

**MINIATURIZED GAS CHROMATOGRAPH-PAUL ION TRAP SYSTEM:
APPLICATIONS TO ENVIRONMENTAL MONITORING**

B. J. Shortt¹, M. R. Darrach¹, Paul M. Holland², and A. Chutjian¹

¹Atomic and Molecular Collisions Group, Jet Propulsion Laboratory,

California Institute of Technology, Pasadena CA

²Thorleaf Research, Inc., Santa Barbara, CA

ABSTRACT

A miniature gas chromatograph (GC) and miniature Paul ion trap (PT) mass spectrometer system has been developed for identifying and quantifying chemical species present in closed environments having a complex mixture of gases. Inherent to the system are high sensitivity, good dynamic range, good PT resolution, low GC flow rates to minimize pump requirements and the need for consumables, and the use of a modular approach to extract and identify volatile organic compounds dissolved in water. Measurements are reported on system response to gaseous species at

concentrations varying over four orders of magnitude. The GCPT has a mass, volume, and power that is, conservatively, 1/20th that of commercial off-the-shelf systems. Potential applications are to spacecraft cabin-air monitoring, robotic planetary exploration, and trace-species detection for (terrestrial) residual gas analysis and environmental monitoring.

INTRODUCTION

Detection of trace amounts of volatile organic compounds (VOCs) in complex gaseous mixtures is a common requirement in environmental monitoring. From NASA's point of view, the quality of

spacecraft breathing air during long-duration human missions is critical to astronaut safety. Real-time cabin air monitoring must identify and quantify a number of chemical contaminants, over a range of concentrations, and often in the presence of high concentrations of interferences such as water vapor, CO₂, and lubricating oils. Target chemical groups include alkanes, alcohols, glycols, aldehydes, ketones, aromatic hydrocarbons, and siloxanes. The system must also have sufficient dynamic range to track the rapid appearance of large amounts of contaminants through a spill or fire; and should have the ability to identify trace amounts of *unknown* species that are not on a targeted list.

Gas chromatography (GC) - mass spectrometry (MS) is a selective, sensitive, analytical tool for the identification and quantification of chemical compounds. While MS alone can identify compounds from their positive- or negative-ion electron-impact fragmentation patterns, it may

encounter difficulty in dealing with mixtures, especially when an analyte is present at low levels. Use of a front-end GC provides rapid separation of complex chemical mixtures. This "predisposition" of the analytical sample presents to the MS a *time-separated sequence* of compounds for detection and identification, allowing trace-level species to be detected in the presence of large backgrounds. The fragmentation spectrum for each compound can be used to identify specific structural features of the molecule, and when correlated with characteristic GC retention times, provides positive target identification.

GCMS instruments for space flight must be robust, use a minimum of consumables, be autonomous, and have minimum mass, volume, and power characteristics. Fortunately, robustness is enhanced by miniaturization. For a dimensional scaling factor k (<1), the mass of an instrument decreases more rapidly (as k^3) than does cross-sectional area (varying as

k^2). Hence the mechanical strength of components is enhanced. Also, electric field strengths increase as k^{-1} due to smaller electrode spacings, so that electrostatic devices require lower operating voltages for a fixed electric field. Finally, small size significantly decreases the amount of analyte required, allowing reductions in other supporting systems such as pumps, getters, adsorbants, and reservoirs.

Described in this paper are recent developments in miniature mass spectrometry and miniature gas chromatography. The approach builds on work in designing and characterizing a miniature quadrupole mass-spectrometer array (QMSA)¹ which has been flown to the International Space Station for ammonia leak detection exterior to the ISS hull². It also builds on the development of a miniature GC that has been coupled to both the QMSA³ and to several Paul ion trap mass spectrometers^{4,5}.

