

ADVANTAGES AND DISADVANTAGES OF DIFFERENT SAMPLING TECHNIQUES FOR SAMPLING VOLATILE ORGANIC HYDROCARBONS IN AIR

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The sampling and analysis of volatile organic compounds (VOC) in air are a great challenge. Air is a matrix very difficult to handle, the pollutants are usually present at very low concentration, so their detection and quantitation require precise sampling, sample preparation, analysis and data evaluation. VOC air samples are almost never sufficiently concentrated to be directly introduced into a capillary GC system via a standard gas-sampling valve. The respective advantages and limitations of these different sampling methods will be reviewed. The observations are based on the results of two sampling campaigns, namely in February-May 1998, in Veszprém, where diffusive samplers were used for the determination of BTEX compounds, and July-August 1998, in Berlin (Germany), where pumped sorbent tubes, passivated canisters and on-line air stream samplers were used for the determination of 54 VOC compounds. VOC measurements contribute to improving our current understanding and will help to clarify what if any remedial action is required.

Keywords: volatile organic compounds; diffusive sampling; gas chromatography

Introduction

Environmental air pollution largely remains a series of unanswered questions: What pollutants are present? At what concentration? Where are they coming from? What harm do they do? Reliable answers to these questions can only be obtained by improving the quality and quantity of air monitoring data collected. Today, a wide range of GC compatible air sampling techniques is available. These include pumped sorbent tubes, passivated canisters, diffusive samplers, semi-continuous on-line air stream sampling. A vast number of VOC concentration measurement and pollution source emission profiles are required before the fate of pollutants in the atmosphere is understood and before the extent and potential hazard of manmade pollution can be correctly assessed.

A large variety of volatile organic compounds (VOC) have been identified recently in ambient air. Many of them have the potential to cause a variety of adverse health effects. These include aliphatic and

aromatic hydrocarbons, chlorinated hydrocarbons and various ketones and aldehydes [1]. Some of these have been suggested as possible carcinogens, such as benzene and 1,1,1-trichloroethane [2]. VOCs in the atmosphere play an important role in the formation and transformation of atmospheric oxidants [3-5]. Understanding the role of VOC requires sound analytical methods for the quantification of these compounds in air in order to locate the major sources of air contamination. These include sample collection and storage, separation of VOCs of interest, and detection and identification.

Hydrocarbons are generally released from anthropogenic sources, vegetation, soils, and oceans, as shown in *Table 1*. In cities anthropogenic sources predominate. Major sources are vehicular exhaust, gasoline evaporation and spillage, leakage of natural gas, emission from petrochemical manufacturing plants and refineries, and chemical solvents [6]. In the industrialized countries, the contribution of biomass burning to the total anthropogenic emissions is

Table 1 Hydrocarbons emitted from anthropogenic and biogenic sources to the air [6]

Source	Emission (Tg year ⁻¹)	Type of hydrocarbons
Anthropogenic sources		
Combustion and chemical industry	36	Mainly alkanes, alkenes and aromatic hydrocarbons
Natural gas	5	Mainly light alkanes
Organic solvents	15	Higher alkanes and aromatic compounds
Biomass burning	40	Mainly light alkanes and alkenes
Biogenic sources		
Foliage emission	830	Mainly isoprene and monoterpenes, some alkenes and alkanes terpenes
Grasslands	47	Light alkanes and higher hydrocarbons
Soil	<3	Mainly ethene
Ocean waters	6-10	Light alkanes and alkenes
Oceans	<26	C ₉ -C ₂₈ alkanes

comparatively minor. In tropics, however, the practices of slash, burn, and shift agriculture, in addition to deforestation, make biomass burning a major source of hydrocarbons at least during the preferred dry season of the year.

WENT [7] pioneered the idea that plants may release substantial amounts of hydrocarbons to the atmosphere, partly by volatilization of essential oils. It appears that isoprene is the predominant hydrocarbons emitted from forest species such as oak, poplar, sycamore, willow, cottonwood and eucalyptus, whereas many other plants, especially conifers, emit primarily monoterpenes. The emission rate from grasslands is small compared with that for hydrocarbons released from foliage, but it is competitive with anthropogenic emissions. Finally, one must consider the ocean as a source of non-methane hydrocarbons. LAMONTAGE et al. [8] have reported that ethane, propane, ethene and propene occur dissolved in marine surface waters with concentration exceeding those expected if the gases were in equilibrium with atmospheric concentration. For certain ocean areas the fluxes can be estimated. The atmosphere above the ocean contains C₉-C₂₈ n-alkanes in addition to low-weight hydrocarbons [9].

