Preconcentration, thermal desorption & analysis of volatile organic compounds

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1. PRECONCENTRATION, THERMAL DESORPTION & ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

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INTRODUCTION

Volatile organic compounds ("VOC") cover a large number of compounds, of which some are toxic (benzene, 1,3-butadiene...) and others are involved in atmospheric chemistry, such as the so-called "ozone precursors". Both benzene and ozone precursors are now covered by European daughter directives [1], [2]. VOC represent a complex mixture and are present in ambient air at low concentrations: from tens of ppbv to sub-ppbv concentration levels. Therefore, their measurement requires preconcentration and high resolution separation. The precise sampling and measurement technique depends on the kind of compounds to be measured. However the principle of the measurement remains the same and can be presented as in Figure 1. Solvent extraction of samples taken on activated carbon will not be covered by this paper, as this procedure is less sensitive and the solvents used are harmful to the environment.
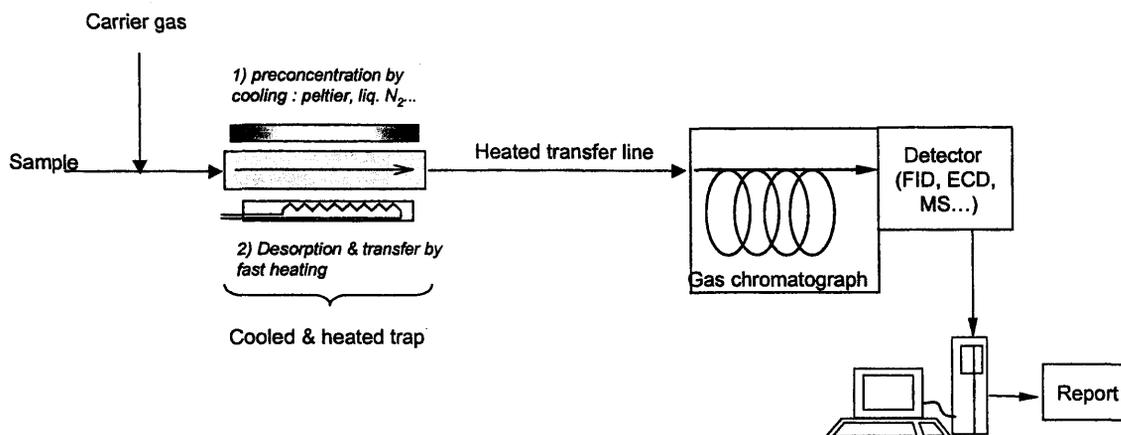

Figure 1 : general principle of preconcentration & analysis.

Typically around a one litre volume of air (either on-line via an in-line drier, by extraction from a canister or via thermal desorption of a tube) is concentrated onto a cooled, sorbent-packed trap. The trap is then quickly heated, under a low flow of helium, to desorb and inject the compounds. This highly concentrated plug of sample is transferred via a heated transfer line, to a capillary chromatographic column, on which the compounds are separated. Each compound gives a signal on a selected detector. The area of each chromatographic peak is related to the mass of compound through response factors determined via calibration.
Specific procedures for different applications will be given for each step.

[1] Directive 2000/69/EC , OJ L 313, 13.12.2000, p 12
[2] Directive 2002/3/EC, OJ L 67, 9.3.2002, p 14

SAMPLING : OZONE PRECURSORS & OTHER VOC...

Depending on the application, sampling can be done using :

– Direct sampling onto the cold trap ("on-line" sampling) : this procedure allows the measurement of a large range of VOC, like ozone precursors and various industrial emissions, from 2 to 10 atoms of carbon, on a quasi-real time basis. Disadvantage is a unique measurement point, e.g. the apparatus can only be used where it is installed. If it is not in a laboratory, but on-site, air conditioning and fluids, as well as a communication line, will be needed.

– Canister sampling : canisters are stainless steel containers, with a specially treated internal surface (electro-polished or fused silica coating) to avoid adsorption of VOC. Sampling can be done either by opening the sampling valve and allowing the ambient air to flow freely into the evacuated canister, or by flushing it with a pump. Advantages of this method are that a whole air sample may be taken at remote locations, which is very useful for the measurement of ozone precursors for instance (see the list in annex), or for the determination of unknown compounds by GC/mass spectrometry. Disadvantages are the cost of canisters (higher than adsorbent tubes) and the difficulties in use : transport (many canisters are 6 litres), cleaning...

