Measurement of vapor-phase organic compounds at high concentrations

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Abstract

Laboratory, industrial, chemical or other waste products may have constituents that evolve volatile organic compounds (VOCs) at very high concentrations. These could pose human health risks during handling, storage and disposal of the waste through inhalation, dermal exposure or explosion. Additionally, the release of VOCs can adversely impact the tropospheric chemistry, and in the case of halogenated compounds, the stratospheric ozone chemistry as well. Very precise and accurate methods exist for measurement of VOCs at trace levels; however, these are inappropriate for the high levels in waste headspace, which often approach saturation vapor pressure. This paper presents an inlet system and analytical method for gas chromatography–mass spectrometry designed specifically for measuring VOC concentrations greater than 10 ppm (v/v) in a gas matrix. The technique is shown to be effective for measuring selected common solvents including alcohols, ketones, halogenated hydrocarbons and aromatic compounds in an air matrix in stainless-steel sampling canisters. This work was performed under a Cooperative Research and Development Agreement between the US Environmental Protection Agency and Graseby/Nutech Corporation.

1. Introduction

The handling, storage and disposal of mixed wastes is subject to a variety of environmental laws and regulations, health and safety rules and transportation regulations. Often there are reporting requirements for potential hazards such as toxicity and flammability due to volatile organic compounds (VOCs) that are present in the gaseous headspace of the waste materials. For purposes of waste characerization, this headspace can be considered as representative of the VOC concentration within the overall waste volume. Thus depending upon the contents of the waste container, concentrations of VOCs can range from a very low part per billion by volume (ppbv) level, as from slowly leaking secondary containment, up to levels in the percent by volume range, where the contents are at saturation vapor pressure from free liquid evaporation. The minimum reporting requirement for compounds of interest is typically 10 to 100 parts per million by volume (ppmv).

Sampling methods for mixed waste headspace generally involve the capture of a gas sample in a bag or rigid container (such as a stainless-steel

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passivated canister) for subsequent laboratory analysis by gas chromatographic (GC) methods. However, analysis of any waste headspace samples containing high concentrations of VOCs cannot be accomplished by standard techniques. Environmental laboratories equipped for air analysis are geared toward trace-level work using method TO-14 [1] (or a related method), which is appropriate for ppbv and sub-ppbv concentrations. The potentially high VOC levels in the waste headspace pose difficulty in sample transfer and processing due to adsorption in the complex gas inlet system and overloading of the analytical column and detector.

To address this issue, various laboratories have made modifications to standard environmental trace-level methods to accommodate high-level samples. The simplest method uses a small syringe aliquot drawn from the sample that is injected into a split-flow GC injection port. Another approach employs a sample loop injection valve to shunt a fixed volume of sample into the analytical system. Some laboratories opt to dilute the high-level samples to concentrations for which their existing instrumentation is suited. These (and possibly other) adaptations to existing techniques have been implemented at various degrees of success. There are some drawbacks to these methods.

The methods involving syringe gas injection of 10 to 100 μl are very operator dependent and tend to suffer from poor precision. The high surface-to-volume ratio of the syringe and the deformable materials in the plunger may affect the sample integrity of the polar constituents in the sample through adsorption and absorption. Sample loop injections through an automated valve are very precise; however, the additional gas flow plumbing and valve surfaces are subject to adsorption of analytes and run-to-run carryover when very-high-level samples are followed by samples with lower concentrations. Finally, though dilution of the sample is very effective in allowing accurate and precise analyses with standard air techniques, this requires additional sample handling by the laboratory personnel, precise pressure or flow gauges, and additional quality assurance and quality control to verify the integrity of the procedure. Each

step in the procedure can introduce errors in the final dilution factor calculation.

This paper presents an automated analysis method and sample injection hardware for GC–mass spectrometry (MS) specifically for high-VOC-concentration samples. It is based upon the injection of a low-volume aliquot from a flowing sample stream through a differential pressure switch, which is functionally similar to work described by Deans [2]. The injection volume is adjustable for sensitivity via computer control without any processing (dilution) or other handling of the sample. The sample stream does not contact any surface other than deactivated fused silica between the sample container and the interior of the analytical column. The method was applied to pressurized gas samples containing compounds including methanol, ethanol, acetone, methyl ethyl ketone, n-butanol, carbon tetrachloride, tetrachloroethylene, benzene and toluene, as well as gasoline vapors. Tests were performed at levels ranging from low ppmv per analyte up to saturation vapor pressure concentrations. This work is a collaborative effort performed under a Cooperative Research and Development Agreement between the Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the US Environmental Protection Agency (EPA) and Graseby/Nutech Corporation.