EXPERIMENTAL CONSIDERATIONS

The GC-Paul Trap (PT) system consists of three basic modules. These are the preconcentrator (PC), the GC injector and column, and the PT mass spectrometer. A schematic diagram of the system is given in Figure 1. Details of the PT have been published elsewhere^{4,5}, and description of the GC (without the PC module) coupled to the miniature QMSA has also been published⁶. By way of summary, the PT is of the hyperboloidal type with an inner radius of $r_0 = 1.000$ cm and a trap center-to-endcap distance of $z_0 = r_0/\sqrt{2}$. The end caps are grounded and the ring electrode carries the ramped radiofrequency potential. The Paul trap was designed at JPL, and fabricated of chemically pure titanium.

A pulsed electron beam produces ions in the trap. The amplitude of the ring voltage controls the number and charge/mass of the trapped ions. Mass analysis of the ions is accomplished by rapidly pulsing "off" the electron ionizer current, pulsing "on" the high voltage of the

channel-type electron multiplier, then ramping the amplitude of the ring voltage. The destabilized ions are ejected through a hole in the end-cap electrode, and are detected by the electron multiplier. The number of detected ions is recorded as a function of the ramp voltage. This becomes the mass spectrum of the ions that were stored in the trap. A complete cycle of trapping and ejection is given in Figure 2 of Ref. 4.

The cycle of ionization, trapping, ejection, and ion detection is repeated at a rate of 50 s^{-1} . The detected ion signal was found to be linear with the trap cycle rate. No helium buffer gas was used, and ions are trapped by the dynamic well depth of the trap itself. The overall sensitivity of the trap is 2×10^{12} counts/torr-s without the preconcentrator, corresponding to a detection limit of about 50 ppb. As the carbon molecular sieve has a different affinity for each chemical compound, it is not possible to state a single value for the

overall sensitivity of the system with the PC. However, enhancements of as high as 50-100 have been measured, which make the system sufficient to meet NASA's cabin-air requirements⁷.

A parameter of interest is the mass resolution of the complete GC-PT system. Narrow full widths at half-maximum and tenth-maximum are essential for clearly separating, to baseline, adjacent mass peaks in order to identify the analytes on the basis of their positive-ion fragmentation patterns. Good baseline resolution is also essential for resolving isotopes (useful in age-dating studies, or to obtain evidence of biological activity) that have adjacent masses with very different abundance, such as the pairs $^{16,17}\text{O}$, and $^{40,41}\text{K}$. The PT used in this study has a resolution of $m/\Delta m \approx 220$ (FWHM) due to an out-of-tolerance machining of one end cap. It is worth noting however that we have routinely reported resolutions as high as⁵ 1565. The mass range of the PT extends from 15 to 100 u. It is determined by the

trap dimensions, the trapping angular frequency, and the amplitude of the radiofrequency voltage.

Data acquisition is controlled by custom software written in C language using a LabWindows/CVI development environment and a National Instruments 6733 multifunction DAQ card. Custom built MOSFET-based pulsing circuits are used to switch the electron beam and detector high voltage “on” and “off” as required. The experimental timing scheme can be varied through the acquisition and control software.

For sample preparation, a stock concentration of a given VOC is first made by injecting the appropriate quantity of liquid (typically several μL) into the septum of a Tedlar bag. Lower concentrations are obtained by successive dilutions of the stock bag into additional Tedlar bags filled with He at one atm. Fresh concentrations of each compound are prepared and tested on the same day. Certified gas tight syringes are

used in each step of the sample preparation procedure. The preconcentrator (PC) consists of a miniature thermal desorption trap containing a carbon molecular sieve (*Carboxen 1000*). The GC is a 10 m DB Wax column with a bore diameter of 100 μm ID and a stationary phase thickness of 0.2 μm .

A miniature pump draws the sample over the PC for a predetermined exposure time, typically 30-120 s. During this time the VOCs present in the sample adsorb onto the PC. Upon completion of the sampling, the PC is back flushed with helium to remove residual atmospheric gas from the system. The PC is then heated to desorb the sample into a much smaller volume, thereby preconcentrating the analytes. A thermocouple mounted on the PC is used to control the desorption temperature, which is typically set to 200C. A flow of He at a pressure of 5 psi carries the desorbed preconcentrated vapor onto the sample loop of the micromachined GC injector. A time

slice of the total vapor desorbed from the PC (approximately 10%) is then injected onto the GC column.

