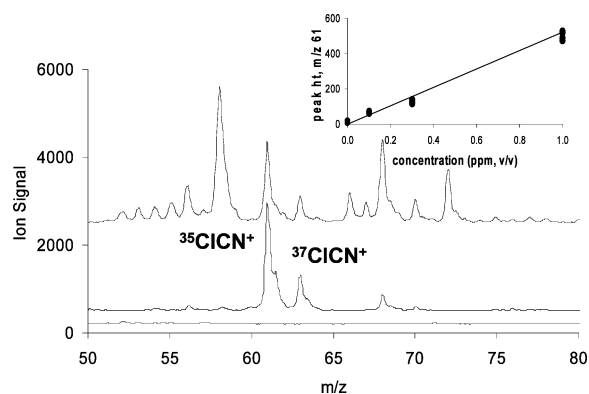


Figure 5. Mass spectra for air blank (bottom trace, offset by 200 intensity units), premade standards of 10.9 ppmv ClCN in N_2 (middle trace, offset by 500 units) and mixed with second-hand smoke interferent (top trace, offset by 2500 intensity units). Inset: calibration curve for ClCN in air; LOD is estimated as 40 ppbv.

in a complex matrix. The figure also suggests the increased certainty of analyte identification when ions of more than 1 m/z (viz. Cl isotope signature) can be used. In contrast, single ion peaks are still useful for preliminary identification of an analyte or as the starting point for tandem mass spectrometry where transitions to characteristic fragment ion masses are sought. More generally, matrix components (including water vapor and possibly other analytes) can decrease analyte ion signal in three ways: (i) reaction with analyte in the sample; (ii) ion/molecule reactions in the vacuum chamber, and (iii) displacement of analyte from the sorbent. Additionally, very abundant matrix ions have the possibility of causing space charge effects, including shifting the apparent m/z assignments of other ions.⁶⁶ In turn, misquantitation results if the m/z shift is not taken into account, with either increases or decreases in apparent analyte ion abundance being possible. Such space charge effects may be mitigated by accumulating ions while simultaneously applying an auxiliary ac waveform to eject the matrix ions. With such a method, Soni et al. were able to detect toluene in water at 500 parts per quadrillion.⁶⁷ Matrix compounds could also generate isobaric interference ions at one or more of the analyte's characteristic ions. In principle, many of these effects can be anticipated and compensated for by calibrating key analytes in the presence of the most commonly encountered interferents for the field application. Suppression effects—due to matrix components or other analytes—are not expected with electron impact ionization, used in this study.

Aldehydes. Acrolein. The PEL of acrolein is 0.1 ppmv and its IDHL is 2 ppmv.⁵² According to the U.S. Environmental Protection Agency, acute inhalation exposure to 10 ppmv or higher levels of acrolein can cause death and lower levels can affect the lungs and the respiratory tract. Sources of acrolein include car exhaust, tobacco smoke, and second-hand smoke.^{68,69} Tang and co-workers recently showed that acrolein causes DNA mutations similar to those found in human lung cancer.⁷⁰

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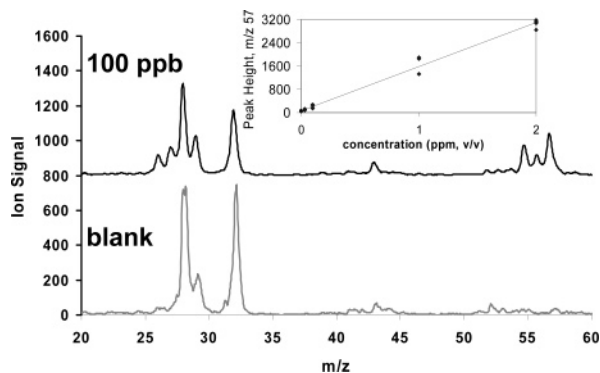


Figure 6. Mass spectrum of 100 ppbv acrolein. Inset: calibration curve.