2. Experimental

Two separate systems were used for this work. The first is an EPA laboratory prototype assembled from available materials with only minor machining of standard fittings and injection port parts, and this is referred to as system 1. The second system is a manufacturer's prototype built by Graseby/Nutech and based upon experience gained from testing of the laboratory prototype. This is referred to as system 2 in the ensuing text.

2.1. System 1

The injection hardware is composed of standard 1/16-in. and 1/8-in. (1 in. = 2.54 cm)

Swagelok fittings and stainless-steel tubing mounted onto a standard split/splitless injection port on a Varian 3400 GC system as configured as part of a Finnigan MAT (San Jose, CA, USA) ITS40 GC–MS ion trap system. The injection port nut was remachined and internally threaded to accept an O-ring fitting that provides a seal as well as mechanical stability. The injection port plumbing of the GC system was bypassed, and the helium purge flow valve was rerouted to provide control of the on/off switching of the helium gas column flow through computer control. A standard Graseby/Nutech 320-01 controller was modified to provide two feedback-regulated temperature zones, one to heat the injection and gas switching assembly, the other to maintain a constant elevated helium temperature. To accommodate the relatively large switching volume, an additional "sweep" flow was used to rapidly remove residual gas. Helium and sample flows are adjusted so that there is always a positive flow at the vent to keep room air from infiltrating into the system. Fig. 1 shows a simple diagram of this injection scheme. Sample is introduced into the analytical column during the time that the helium flow is off. This time was empirically chosen (0.01 min) so that saturated pressure VOCs presented well-resolved and well-formed chromatographic peaks.

2.2. System 2

The large, complex configuration of system 1 was redesigned into a small solid steel block drilled with appropriate channels to provide the switching body. Connection tubes were welded into place, and the whole assembly was passivated with a deactivated fused-silica layer, a proprietary process (Silcosteel) from Restek (Bellefonte, PA, USA). Helium pressure and flow were controlled with a dedicated single-stage regulator and fine metering valve. The injector was imbedded in a temperature-controlled zone and installed on top of a Hewlett-Packard (HP; Palo Alto, CA, USA) HP-5890 gas chromatograph with an HP-5971 mass spectrometer as the detector. An external Graseby/Nutech Series 2000 controller was interfaced directly into the Windows-based (Microsoft) HP Chemstation software so that the GC–MS system and the injection system could be operated directly from the GC–MS system computer. Fig. 2 shows a diagram of the simplified system. The injection volume was set by adjusting the helium "time off" parameter empirically to achieve good chromatography.
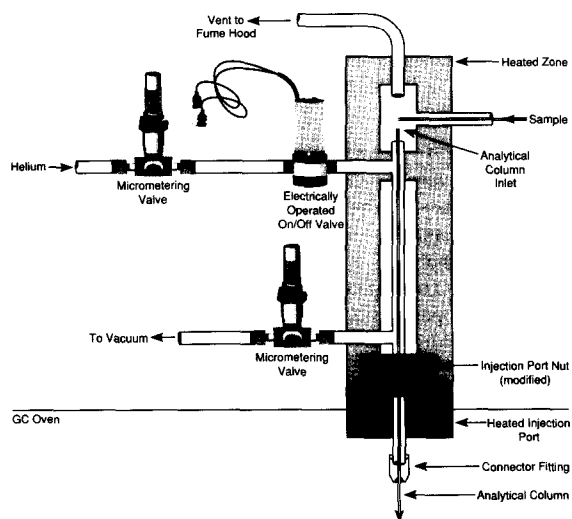

Fig. 1. Diagram of system 1 (laboratory prototype) sample injection hardware. Sample flow is briefly shunted onto the analytical column when the helium valve is placed in the off state. The injection volume of the "switch" is always swept through the coaxial flow around the outside of the analytical column. Helium and sample flows are set to always provide positive flow at the vent.