RESULTS AND DISCUSSION

The analytes selected for demonstration of the CGPT system were based on NASAs requirements for space cabin-air safety. The complete list of species and required minimum detection limits (MDLs) are available at the NASA website ⁷. The analytes studied herein are a subset of that longer list.

A range of preconcentrator exposure times (30-120 s) was used for determination of the lowest limit of detection (LLD – we use this notation to distinguish it from the NASA-required MDL). As such the LLDs have been normalized so that the detection limits reflect the expected levels for a 60 s preconcentrator exposure. Measurements (not shown here) give a linear response of signal to PC exposure time. As such the normalization to a common exposure time was deemed valid. Results of the present

GCPT measurements for six gases are given in Table 1. The range of LLDs reflects the fact that the carbon-based PC has a different affinity for each organic compound. The LLDs reported are, except for acetaldehyde and hexamethylcyclotrisiloxane, below the MDLs required by NASA. For example, the LLD for furan is 10 times below the specified limit, and the LLD for ethanol is 2500 times below the required level.

Positive identification of each species at its LLD has been made on the basis of its characteristic GC elution time and its unique fragmentation pattern. The fragmentation patterns were compared with the NIST/EPA/NIH mass spectral library. In all cases the agreement between database and experimental patterns is excellent. Small variations in the relative abundance of mass fragments for a given compound were observed. This is very likely due to the fact that the ionization energy of electrons inside the PT is somewhat uncertain. Electrons are injected into the trap with a low value of the

rf trapping voltage present. This leads to an acceleration of the electron beam, and to a different ionization impact cross section (and branching fractions) than encountered for the case of the NIST tabulation at the standard 70 eV ionization energy.

The dynamic linear range of the system is shown in Figure 2. Measurements were made using standard dilutions of benzene using Tedlar gas sampling bags and gas-tight syringes. The criterion applied to determine the LLD of a species is that the integrated area of the GC elution peak should contain 1000 net counts. As such, it is evident from Figure 2 that the LLD for benzene for a 120 s PC exposure is approximately 0.2 ppb. Hence the linear dynamic range of the system extends over at least five orders of magnitude. It was necessary to decrease the PC exposure time for mixtures with benzene present at greater than about 0.1 ppm. This was done to prevent a roll-off of the curve due to space charge effects in the ion trap described

above. The data points above 0.1 ppm have been normalized to account for the shorter PC exposure time.

In order to explore the GCPTs suitability for real-time, cabin-air monitoring, the response to several complex gas mixtures with varying constituent concentrations was investigated. Excellent separations have been obtained with several six-component mixtures. These were: (a) a BTEX sample at component concentrations of 14 ppb, and (b) a mixture of acetone, ethyl acetate, 2-butanone, benzene, ethanol, and toluene at component concentrations of 0.4-21 ppb. An example of the system's ability to perform separation and identifications, as well as the effect of interferences, is shown in Figure 3. The interferences in this case were chosen to mimic those encountered in a spacecraft cabin atmosphere. A Tedlar bag was prepared with acetone and benzene at concentrations of 17 and 21 ppb respectively. GCPT analysis yielded two

peaks at elution times of 80 s and 180 s. Examination of the mass spectra during these elution peaks confirmed the peaks as acetone and benzene. A second Tedlar bag was prepared with identical acetone and benzene concentrations, and with the following contaminants added: hydrogen at 400 ppm, carbon dioxide at 1% and freon 113 at 150 mg/m³. As can be seen from Fig. 3 the presence of the contaminants did not affect the system's ability to identify and quantify the desired compounds.