Different Sampling Techniques for Sampling Volatile Organic Hydrocarbons in Air

Whole Air Sampling

Whole air sampling procedures, using passivated stainless steel canisters, Tedlar bags or some other suitable container, have been developed primarily for apolar species ranging in volatility from acetylene to trichlorobenzene. Passivated stainless steel canisters, in particular, have been extensively evaluated in the US for "Air Toxics" and C₂-C₉ hydrocarbons. During analysis an aliquot of canister air is drawn into the focusing trap using a pump and mass flow controller. Canisters and bags offer advantages for sampling very

volatile components which cannot be quantitatively retained on conventional sorbents at ambient temperature and also benefit from low artifact interferences provided the containers are well cleaned. However, canisters are expensive to buy and transport, and can be difficult to clean once contaminated. Specific conditions in terms of temperature, humidity and pressure are also required for the air inside the canister if the full range of target analytes is to be monitored without loss of high boilers.

Collecting grab samples or air using canister is simply achieved by opening a valve on an evacuated canister and closing it again once the pressure inside approaches atmospheric. However, the collection of time weighted average sample requires relative complex apparatus, which can be difficult to assemble and operate in the field. Most canister methods also specify that only a relatively small air sample volume should be transferred from the canister to the GC analytical system and this limits the sensitivity of the method.

Air Sampling Using Sorbent Tubes

Sorbent tubes provide a much lower cost, more practical and more versatile alternative to canisters or other containers for most VOC air monitoring applications. They are not suitable for collecting ultra volatile components such as C₂ hydrocarbons at ambient temperature, but are compatible with both apolar and polar compounds and offer quantitative retention of organics ranging in volatility from C₃ hydrocarbons. Some inorganic vapors such as N₂O and CS₂ can also be quantitatively collected at ambient temperature. Other advantages include the collection of several liter air sampling if required that the sample tubes are clean and ready for immediate reuse at least 10 times before the sorbent needs replacing. One limitation of sample tubes is that artifacts from the sorbent material may interfere with component analysis unless strict conditioning and storage procedures are applied.

Active Sampling

Air is usually pumped into one or more sorbent tubes using a personal monitoring pump. Several replicate samples may be collected in parallel using constant flow type pumps in instances where a repeat analysis capability is essential. The direction of the gas flow is always reversed during thermal desorption so that the higher boiling compounds are backflushed easily from the sampling end of the tube. If the target analytes cover a wide volatility range, tubes may be packed with series of sorbents of increasing strength.

Diffusive Sampling

Diffusive sampling has long been available as an alternative to active sampling in occupational hygiene to

determine the concentrations of toxic volatile organic compounds in workplace air. Nowadays, this technique is widely used in environmental monitoring. Diffusive sampling has many advantages including increased sampling time, simplicity and lower unit sample cost. In this method volatile organic compounds are taken up by an adsorbent from the air at the rate controlled by diffusion. This is most suited to monitoring individual organic compounds or a narrow volatility range of components as only one sorbent can be used at any one time. Several different monitors may be worn or placed simultaneously if required. The relatively slow sampling rate restricts detection limits around 1-10 ppb for normal 24 h sampling period. Long term (3-28 days) diffusive sampling times are currently under evaluation and may be used for the ppt detection limits.

On-Line Air Stream Sampling

Semi-continuous on-line air sampling and GC analysis is a relatively new technique with applications ranging from urban air quality testing to occupational hygiene. The procedure involves a volume of air being pumped directly into the focusing trap via an inert mass flow controller. After sample collection, the trap heats rapidly, transfers the sample to the GC analytical column and initiates the GC separation. As soon as the trap recools the system is ready to collect the next sample. The chromatographic analysis of the previous sample continues while the next sample is collected.