2.3. Performance tests

All performance tests were based on compressed gas samples in humidified zero grade air or in nitrogen. These were prepared in 6-l-volume Summa-polished canisters from SIS (Moscow, ID, USA). Each sample was fitted with a dedicated fused-silica transfer line and reducing union fitting. All analyses were performed by using full-scan MS data acquisition. For quantitation, the characteristic ion (typically the base peak ion) was extracted from the total ion chromatogram, and the resulting trace was integrated.
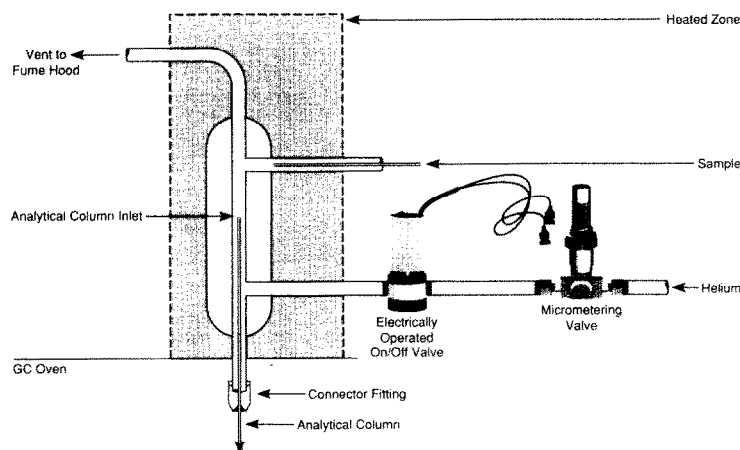
Fig. 2. Diagram of system 2 (commercial prototype) sample injection hardware. This simplified system is a single machined piece internally coated with deactivated fused silica. Sample flow is briefly shunted onto the analytical column when the helium flow is interrupted by the helium on/off valve. The extremely low dead volume does not require an additional sweeping flow as in system 1.

Initial tests

The first developmental tests were performed by using high-level samples prepared in the laboratory by injecting 100 or 200 μl (each) of a variety of liquid analytes (and water) into evacuated 6-l canisters and pressurizing to 3 atm absolute pressure (30 p.s.i.g.; 1 atm = 101 325 Pa, 1 p.s.i. = 6894.76 Pa) with zero-grade air.

Depending upon the compound, these samples were at or near saturation vapor pressure for the analytes. Some typical analyte mixtures are given in Table 1. Lower level samples (at 10 or 20 ppmv), composed of primary working standards from method TO-14 [1] calibration mixtures available in the laboratory, were used to test the sensitivity range and to optimize analytical pa-

Table 1
Analyte mixtures used to optimize analytical parameters

High level 1	High level 2	High level 3
Methanol	Methanol	Methanol
Ethanol	Ethanol	Ethanol
2-Propanone (acetone)	2-Propanone (acetone)	1,1'-Oxybisethane (diethyl ether)
2-Butanone (methyl ethyl ketone)	Dichloromethane	2-Propanone (acetone)
2-Propanol	n-Hexane	Dichloromethane
n-Butanol	Methylbenzene (toluene)	Cyclohexane
	Tetrachloroethene	Tetrachloromethane (carbon tetrachloride)
	Nitrobenzene	Benzene
	Naphthalene	Fluorobenzene
		n-Butanol
		Methylbenzene (toluene)
		Tetrachloroethene
		Ethylbenzene
		1,2-Dimethylbenzene (o-xylene)
		Benzene methanol (benzyl alcohol)
		Nitrobenzene

*Common names of the chemicals are in parentheses.

rameters. The method TO-14 list of compounds is composed of 40 specific "non-polar" VOCs ranging in volatility from the very volatile Freons up to the marginally volatile aromatic hydrocarbons and halogenated aromatic hydrocarbons.

Quantitative precision tests

For system 1, replicate precision tests were performed using high-level samples prepared in the laboratory (as listed in Table 1, columns 1 and 2); for system 2, moderately-high-level standards that were obtained through the AREAL Quality Assurance Division were used. The compounds and concentrations used for system 2 precision tests are listed in Table 3. The area of the integrated extracted ion profile of an analyte's characteristic ion was used for quantitation. All quantitation was based on external standards from various available sources.