Finally, the specifications of the mini-GCPT system can be compared to those of a commercial ion trap system. From this comparison (shown in Table 2) one sees the mass range, resolution, sensitivity, and dynamic range of the two systems are comparable; but with a mass-volume-power of the present system that is 10-20 less than the commercial unit.

A number of improvements to the GCPT system are in progress or planned.

(1) Temperature focusing can be used to

collect all of the material desorbed from the PC for injection onto the GC column. (2) Miniature electronics, especially of the air-core transformer, can significantly reduce the mass-volume-power of the system. (3) With an additional water-extraction module, the GCPT system can be used for water-purity monitoring on spacecraft. Efforts in these three areas are underway in our laboratory.

CONCLUSIONS

A miniaturized GCPT system capable of identifying and quantifying target compounds to the 0.4-0.6 parts-per-billion level has been developed. Good dynamic range, GC separation, and mass resolution of the system have been demonstrated, as well as the ability to deal with interferences commonly found in spacecraft cabin air.

ACKNOWLEDGMENTS

BJS acknowledges support through the Caltech Postdoctoral Scholars Program. This work was carried out at the Jet Propulsion Laboratory, California Institute

of Technology, and was supported by the
National Aeronautics and Space
Administration through agreement with the
California Institute of Technology.

REFERENCES

- [1] Orient, O. J.; Chutjian, A.; Garkanian, V. *Rev. Sci. Instr.* **1997**, *68*, 1393.
- [2] Abbasi, T.; Christensen, M.; Villemarette, M.; Darrach, M.; Chutjian, A. *SAE Technical Paper Series 2001-10-2405*; SAE: Warrendale, PA, 2001.
- [3] Chutjian, A.; Darrach, M. R.; Garkanian, V.; Jackson, S. P.; Molsberry, T. D.; Orient, O. J.; Karmon, D.; Holland, P. M.; Aalami, D. *SAE Technical Paper Series 2000-01-2300*; SAE: Warrendale, PA, 2000.
- [4] Orient, O. J.; Chutjian, A. *Rev. Sci. Instr.* **2000**, *73*, 2157.
- [5] Orient, O. J.; Chutjian, A. *Rev. Sci. Instr.* **2003**, *74*, 2936.
- [6] Holland, P. M.; Chutjian, A.; Darrach, M. R.; Orient, O. J. *Proc. SPIE* **2003**, *4878*, 1; Eds. Bearman G. H., Beauchamp, P. M.; Bellingham, WA.
- [7] See <http://www.jsc.nasa.gov/toxicology/SMACSDB.pdf>

Table 1. Summary to date of the Lowest Limits of Detection (LLDs) and NASAs required
 Minimum Detection Level (MDL) for Six Volatile Organic Compounds as measured
 with the miniature GCPT system.

compound	MDL/LLD (ppb)	compound	MDL/LLD (ppb)
acetaldehyde	100/136	freon 113	2000/9
benzene	10/0.4	isoprene	50/0.8
dichloromethane	30/0.7	octamethylcyclotrisiloxane	50/4

Table 2. Comparison of the JPL miniature GCPT system with a Commercial-off-the-Shelf system. The miniature GCPT system data include all electronics, with a 10 ℓ /s turbomolecular pump. Data in brackets are estimates with miniature electronics currently under development.

Component	Miniature GCPT System	Commercial GCPT System
mass spectrometer type:	Paul ion trap	Paul ion trap
ionization mode:	electron impact (70 eV nominal energy)	electron impact (70 eV nominal energy)
mass range: (u):	15-100 ^a	10-1000
mass resolution ($m/\Delta m$):	1565 ^b	comparable
system sensitivity:	2×10^{12} counts/torr-s ^c	comparable
dynamic range ^d	10^5	10^5 - 10^6
system mass (kg):	5.4 [4.6] ^e	130
system volume (L)	1.6 [1.5] ^e	304
system power (W)	42 [35] ^e	4000