Figure 6 depicts the mass spectrum of 100 ppbv acrolein in air. The molecular cation, M^+ , is at 56 Th. An ion with approximately twice the abundance of the molecular cation occurs at 57 Th, presumably due to MH^+ , which would be the result of ion/molecule reactions that are favored in ion traps. This peak is not present in the NIST mass spectrum⁵³ nor in that reported by Choudhury,⁷¹ who analyzed acrolein in water using membrane introduction with EI. Another prominent peak occurs at 55 Th, due to $[M - H]^+$. The large abundance of $[M - H]^+$ fragment ion is characteristic for aliphatic aldehydes generally⁷² and for acrolein specifically.⁷¹ Formation of $[M - H]^+$ from both the protonated molecular species⁷³ and the molecular radical cation⁷⁴ has been proposed. Peaks from m/z 26 to 29 are consistent with previously reported EI spectra. The peak at m/z 32 is residual oxygen. Other peaks at m/z 52, 53, and 54, although at very low levels, appear to correlate with the introduction of acrolein into the instrument. These peaks are also not present in the EI spectra of NIST or the Choudhury study. These small peaks may be due to multiple hydrogen losses from the species at m/z 55, 56, or 57 given what may be a complex ionization environment. Peaks from m/z 42 to 46 are due to sorbent. The LOD of 30 ppb compares favorably with Dettmer et al., who examined concentrations of ~100 ppb using a Carboxograph 5 sorbent trap interfaced to GC-FID with sampling time of 10 min and desorption time of 5 min.⁷⁵

Formaldehyde. Formaldehyde is a colorless, flammable gas at room temperature, with a “pungent and suffocating odor.”⁵¹ PEL is 0.8 ppmv, and IDLH concentration is 20 ppmv.⁵² Figure 7 shows spectra for two formaldehyde samples with different concentrations as well as a blank sample. At 3 ppmv, the protonated molecule, H_2COH^+ , appears as a shoulder at m/z 31 on the very large O_2^+ peak at m/z 32. At 29 ppmv, the shoulder has developed into a large peak. In addition, a peak at m/z 61, due to the

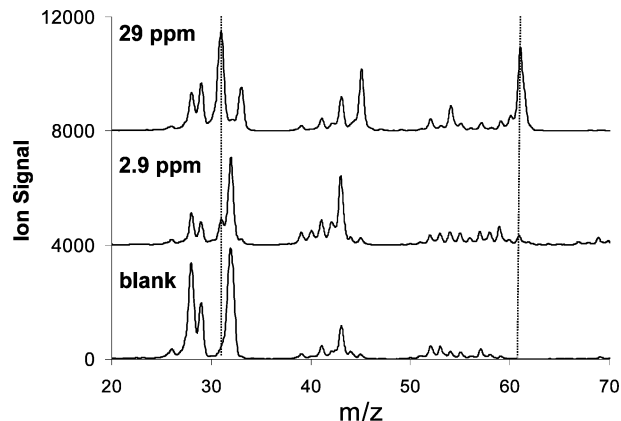


Figure 7. Mass spectra of a blank (air), 2.9 (offset by 4000 intensity units) and 29 ppmv (offset by 8000) formaldehyde. The growth of protonated formaldehyde at m/z 31 can be observed as well as that of protonated formaldehyde dimer at m/z 61. Dotted lines are added at m/z 31 and 61 to guide the eye.

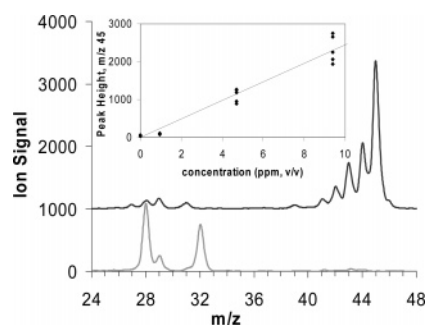


Figure 8. Mass spectrum for ethylene oxide. Lower curve is air blank, and upper curve is 9.38 ppmv, offset by 1000 intensity units. Inset: calibration curve for ethylene oxide, peak height of m/z 45 vs concentration.

protonated formaldehyde dimer, $(H_2CO)_2H^+$, appears for both concentrations. The peak heights at both 31 and 61 Th are proportional to the formaldehyde concentration. Signals at m/z 39, 41, 43, and 45 are from the sorbent (as may be affirmed by inspection of, for example, the blank spectrum in Figure 2). Other peaks that correlate with formaldehyde concentration are at m/z 33 and 45. Formaldehyde is produced by the catalytic oxidation of methanol; the latter's possible presence as a contaminant would explain the peak at m/z 33. Also, further oxidation during the production of formaldehyde would produce traces of formic acid (molecular weight of 46), which may explain the peak at m/z 45.