Sample contamination and carryover tests

Once system 2 was tested and optimized, the efficacy of the methodology in a complex matrix was demonstrated by using a very challenging mixture —raw gasoline headspace. Various samples were prepared by injecting 5 ml of gasoline into evacuated canisters and pressurizing to 2 atm gauge. Sample blanks were prepared by injecting organic-free deionized water in place of the gasoline. For these tests, three different formulations of gasoline were obtained from the AREAL Mobile Source Emissions Research Branch: unleaded 87 octane with no oxygenates, with methanol additive, and with methyl *tert.*-butyl ether (MTBE) additive. For these tests, the gasoline headspace samples were analyzed with interspersed blank samples to test for sample cross-contamination and to determine if the oxygenated additives could be detected in the very complex hydrocarbon matrix.

2.4. Sample introduction

For all analytical tests, the sample mixture was released from the canister through a 50 cm × 0.25 mm I.D. deactivated fused-silica tube into the analytical system inlet. The resulting transfer flow was in the range of 100 to 250 ml/min,

depending upon canister pressure. Only a small aliquot of this constant flow was introduced onto the analytical column through the valveless switch, as the helium flow was briefly interrupted by the helium control valve. (See Figs. 1 and 2 for system diagrams). Injection of sample in this fashion is very precise, and the sample amount can be adjusted through a software parameter that determines the time interval that the helium control valve is off. This time interval was chosen empirically to achieve optimal chromatography for each system and then left unchanged for all tests. An exact injection volume could not be accurately determined because of gas turbulence during the switching pulses, dead volume mixing within the switch volume, and the unknown valve response time. Calculated injection volumes were 12.5 μl for system 1 and 100 μl for system 2.

3. Results and discussion

The major part of the initial development work was performed on system 1 with a wide variety of compound mixtures and other real-world matrices. Once the specific technique was
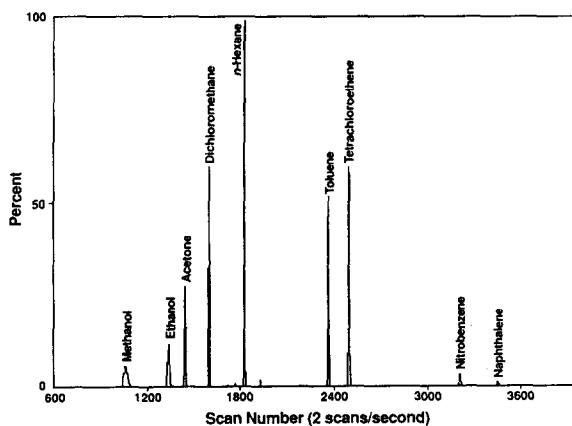

Fig. 3. Example chromatogram of mixed waste headspace precision test of system 1. Compounds are at (or near) saturation vapor pressure in a humid air matrix in a 6-l-volume canister. Column: J & W DB-5 (30 m × 0.25 mm I.D., 1-μm phase). GC oven: 2-min hold at −50°C, ramp 8°C/min to 200°C.

Table 2
System 1 precision test results for high-level mixture 2

Compound	R.S.D. (%) (n = 7)
Methanol	6.92
Ethanol	6.19
2-Propanone (acetone)	6.99
Dichloromethane	5.15
n-Hexane	5.75
Methylbenzene (toluene)	5.39
Tetrachloroethene	6.44
Nitrobenzene	7.94
Naphthalene	9.35

Seven replicate runs, statistics based on single ion extracted profile areas. Common names of the chemicals are in parentheses.

developed, high-level headspace samples were more rigorously tested. An example chromatogram of a precision test is given in Fig. 3, and the results for a seven-repeat-analysis sequence are shown in Table 2. In this demonstration, the sample concentrations were near or at saturation vapor pressure. Note that the chromatography is

clean and that the precision data indicate a typical run-to-run scatter of 5 to 7% relative standard deviation (R.S.D.). Nitrobenzene's and naphthalene's greater errors at about 8 and 9% R.S.D. are most likely due to the low vapor pressure and marginal suitability for storage in canisters for these compounds. For this particular test, a J & W (Folsom, CA, USA) DB-5, 30 m × 0.25 mm I.D. capillary column with 1-μm stationary phase was used with a GC oven temperature profile consisting of a 2-min hold at $-50°C$ with a ramp to $+200°C$ at 8°C/min. The calculated injection volume was about 12.5 μl. In other tests, J & W DB-1701, Restek Rtx-5 and Restek Rtx-1301 columns (each with appropriate oven temperature programs) were used with good results.