Experimental Section

Sampling, Instrumentation, Operating parameters, Procedures

Between February and May 1998, samples were taken in Veszprém by diffusive sampling with standard Perkin-Elmer sample tubes ($A = 0.2 \text{ cm}^2$; $L = 1.5 \text{ cm}$) filled with 250 mg of Tenax TA adsorbent for the determination of BTEX (benzene, toluene, ethylbenzene, m,p-xylene) compounds. The sampling sites were selected to cover a range of sampling locations from heavily polluted downtown areas to less polluted urban locations. The locations were as follows (in the order of decreasing level of pollution):

- Site A. In the downtown of Veszprém, a medium-sized town in the northwestern part of Hungary, near a busy crossroads, 5 m above ground level.
- Site B. In the suburb of Veszprém, with moderate urban traffic, 5 m above ground level.
- Site C. In a conurban location near Veszprém, 5 m above ground level, low level of pollution is expected.

At each sampling site three of each type of adsorbent tubes were applied simultaneously.

Samples were analysed with a gas chromatograph coupled to a Perkin Elmer ATD 400 automatic thermal

desorber. Gas chromatograph: GC 6000 Vega Series 2, column SPB-1, 15 m, 0.53 mm i.d., film 1.5 μm . An IBM compatible PC was used for data acquisition and processing.

In July and August 1998, air samples were collected over Berlin (Germany) on board of an airplane using stainless steel canisters $V = 800 \text{ cm}^3$, $p = 3 \text{ bars}$. The samples were analysed in two ways: 1. directly introducing the sample into a GC-MS-FID system using cryogenic focusing, and 2. trapping the components on solid adsorbent which was followed by thermal desorption, cryogenic enrichment and GC-MS analysis. Both sampling techniques are suitable for detecting very low concentrations of volatile organic compounds.

System 1: The collected samples were analysed directly from the canister by a gas chromatograph: Fisons Instruments GC 8000 Series, column DB-1, 60 m, 0.25 mm i.d., film 1.50 μm , coupled with an MD-800 mass spectrometer and FID.

System 2: Three different adsorbents were used in a multilayer-bed tube for trapping the VOS's: Carbotrap C 20/40 mesh (for relative high molecular weight airborne contaminants), Carbotrap 20/40 mesh (for C5-C9 compounds) and Carbosieve SIII 60/80 mesh (for small airborne molecules such as C2 hydrocarbons). Samples were analysed with a gas chromatograph coupled to a AMA System DA816/KA-D4 automatic thermal desorber: focuser temperature: -80 $^{\circ}\text{C}$ (2 min), desorption: 300 $^{\circ}\text{C}$ for 5 min, injection to GC Focuser: 250 $^{\circ}\text{C}$ for 2 min, conditioning: Tubes: 350 $^{\circ}\text{C}$ for 20 min, Focuser: 250 $^{\circ}\text{C}$ for 20 min. Quartz Tube: 15 cm, 6 mm O.D., 4 mm I.D. were used in the analysis. Gas chromatograph: Fisons Instruments GC 8000 Series, column Permabond OV-624-DF, 50 m, 0.25 mm I.D., film 1.40 μm . VG-Quattro Fisons Instruments triple quadrupole mass spectrometer 4000, EI+, electron energy 70 eV, scan range 22-350 AMU (atomic mass unit), scan time 1.0 s, transferline temperature 150 $^{\circ}\text{C}$, source temperature 150 $^{\circ}\text{C}$, acquisition time 41 min, tune reference compound is Heptacosane (perfluorotributyl-amine).

The carrier gas was helium (Linde 4.6), flow rate 1 $\text{cm}^3 \text{ min}^{-1}$. ALL-Pure Gas Specific Purifier Module and Helium purifier from Alltech was used as helium purifier. Different gas standards were used for making the calibration curves: a: Matheson Gas Products TO-14 Enviro-Mat Ozone Precursor Cat.#34420 Lot#12713 55 compound 1ppm, b: Linde 20 ppb Ethane, n-Butane, Benzene, Toluene and c: Internal Standard 10 ppb Dichloromethane-D2, Acetone-D6, Cyclohexane-D12, Benzene-D6, Toluene-D8.