– Active sampling : this is done by pumping ambient air through a tube filled with carefully selected adsorbent. Tubes can be packed with one, 2 or three different adsorbents, which allows the sampling of a wide range of compounds. Examples of largely used single bed tubes are for BTEX and C5 to C9 : Carbotrap, Carbopack, Carbograph, Tenax. C3 to C5, and the lighter chlorinated compounds, can be sampled on Carbosieve SIII or Carboxen 1000. Examples of tubes with combination of adsorbents are : Carbopack C (C10-C15), Carbopack B (C6-C9), Carbosieve SIII (C3-C5). These tubes can be used for sampling ozone precursors, except the C2 (ethane, ethene and ethyne), and formaldehyde. Duration of sampling depends on the flow rate of the pump and the volume of air, but extends typically from some minutes to a few hours. There are examples of sampling over 15 days period (BTEX sampling in UK).

– Passive sampling (1- 15 days) : tubes are packed with only one adsorbent, and open to ambient air at one end, letting the compounds diffuse freely onto the surface of the adsorbents. Typical use is for BTEX sampling (French experience). There have also been attempts for light compounds (1,3-butadiene...). Advantages are the lightweight of the method (on-site, tubes are protected in a shelter, but no pump is needed), and integration over a period of time up to several weeks. This is particularly useful for determining the mean value of benzene concentrations for instance...

PRECONCENTRATION

The preconcentration step covers the enrichment of the VOC (sampled from 0.5 to 4 litres of air) on a cold trap. This step is followed by a "flash" desorption to transfer very quickly the sample to the analytical system. The cold trap system can be constituted of one or more traps, containing different adsorbents. If the sample comes from a canister or is directly pumped through the cold trap, thermal desorption is operated in a single stage mode. Two stage desorption is used when the sample comes from the primary thermal desorption of an adsorbent tube (either active or passive).

The flow-rates of carrier gas required for efficient desorption of the trap are generally too high for the capillary columns of the GC : there is generally an outlet split of this carrier gas flow.

The preconcentration step can be manual, but for ambient air studies involving a large number of measurements, it is generally automated, either for the on-line sampling or the

primary desorption of numbers of tubes. The most representative examples of preconcentration apparatus presently available on the market are given below.

PERKIN ELMER Turbomatrix : 1 trap, 2 zones

This system comprises one trap which is cooled by a Peltier effect to − 30 °C. For the measurement of ozone precursors in ambient air, this trap contains two adsorbents : Carbotrap or Carbopack B + Carbosieve SIII. This combination allows the preconcentration of hydrocarbons from C2 to C10. The trap is desorbed under a reverse flow of the carrier gas, in order to protect the adsorbent for the light compounds from being contaminated by the heavier compounds.

The system can desorb adsorbent tubes which are placed on a carrousel (up to 50 tubes) or can be supplied with an on-line introduction option, which is also used to sample air from canisters. This on-line injection is presented in Figure 2. On this path, sample goes through a Nafion drier. This is not the case for the compounds with are extracted from an adsorbent tube.

Major advantages of this system are that preconcentration is made in one step, and there is no need of a coolant like liquid nitrogen. Disadvantage is that the sample coming from an adsorbent tube does not go through the drying device, and if there is a high amount of water trapped on the tube, there may be a small ice ball on the cold trap. Repeated desorptions of large amounts of water lead to a permanent damage of the adsorbents, and to a reduced lifetime of the trap. Also, the injection of quantities of water on the chromatographic column leads to analytical problems. This phenomenon can be overcome by either limiting the volume of air sampled on the tube (see for instance US EPA TO17 [3]), sampling through a cooler device to condense water, or using a dry purge of the tube by the carrier gas before analysis.
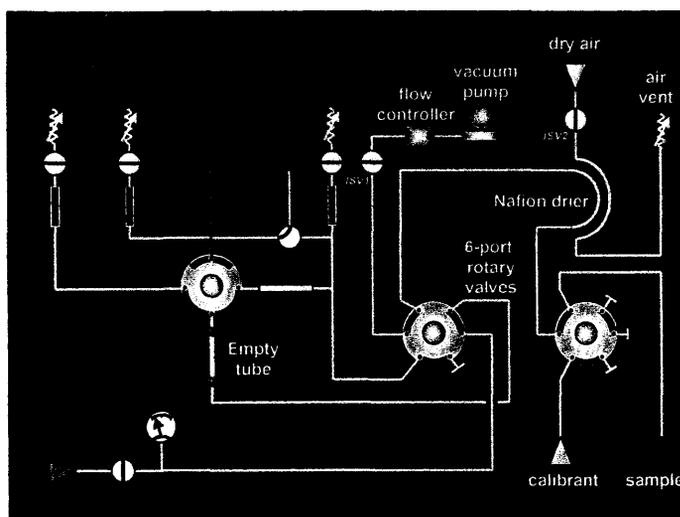

Figure 2 : Perkin Elmer Turbomatrix preconcentrator

ENTECH P7100 : 3 traps in line

This preconcentrator, shown in Figure 3, contains three traps in line, with two different adsorbing materials, and was specially designed to analyse, with a GC and a mass

[3] US EPA (1997) : « Compendium method TO-17 : Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes ». January 1997

spectrometric detection, air samples from canisters, following US EPA TO-14 [4]. Different temperature programs of the three traps can be used, depending on the application. For measurement of VOC in ambient air, "microscale purge and trap" is the most suitable program :

- The first trap is packed with glass beads and cooled at − 150 °C with liquid nitrogen : there, VOC are concentrated, and water condensed, though oxygen, nitrogen and argon are not trapped and go to the vent. The transfer of the compounds to the second trap starts before the heating of the first trap This trap is heated to ambient temperature, allowing the VOC to be transferred by the helium flow on the second trap, though water remains liquid on the glass beads and is eliminated during the bakeout of this trap.

