The Use of a Programmable Temperature Vaporizer in the Thermal Desorption Mode for the Quantitative Analysis of Airborne Volatiles

A. Samman and **S. Grant Wyllie**
Faculty of Science and Technology, University of Western Sydney, Hawkesbury, Richmond, NSW, Australia

Abstract

A Tenax packed trap constructed from a programmable temperature vaporizer (PTV) injection liner was used to collect volatiles that were subsequently analyzed by thermal desorption in the PTV directly into a gas chromatography column. The limits of detection and quantitation, range, and linearity of the method were evaluated using BTEXs as test materials.

Introduction

The growing availability of programmable temperature vaporizers (PTV) as injection systems on gas chromatographs (GCs) provides a great variety of injection modes that can be used to solve particular analytical problems. In particular, their ability to operate in the thermal desorption mode provides the potential for a less costly means of carrying out the quantitative analysis of organic volatiles, such as those found in polluted air samples. This investigation describes an active sampling (1) analysis procedure for airborne volatiles based on the use of a PTV, an absorbent trap, and an air sampler and evaluates the potential analytical performance of this approach in terms of its limits of detection and quantitation, reproducibility, and working range using a model system designed to duplicate field conditions as closely as possible.

Experimental

Air sampler

A Giliar 5 Tri-Mode air sampler (Gilian Instrument Corporation, Wayne, NJ) was used to draw air through the traps. Air sampler calibration and flow rate adjustment were achieved using a Gilibrator-2 primary flow calibrator.

GC

GC was carried out on a Hewlett-Packard (Palo Alto, CA) model 5890 series II fitted with a flame ionization detector (FID) and an Ai OPTIC 600 (Ai Cambridge, Cambridge, England) PTV injection system operating in the split mode (split ratio, 1:20). The conditions for trap desorption were as follows: initial injector port temperature, 35°C; once the trap was inserted into the injector port, the temperature was increased to 230°C at a rate of 16°C/s. This temperature was maintained until the run was completed. The FID temperature was 240°C, and the carrier gas was helium. A capillary column (SGE BP1, 23 m × 0.22-mm i.d., 1-µm film thickness, SGE, Victoria, Australia) was used for all analyses. The column was programmed as follows: initial temperature, 40°C; initial time, 20 s; ramp rate, 20°C/min; final temperature, 100°C; final time, 13 min.

A 0.5-µL microsyringe (Hamilton 7000 series, Reno, NV) fitted with a constant volume delivery attachment was used to inject all samples.

Data integration software

Data were acquired and integrated using DAPA software version 4.52 (DAPA, Perth, Australia).

Trap construction

Standard Ai pyrex PTV injector liners packed with Tenax TA (Alltech, Deerfield, IL, 80–90 mg, 35/60 mesh) between silanized glass wool plugs were conditioned at 350°C for 4–6 h in a continuous flow of nitrogen (10 mL/min). After the completion of the conditioning process, the traps were removed, capped immediately with Teflon caps, cooled, and stored at room temperature.

Determination of the breakthrough volume of the traps

Benzene was used as a representative of the BTEX group of compounds (benzene, toluene, ethylbenzene, and xylene). Benzene in methanol (140 ppm) was injected (0.5 µL) into the dynamic headspace model system (DHMS), and various volumes of air (1, 2, 4, and 6 L at 20 mL/min) were drawn through the system. Eight replicates were used at each air volume. The contents of the traps were analyzed under the conditions previously described.

Determination of the storage stability of sample trapped on the Tenax TA traps

Four replicate injections (0.5 µL) of a standard BTEX solution (8000 ppm) were made into the DHMS, and the air sampler was

adjusted to draw 2 L of air through the system (20 mL/min). Four sets of Tenax TA traps (each set consists of a front and back liner) were collected. The first trap from each group was desorbed on the same day of sampling, the other 3 traps of each group were stored in a refrigerator at 4°C. The second, third, and fourth trap of each group were desorbed and analyzed after 2 days, 1 week, and 2 weeks, respectively.

Statistical analysis

Linear regression was used to calculate the residual standard deviation (σ) using Microsoft (Redmond, WA) Excel version 5. The residual standard deviation was then used to calculate the limit of detection (LOD) and limit of quantification (LOQ) of the selected volatile organic compounds (VOCs).

Construction of the DHMS

The DHMS consisted of a glass chamber (150-mL quickfit conical flask) fitted with inlet and outlet fittings and an injection septum. The inlet of the chamber was connected to a charcoal trap. Two traps (front and back) were connected in series to the chamber's outlet. All fittings and caps used in constructing the system were made of poly(tetrafluoroethylene) materials. All connecting tubes were either silicone rubber or stainless steel (316 ss and 3.1-mm i.d.). The sample containing the selected compounds was introduced into the chamber via the septum port using a microsyringe. A known volume of air was then pumped through the system at a preset rate to transfer the sample to the trap.