^a expandable to the range 1-1000 u using two rf oscillators

^b as reported in Ref. 5, but the resolution was $m/\Delta m=220$ herein

^c without the PC, see Table 1 for LLDs with the PC

^d can be increased by a factor of 3-5 with faster detecting electronics

^e includes a 10 ℓ /s turbomolecular pump and a 4.5 ℓ /m scroll backing pump

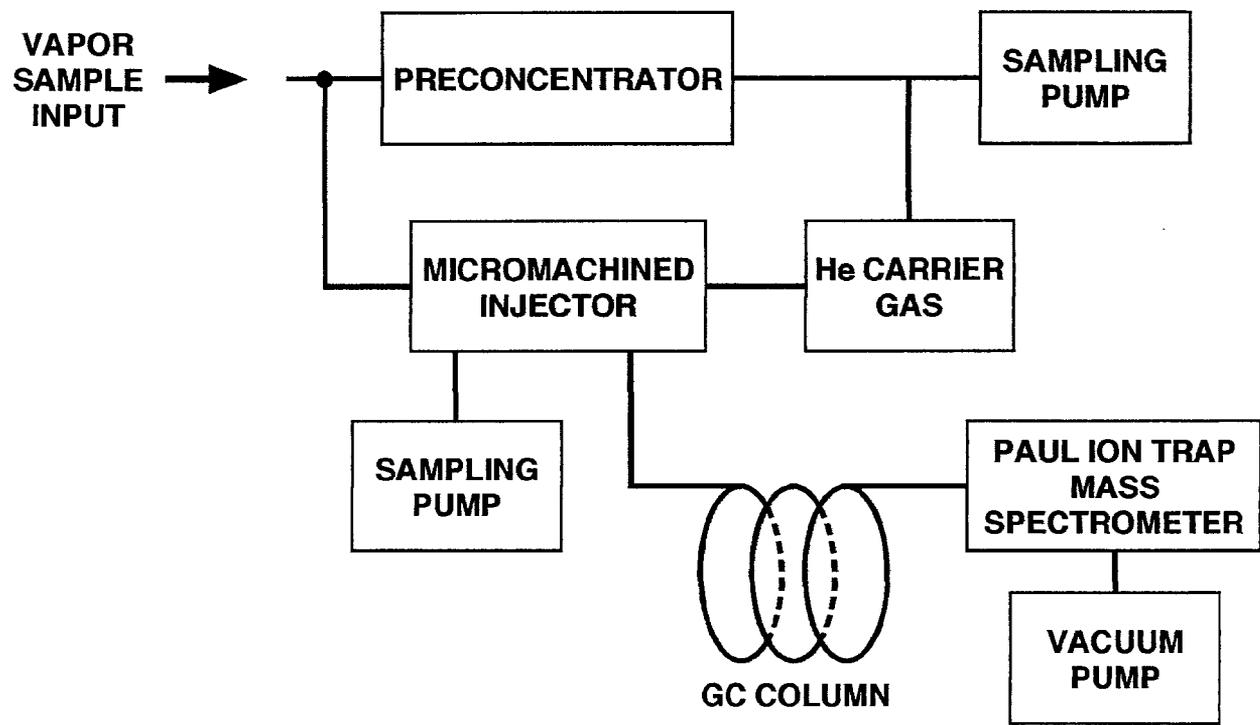


Figure 1. Schematic diagram of the miniature GC-Paul Trap system.