Results and Discussion

Aromatic hydrocarbons were analysed in Veszprém. The samples were collected using diffusive sampling. A few of these results are presented in this paper to illustrate the usefulness of this method (Table 2). The concentration of benzene, toluene, ethylbenzene and

Table 2 The concentration of BTEX compounds in different parts of Veszprém

	Site A. $\mu\text{g m}^{-3}$	Site B. $\mu\text{g m}^{-3}$	Site C. $\mu\text{g m}^{-3}$
Benzene	5.75±0.15	1.52±0.04	1.09±0.01
Toluene	16.72±0.50	5.45±0.15	2.95±0.06
Ethyl-benzene	4.01±0.10	1.15±0.03	0.44±0.01
m,p-Xylene	13.07±0.41	2.52±0.05	0.97±0.02

Table 3 The concentration (c) of volatile organic hydrocarbons found above detection limits over Berlin

Name	c ($\mu\text{g m}^{-3}$)	Name	c ($\mu\text{g m}^{-3}$)
Propene	0.69	Hexane	8.30
Propane	0.04	trans-2-Hexene	0.23
i-Butane	0.57	cis-2-Hexene	0.17
1-Butene	1.90	Methyl-cyclopentane	0.37
3-Methyl-1-Butene	0.07	2-Methylhexane	0.18
2-Methylbutane	0.30	Cyclohexane	1.02
Pentane	0.38	3-Methyl-Hexane	0.24
trans-2-Pentene	0.12	Benzene	2.22
Isoprene	0.80	2,2,4-Trimethylpentane	0.90
		Heptane	0.74
cis-2-Pentene	0.14	Methylcyclohexane	0.28
2,2-Dimethylbutane	0.45	2,3,4-Trimethylpentane	0.13
4-Methyl-1-Pentene	0.07	2-Methylheptane	0.22
		3-Methylheptane	0.43
Cyclopentene	0.16	Ethylbenzene	1.37
2-Methylpentane	0.16	Styrene	0.14
Cyclopentane	0.14	α -Pinene	3.28
3-Methylpentane	0.28	β -Pinene	0.57
2-Methyl-1-Pentene	0.68		

m,p-xylene was highly variable in the city depending on location. The concentration ranged from 0.44 to 16.72 $\mu\text{g m}^{-3}$. The concentration of all the aromatic hydrocarbons was highly correlated with each other ($r^2 \geq 0.95$) which suggests the presence of only one major emission source. This is probably due to the high traffic in Veszprém. The benzene: toluene: ethyl-benzene: m,p-xylene ratios were on average = 1: 3.1: 0.6: 2, respectively. The high toluene/benzene ratio suggests the proximity of traffic emission sources [10].

Diffusive sampling is an inexpensive and reliable method for monitoring long term average concentration of hydrocarbons in the environment. The precision of the method has been determined by parallel sampling, and is roughly 3 %. One week sampling period is sufficient to obtain time-weighted average concentrations of aromatic hydrocarbons with a fair degree of accuracy. Results are shown in Table 2.

In July and August 1998, air samples were collected over Berlin (Germany) on board of an airplane using stainless steel canisters for the determination of 54 VOCs.

The following advantages of stainless steel canister sampling were established:

1. well-suited for grab sampling of C2-C8 hydrocarbons. The risk for irreversible losses due to wall adsorption increase with increasing boiling point and polarity of the analytes,
2. very low blank levels can be obtained,

3. the samples can be stored for several weeks without changes in sample composition.

However, the technique has some disadvantages:

1. the bottles are heavy, therefore the transportation is limited,
2. the special inert bottle surface and the clean shut-off valves makes it rather expensive,
3. the sample may contain significant amount of water, which should be removed before analysis, resulting in evaporative losses of the less volatile ($>\text{C}_8$ hydrocarbons) compounds.

By trapping the compounds on a solid sorbent, this latter limitation is largely overcome.

The concentrations of volatile organic hydrocarbons in a selected sample are given in Table 3. Different classes of organic compounds were found: alkanes, alkenes, aromatic hydrocarbons and terpenes. The precision of the measurements was ± 5 to 20 %.

Conclusion

Different sampling techniques are available for the sampling of volatile organic compounds in air. This fact, in itself, indicates that each of them has its field of application. We have shown that each has advantages and limitations but they are not really comparable. The selection of a sampling technique is primarily governed by the objective of the analysis. If long-term time-weighted average concentrations of VOCs are needed for monitoring, diffusive sampling is the only feasible method. Sampling aboard an airplane requires instantaneous and more sensitive methods, such as grab sampling. Active sampling is probably the most common of all air sampling techniques, now being challenged by diffusive sampling on one side and automated semi-continuous sampling on another. One should remember, however that sampling is only a part of a system on which the quality of the analytical data relies.

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