Trap restriction factors

Because the traps provide flow resistance, the actual flow through the trap in relation to the nominal flow set on the air pump was measured. This restriction factor was measured for each trap.

Sample introduction

The reproducibility of the syringe used for manual injection into either the GC or the DHMS was evaluated using a series of 32 injections of a standard solution of benzene in methanol into the GC.

Minimum sweep volume of the DHMS

To enable the quantitative comparison to be made, the volume of sweep air required to completely transfer the sample from the DHMS vaporization chamber to the trap was determined. A series of volume recovery determinations showed that a total of 1.5 L of swept air was required for complete transfer in this system.

Results and Discussion

The method is based on using the injection liner of a PTV packed with an absorbent as the sample collection medium (trap). The packed liner is inserted into the PTV and thermally desorbed under controlled conditions directly into the analytical column. This method has been shown to have useful applications for volatiles analysis in a nonquantitative manner (2). The overall quantitative analytical performance of such a system is determined by the sample capacity of the trap, the stability and adsorption/desorption characteristics of the trapping material, and the sensitivity of the GC.

The sample capacity of the trap can be expressed in terms of its BTV. Although a number of definitions of BTV have been suggested (3,4) for this work, the BTV was defined as the volume of air that could be passed through the trap that resulted in the loss of less than 10% of the applied sample. The BTV is determined primarily by the amount and nature of the adsorbent, the configuration of the trap, and the sampling flow rate. In this case, the configuration and capacity of the trap were determined by the dimensions of the PTV liner. The characteristics of the adsorbent were also dependent on parameters imposed by the use of a PTV as the thermal desorber, because the use of cryofocusing in the GC was avoided in the present experiment. Therefore, the adsorbent was required to desorb the analyte with sufficient rapidness upon heating to produce a sufficiently narrow sample injection band that maintained normal GC resolution. Of the adsorbents tested, Tenax TA gave the most satisfactory combination of adequate sample capacity, durability, and suitable desorption performance and was adopted for all further work. This finding is in accord with those of Herraiz et al. (5,6), who evaluated the use of a PTV injector in the thermal desorption mode for the analysis of volatile compounds at low concentrations (albeit in a somewhat different experimental context to that used in this work).

Design and validation of test system

Evaluation of the limits of the method in terms of range, reproducibility, and linearity required the design of the system to deliver known quantities of analyte in known quantities of air at a given flow rate to the trapping system. The simple dynamic headspace model system (described in the Experimental section) coupled with an air sampler pump proved adequate for this task. Known amounts of the various analytes were injected into the system using a microsyringe and swept by a calibrated volume of air into the trapping system. Subsequent analysis of the traps both quantitated the analyte and showed whether sample breakthrough had occurred.

Sample injection variability will contribute to errors in quantitation and reproducibility using this test method. This was evaluated by analyzing the peak areas from 32 manual injections of benzene standard. The data showed a relative standard deviation (RSD) of 4.58% ($n = 32$). Therefore, this represents the minimum error that can be expected with this procedure.

A comparison was made between the peak areas obtained from injecting a specific amount of test sample into the test system followed by trapping and desorption and a direct injection of the same amount into the GC. No significant differences in peak areas or RSD values between the 2 injection systems were found (8 replicates each).

The accuracy and reproducibility of the test system were therefore established.

Determination of breakthrough volume

For the BTEX group of compounds chosen as test compounds, the BTV was determined by that of benzene, the lowest boiling and least strongly absorbed member of the group. The minimum BTV value for benzene on the traps employed was found to be

2.0 L at a collection flow rate of 20 mL air/min. Under these conditions, the recovery of benzene was greater than 95% (8 replicates) and hence conformed to the definition given previously. All subsequently used traps were required to meet this specification.

Method detection limits

The equations used to determine the minimum detectable amount (MDA) and minimum quantifiable amount (MQA) for the method were derived from general equations recommended by the International Conference on Harmonisation (7) to determine the LOD and LOQ for a specific compound. These equations were as follows:

$$MDA = \frac{3.3\sigma}{S} \quad \text{Eq. 1}$$

$$MQA = \frac{10\sigma}{S} \quad \text{Eq. 2}$$

where S is the slope of the calibration curve for a specific compound in the range of the detection limit and σ is the residual standard deviation of the regression line.

The MQA is the minimum amount of a particular compound that can be measured with quantitatively meaningful reliability. At this value, the relative confidence in the detected value is approximately ± 30% at the 95% probability level (8).

A typical calibration curve for benzene at concentrations close to the detection limit is shown in Figure 1. This curve, based on the determination of 8 replicates at each concentration, has a linear regression coefficient r^2 of 0.998. Very similar results were obtained for the other members of the BTEX family. The MDA and MQA for the BTEXs obtained using the test protocol are shown in Table I.

Clearly, the overall method sensitivity is dependent on the sensitivity of the GC used, a parameter determined by the characteristics of the detector and the instrument configuration (in this case, particularly the injector configuration). These factors need to be taken into account when evaluating the values in Table I.