The optimized system 2 was similarly tested for precision by using a nominal 100-ppmv-percompound mixture and a prepared mixture with a variety of concentrations for each compound. Results for these two tests are given in Table 3. For this particular series of tests, a Restek Rtx1301 30 m × 0.25 mm I.D. column with 1-μm stationary phase was used. The oven tempera-

Table 3
System 2 precision test results for two mixtures

Compound	Test 1		Test 2	
	ppmv	R.S.D. (%)	ppmv	R.S.D. (%)
Methanol	86.5	4.95	725	6.28
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	86.1	4.16	787	2.24
2-Propanone (acetone)	119	3.83	769	2.49
Dichloromethane	105	4.31	793	2.28
1,1-Dichloroethane	103	4.34	836	2.93
2-Butanone (methyl ethyl ketone)	106	2.78	117	2.83
Trichloromethane (chloroform)	92.6	3.32	731	1.80
1,1,1-Trichloroethane (methylchloroform)	91.1	3.47	325	1.47
Tetrachloromethane (carbon tetrachloride)	89.4	4.11	181	2.45
Trichloroethene	79.1	5.47	104	2.89
4-Methyl-2-pentanone	96.1	4.62	72.0	2.79
Methylbenzene (toluene)	91.1	3.28	172	2.32
Tetrachloroethene	79.9	5.04	19.8	2.10
1,4-Dimethylbenzene (p-xylene)	94.6	3.52	31.8	2.26
1,1,2,2-Tetrachloroethane	96.2	3.68	25.9	2.20

Seven replicate runs for each mixture. Statistics based upon single ion extracted profile areas. Common names of the chemicals are in parentheses.
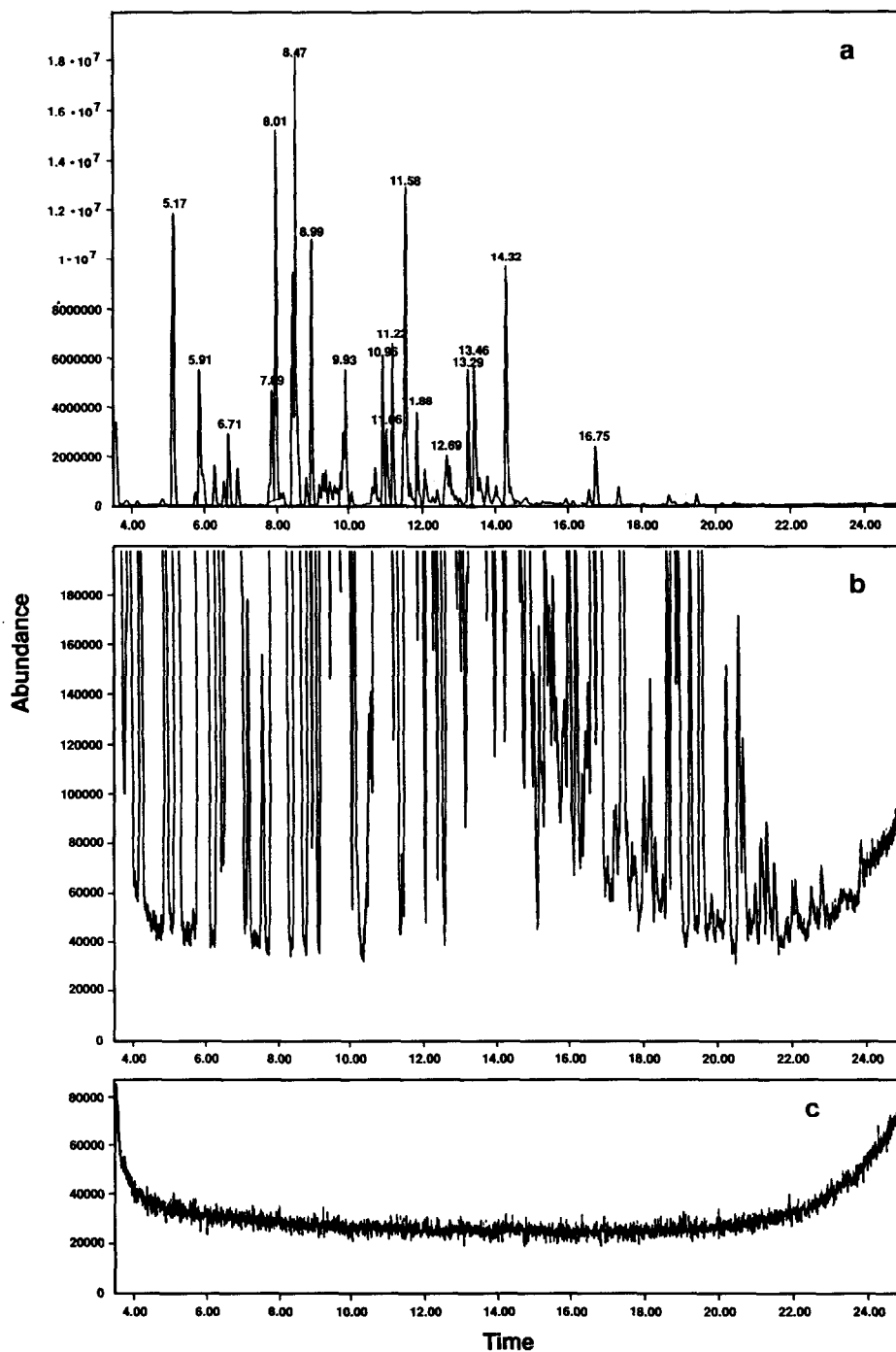
Fig. 4. Example chromatograms demonstrating sample integrity of system 2: (a) headspace of gasoline saturation vapor pressure, full scale; (b) headspace of same sample, chromatogram expanded vertically; (c) humid zero air sample run immediately after gasoline headspace, same scale as (b). Column: Restek Rtx-1301 (30 m × 0.25 mm I.D., 1-μm phase). GC oven: 2-min hold at 5°C, ramp 10°C/min to 200°C. Time in min.