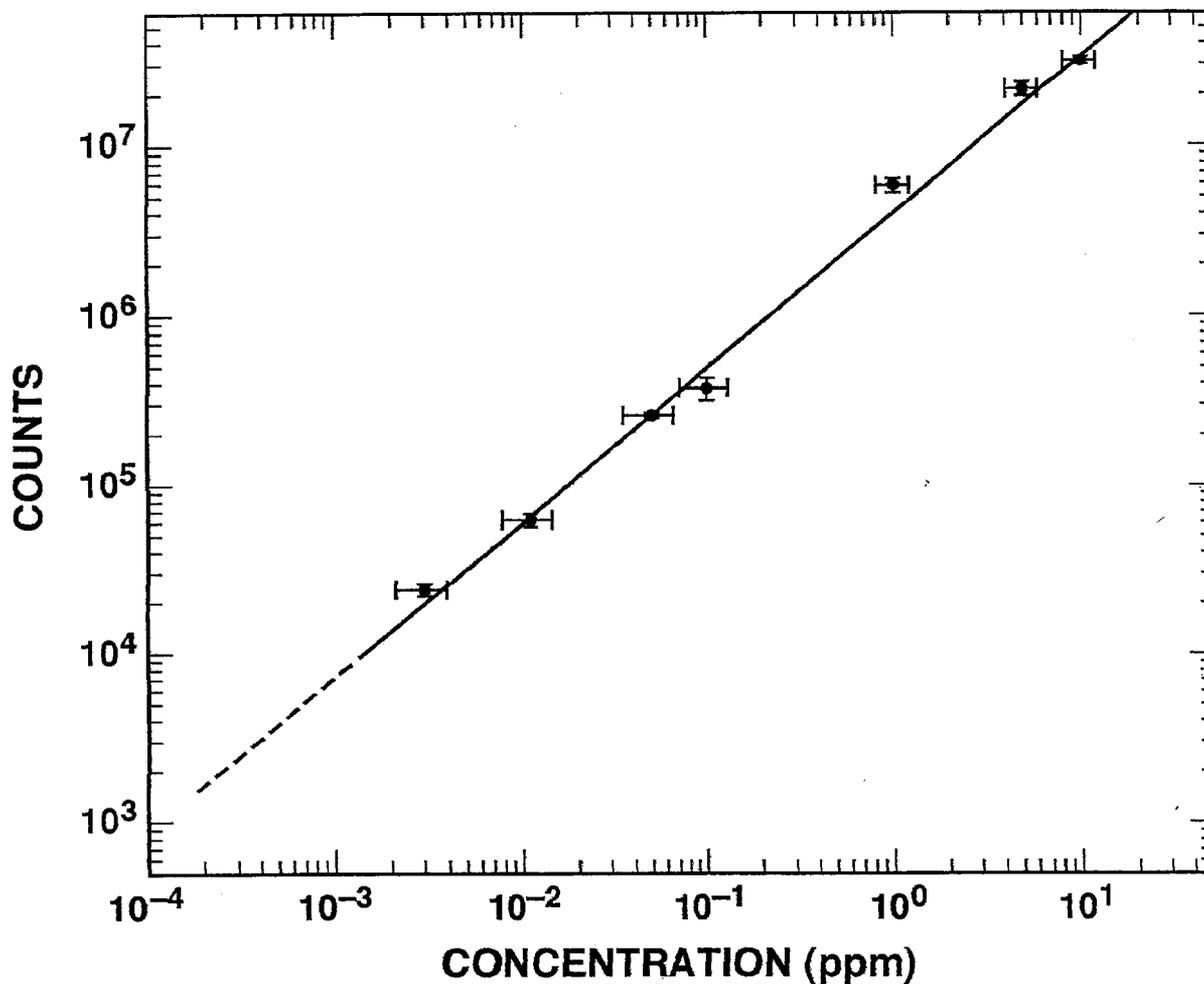


Figure 2. Dynamic linear range of the GCPT system as measured for benzene. The benzene was exposed to the PC for 120 s at and below 1 ppm concentrations, and for 2 s above 1 ppm. The slope of the measured portion (—) is 0.912 ± 0.008 . The dynamic range considering both the measured portion, and the extrapolated portion corresponding to an LLD of 0.2 ppb (----), is 5 orders of magnitude.