Method LOD and LOQ

The total method LODs and LOQs depend on the BTV value and the instrumental sensitivity as expressed by the MDA and MDQ discussed previously. The total method LOD and LOQ can be obtained as follows:

Method LOD (ng/L) = MDA (ng)/sample volume (L) Eq. 3
Method LOQ (ng/L) = MQA (ng)/sample volume (L) Eq. 4

Table II shows the method LODs and LOQs obtained for the BTEX group of compounds by this method. The method is therefore capable of quantitatively determining organic volatiles in the range of concentrations often encountered in air samples (9).

Method linearity

The range of concentrations over which the method exhibits linear response is an important parameter for methods that may encounter analytes of wide concentration ranges. Figure 2 illustrates a typical calibration curve (for toluene) shown by the components of the BTEX group using the methodology described previously. All of the compounds in this group showed linear behavior (r^2 < 0.988) from the MQA to the largest sample size tested (4000 ng). The method is therefore applicable in situations where a wide concentration range of analytes may be encountered.

Storage stability

It has been shown that samples of volatiles collected on Carbopack B (Supelco) can be stored for 1 week without significant losses (10). Because it is likely in a field situation that

Table I. Method MDAs and MQAs for BTEXs

Compound	MDA (ng)	MQA (ng)
Benzene	0.49	1.50
Toluene	0.65	1.97
Ethylbenzene	0.64	1.93
o-Xylene	1.34	4.06
m- and *p*-Xylene	1.23	3.74

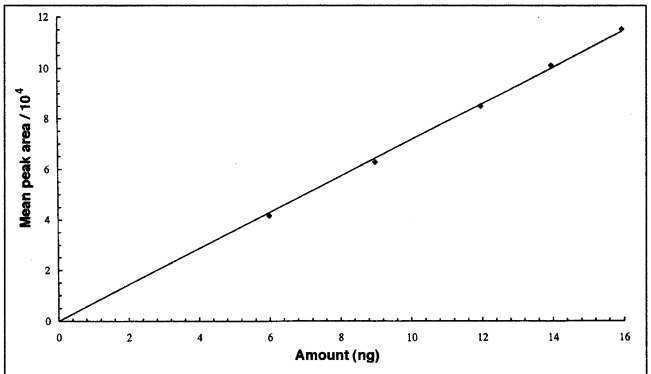

Figure 1. Typical calibration curve for the determination of method MDA and MQA (benzene used as an example).

Table II. Method LODs and LOQs for BTEXs

Compound	LOD (ng/L)	LOQ (ng/L)
Benzene	0.245	0.742
Toluene	0.325	0.985
Ethylbenzene	0.320	0.970
o-Xylene	0.670	2.03
m- and *p*-Xylene	0.615	1.86

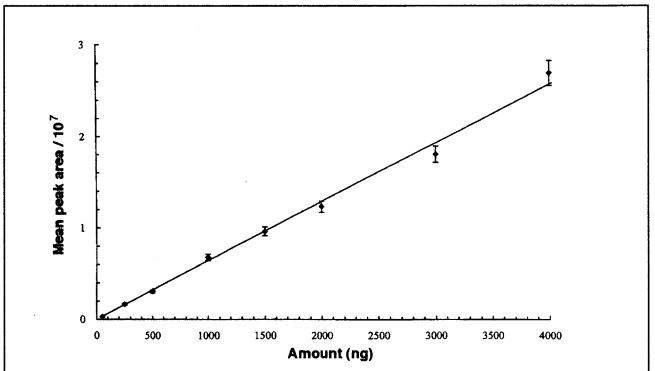

Figure 2. Typical calibration curve for determination of method working range (toluene used as an example).

samples may not be able to be analyzed immediately, the recovery of BTEX samples collected in Tenax TA packed traps and stored at 4°C for periods of up to 2 weeks was evaluated. Recovery of the total sample group averaged 98% on the day of collection, 92% on the second day, 90% on the seventh day, and 81% on the 14th day. There were no significant differences between the losses of the various group components. Although this loss of sample may be able to be minimized by more rigorous storage conditions (e.g., storage at –18°C), the results of this experiment suggest that analysis as soon as possible after sample collection will provide the most reliable analytical outcomes.

Conclusion

The results obtained for this method for the sampling and analysis of VOCs in air have shown that the combination of active sampling on Tenax traps followed by thermal desorption using a PTV coupled to a GC has LODs and LOQs in the correct range for regulatory requirements. There is also an adequate linear range to cover most sample concentrations encountered in the environment. For laboratories that do not have the complex instrumentation usually associated with the automated analysis of airborne volatiles, this approach may provide a simpler and less expensive solution for dealing with small sample numbers or nonstandard sampling environments. However, as with any quantitative technique, careful calibration using the target analytes is needed. Its utility in the analysis of volatiles from natural sources has already been demonstrated (11,12).

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