ture program consisted of a 2-min hold at 5°C with a 10°C/min ramp to 200°C. The injection volume was calculated to be 100 μl.

These results are excellent considering the very-high-level concentrations and the associated potential for contamination within the system.
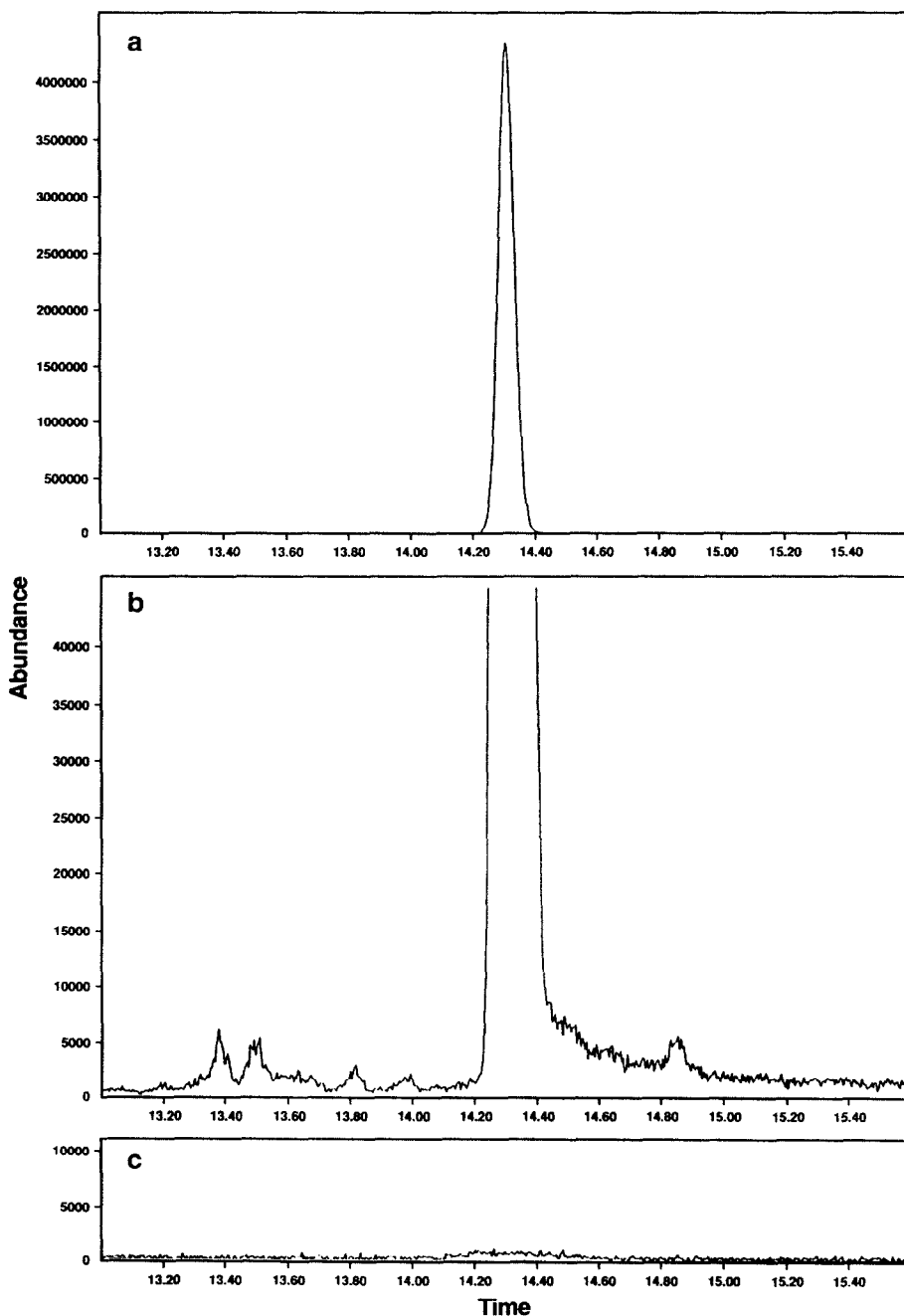