- The second trap is packed with Tenax and cooled at − 10 °C : the organic compounds are trapped but not carbon dioxide. This allows the removal of CO_2 before injection on the column and in the mass spectrometer.

- The third trap is a single piece of deactivated column and is only used for cryofocussing of the compounds.

Advantages of this system are a good removal of water and carbon dioxide, which is necessary for a good analysis on the mass spectrometer. Disadvantages are the needs for liquid nitrogen, some loss of the more polar compounds in water on the first trap, and in some cases the breakthrough of the lighter compounds (C2 mainly) on the Tenax trap. The latter case can be solved by changing either the adsorbent (Carbotrap or Carbograph) or the temperature program.

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[4] US EPA (1999) : « Compendium method TO-14A : Determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography ». 2nd edition, January 1999
Compendium methods can be dowloaded from the EPA web site :
http://www.epa.gov/ttn/amtic/airtox.html

For further information on the subject, see also :
- McCLENNY W. A., PLEIL J. D., EVANS G. F., OLIVER K. D., HOLDREN M. W., WINBERRY W. T. (1991) : « Canister-based method for monitoring toxic VOCs in ambient air ». J Air Waste Manag. Assoc., vol 41, n° 10, pp 1308-1318.
- TOLAI B., HLAVAY J., MOLLER D., PRUMKE H.-J., BECKER H., DOSTLER M. (2000) : « Combination of canister and solid adsorbent sampling techniques for determination of volatile organic hydrocarbons ». Microchem. Jal, vol 67, pp 163-169.
- SKOV H., LINDSKOG A., PALMGREN F., CHRISTENSEN (2001) C. S. : « An overview of commonly used methods for measuring benzene in ambient air ». Atmosph. Envir., Vol 35 suppl. 1, pp S141-S148
- MARKES, application note n° 12, « About thermal desorption : an introduction ». Can be downloaded from the web site :
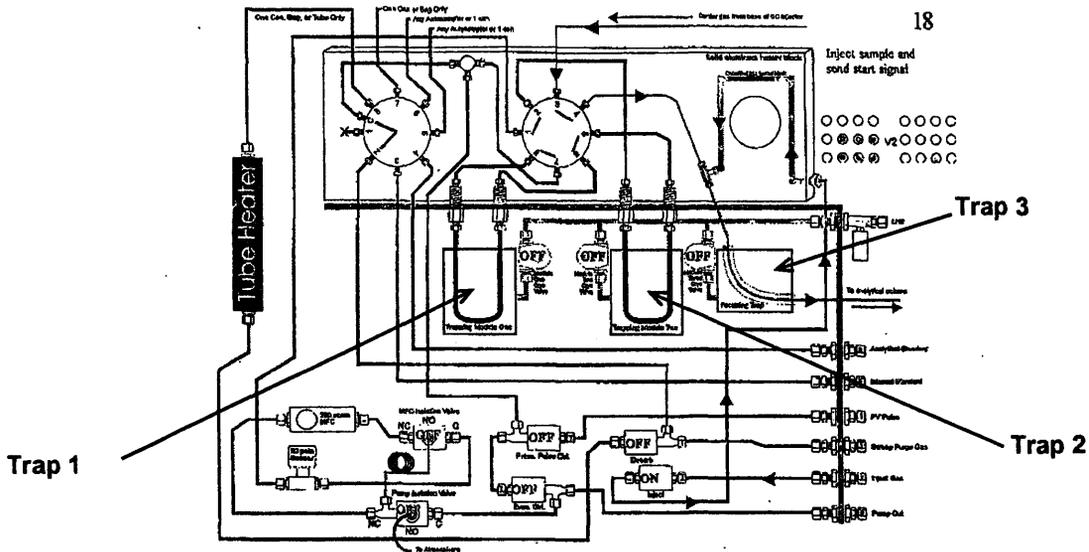http://www.markes.com/technicalhelp/publications/default.asp

Figure 3 : pneumatics of Entech preconcentrator

MARKES International Ltd UNITY : 1 trap, recollection possible

The principle of this system is very similar to that of the Perkin Elmer Turbomatrix preconcentrator: in that it uses Peltier cooling and allows both on-line sampling and tube desorption. The original feature of the Markes system is that the split part of the sample which comes from the primary desorption of a tube (see in