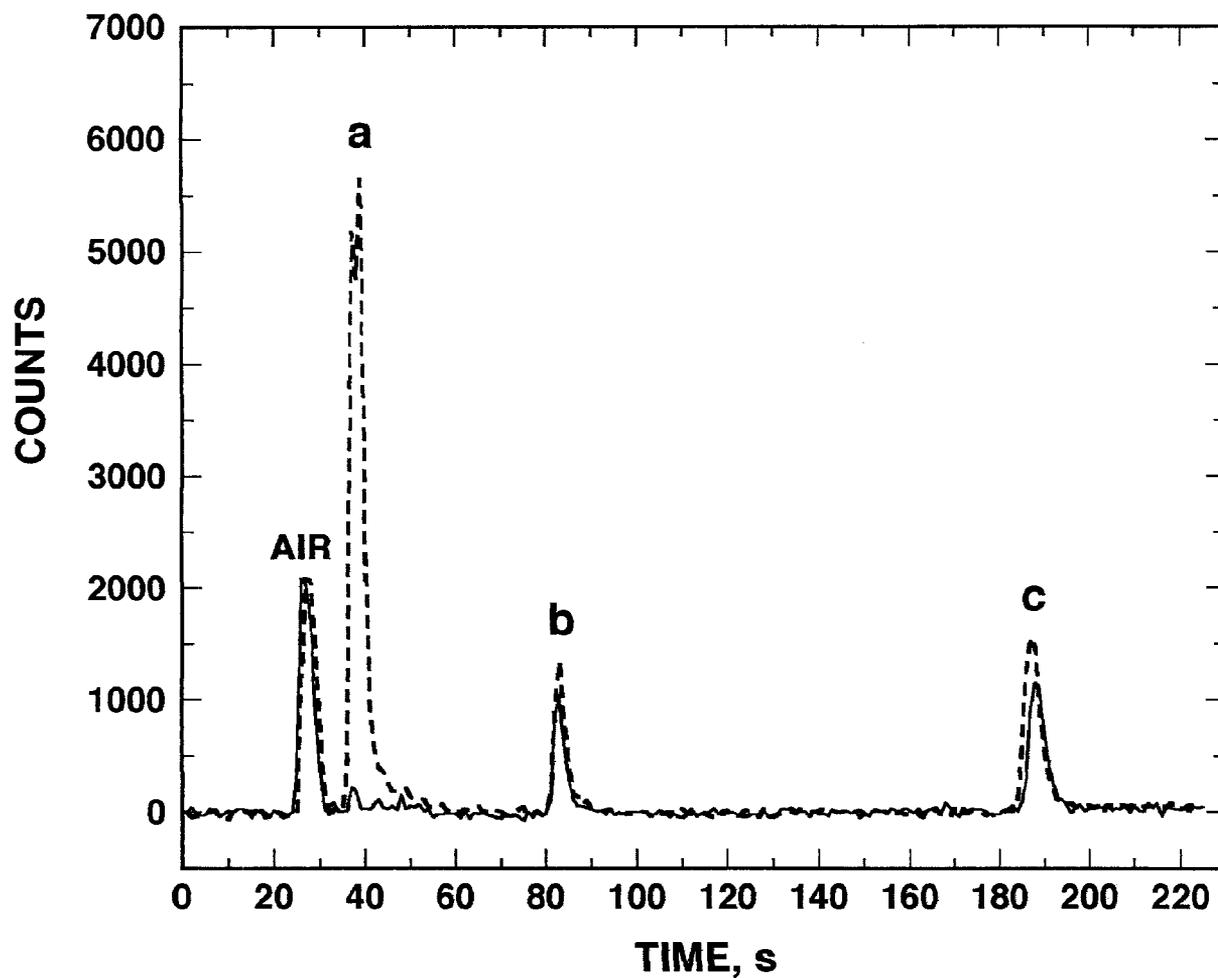


Figure 3. Shown are an ion chromatogram of a mixture of acetone (17 ppb) and benzene (21 ppb) (—); and a second ion chromatogram of the same mixture with added CO₂ (1%), H₂ (400 ppm), and freon 113 (150 mg/m³) to show effects of interferences (-----). The peaks correspond to (a) freon 113, (b) acetone, and (c) benzene.