Fig. 5. (a), (b), (c) Example extracted ion 91 chromatograms corresponding to Fig. 4a, b and c, respectively, for the toluene constituent of gasoline headspace demonstrating run-to-run sample integrity. Time in min.

Upon detailed analysis of individual chromato-grams, we noticed a slight systematic decline in the overall HP-5971 MS response throughout the day, which contributed to the aggregate error. It was estimated that only about half of the R.S.D. should be attributed to the injection system.
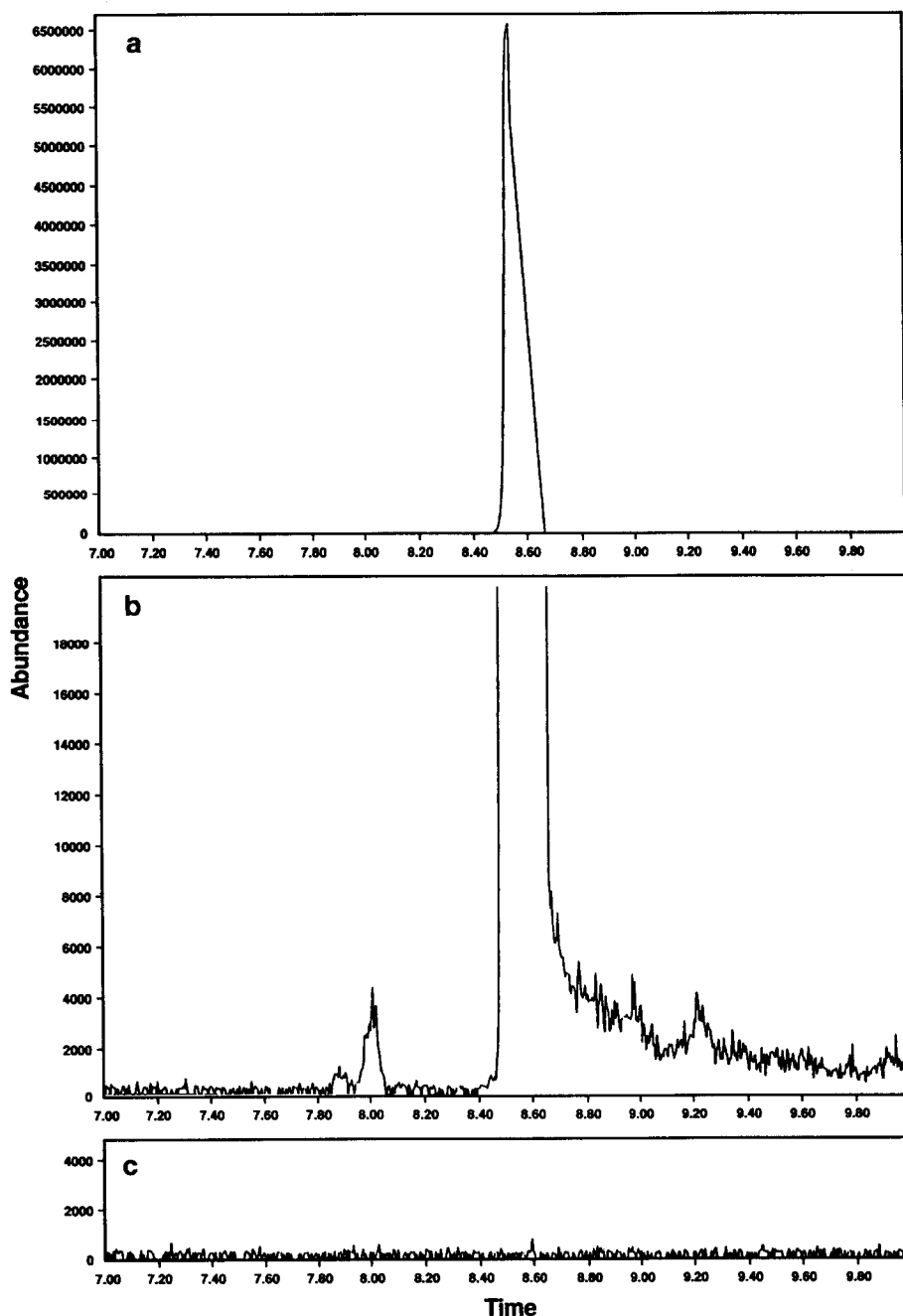