Ethylene Oxide. The PEL of ethylene oxide has been set at 1 ppmv and the IDLH at 799 ppmv.⁵² In the spectrum (Figure 8), the largest peak is due to the protonated molecule, $C_2H_4OH^+$, at m/z 45 ($PA = 774.2$ kJ/mol).⁶⁰ The molecular ion is observed at m/z 44, and a succession of hydrogen-losses yield peaks at m/z 43, 42, and 41, while ions of m/z 31 and 27 are due to the fragments H_3CO^+ and $C_2H_5^+$, respectively. Response of m/z 45 is linear from the LOD of 200 ppbv to 9.4 ppmv. In previous work from this laboratory, the protonated species at 45 Th was created by APCI and monitored by a commercial bench top mass spectrometer, with LOD of 6 ppbv.⁵⁰ Tsai and colleagues invented an SPME fiber-based sampling device to be worn by personnel; the PEL concentration could be detected after 1 h of sampling.

Ethyl Parathion. The organophosphate insecticide ethyl parathion has a PEL of 8.4 ppbv, while the IDLH level is 840 ppbv.⁵²

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The most abundant ion in the mini instrument's spectrum occurs at 97 Th, identified previously as a major fragment ion peak obtained under EI conditions.^{53,76} The NIST database shows the most intense ion at m/z 291, M^+ , m/z 97 is the third most intense peak at ~65% relative to m/z 291. We observe no higher mass fragments; the signal at m/z 97 is by orders of magnitude the most intense ion peak for ethyl parathion under our conditions. The estimated LOD is 800 parts per trillion, the lowest LOD of the nine analytes. This seems roughly comparable with Riter's LOD of 50 ppb for the pesticide lindane using SS-MIMS with a PDMS stationary phase and a sampling time of 10 s.⁴⁹ Our results also demonstrate the excellent efficiency of the sorbent (Tenax TA/HayeSep C) in preconcentrating organic compounds with significant hydrophobic character, like parathion. Nonetheless, this sorbent, although not optimized for the task, has also performed remarkably well even with low molecular weight inorganic gases like SO_2 and HCN.

Detection limits reported here, of course, obtain for the experimental conditions and parameters used, including the 2-min total analysis time. The sorbent trap is the rate-limiting step in the experiment; acquisition of mass spectra can be as short as 1 s (20 mass spectra at 50 ms each). Sampling time, as well as details of the desorption profile, affects time-sensitivity trade-offs. So, for example, sampling times could be cut as much as 10-fold, with presumably a 10-fold decrease in sensitivity. Heating and post-sample cleaning may also be reduced; decreasing overall analysis times per sample to as little as 30 s with incremental changes to the trap. Conceivably, given the very short times achieved by Riter et al. with SS-MIMS,⁴⁹ SPME, or SS-MIMS with coaxial heating could take only 10 s, thereby coming very close to the 5-s goal.

CONCLUSION

A miniature, handheld mass spectrometer, applied to the problem of atmospheric monitoring of toxic industrial compounds, has been used successfully to determine nine analytes of interest, with LODs between 800 pptv and 3 ppmv. For eight of nine analytes, the LOD ranged from 3.5 to 130 times smaller than the PEL. These results underscore the utility and potentially broad

applicability of handheld mass spectrometers for the detection, identification, and quantitation of gaseous species in the field. Monitoring of industrial and urban atmospheres as well as accident sites is indicated. MS provides specific identification, based on the mass-to-charge ratios of the characteristic ions of the compounds of interest. Deployment of hand-portable instruments in the field will allow improved decision-making, especially in the early stages of a crisis involving the release of toxic gaseous species.

The current instrument also compares favorably with our previous miniature instrument, the Version 8 cylindrical ion trap-based mass spectrometer with atmospheric inlet.⁶³ That instrument produced LODs of 1–10 ppbv using APCI, with linear dynamic ranges of 1–2 orders of magnitude, whereas the performance of the current much smaller instrument includes LODs ranging from 1 to 200 ppbv, but with similar linear dynamic range. The current study emphasizes that the pumping limitations of small instruments can be overcome. A sorbent trap with appropriately chosen sorbent material was demonstrated to good effect. We anticipate that the Mini 10 will be amenable to new inlet configurations and ionization methods in the future. We also anticipate further reduction in the size of related systems and work on this and on the addition of other ionization and introduction methods, including atmospheric pressure sampling methods.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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