Fig. 6. (a), (b), (c) Example extracted ion 73 chromatograms corresponding to Fig. 4a, b and c, respectively, for the MBTE constituent of gasoline headspace demonstrating run-to-run sample integrity. Time in min.

Numerous tests with blanks on both system 1 and system 2 showed no measurable cross-contamination or carryover from a previous high-concentration sample. A worst-case example, as run with system 2, is presented in the total ion chromatograms in Fig. 4; here, the analysis of the headspace of raw gasoline with MTBE as an additive was followed immediately by the analysis of a humidified zero air sample. The comparison between the expanded vertical scale of the gasoline headspace chromatogram and the blank chromatogram shows this graphically.

For further investigation of possible cross-contamination, Figs. 5 and 6 show detailed sets of extracted ion chromatograms in which toluene and MTBE are used as examples. Here, the full-scale peak, an expanded peak (scale factor of 100), and the correspondingly scaled blank sample chromatogram are shown. Note that there is no measurable carryover into the blank sample.

4. Conclusions

The presented methods and hardware configurations are effective at determining the high-level VOC concentrations in a gas matrix. Even a simple configuration (system 1), as constructed in the research laboratory, was capable of precise headspace analysis (5 to 9% R.S.D.) of high-level VOCs. The optimized system 2 switching device, constructed from a single machined and welded part and then internally coated with fused silica, performed with about a factor of 2 better precision (1.5 to 6% R.S.D.). This type of injection switching performs well within the typical requirement of 20% R.S.D., and it is relatively simple because it requires no syringes, sampling valves, or high-level multiple dilution steps, which require additional laboratory preparation time. Both polar and non-polar VOCs can be analyzed in a single chromatographic run with excellent precision. The absence of run-to-run sample cross-contamination reduces the need for frequent blank checks, thus reducing the overall quality control overhead. With a single parameter setting, the system has a dynamic range of analysis from 10 ppmv up to saturation vapor pressure of a variety of VOCs. Finally, the system is suitable for any type of modern capillary column GC–MS system employing a direct column GC–MS interface.

5. Disclaimer

The research described in this article has been performed under a Cooperative Research and Development Agreement between the US Environmental Protection Agency and Graseby/Nutech Corporation. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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