Figure 4) and/or from the second stage desorption of the trap, can be recollected on a second tube. This uniquely overcomes the one-shot nature of thermal desorption and permits a second reanalysis of a sample, which is normally impossible on tubes which have been desorbed.
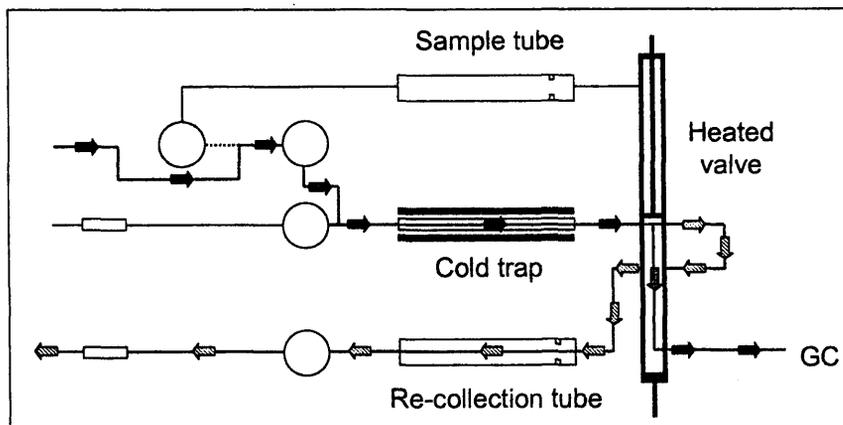

Figure 4 : SecureTD™: re-collection of the split part of the sample (Markes International Ltd)

ANALYSIS : SEPARATION

Separation of the individual compounds to be analysed is made on a gas chromatograph, equipped with one or two capillary columns. Systems with two columns and two detectors were developed because it is nearly impossible, due to the difference in their boiling points, to analyse on the same column, with the same accuracy, compounds as different as ethane

and trimethylbenzenes. If the target compounds are within a limited range, like BTX, a gas chromatograph with a single column can be used. The range of compounds eluted can be increased by starting the oven program at sub-ambient temperatures, with a cooling by carbon dioxide injection. This may allow a good separation of compounds from C4 to C9-C10 for example. But the quantitative recovery of C2 to C9 cannot be performed on a single column. If a GC with dual column is not available, the analysis of the ozone precursors as imposed by the EC Directive requires 2 GC.

Hydrocarbons are analysed on apolar columns, the lighter compounds (C2-C5) are generally separated on a Plot Alumina (KCl or NA_2SO_4 washed), the heavier compounds (C6-C10) on a methyl silicone column : CPSIL5, DB1...

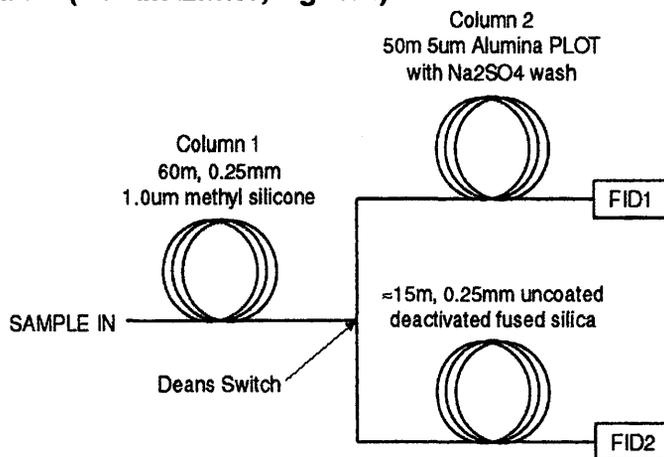## GC : double column (Perkin Elmer, Agilent)

Figure 5 : scheme of dual column chromatographs (Markes)

Figure 5 represents a GC fitted with 2 columns, with a device called "Deans switch", which splits the family of hydrocarbons between the light and the heavy compounds. All the compounds are injected on the methyl silicone column. The light compounds pass virtually unretained though this column, and are directed, through the Deans switch, onto the alumina column and detector 1. After some minutes (typically 10 to 13), all the C2-C5 compounds are on the Plot column, the Deans switch operates, and the heavier compounds, which are now eluted, are directed, through a deactivated uncoated retention gap, to the second detector. The two chromatograms are recorded at the same time : Figure 6 gives an exempla of the analysis of a calibration mixture containing 30 VOC from C2 to C9. Equilibrium in the carrier gas pressures between the different columns is critical, and rather difficult to adjust. Once it is adjusted, if the system is stable, the retention times on both columns for all the analysed compounds should remain stable for at least several weeks. This device can be installed on GCs from Perkin Elmer and Agilent.
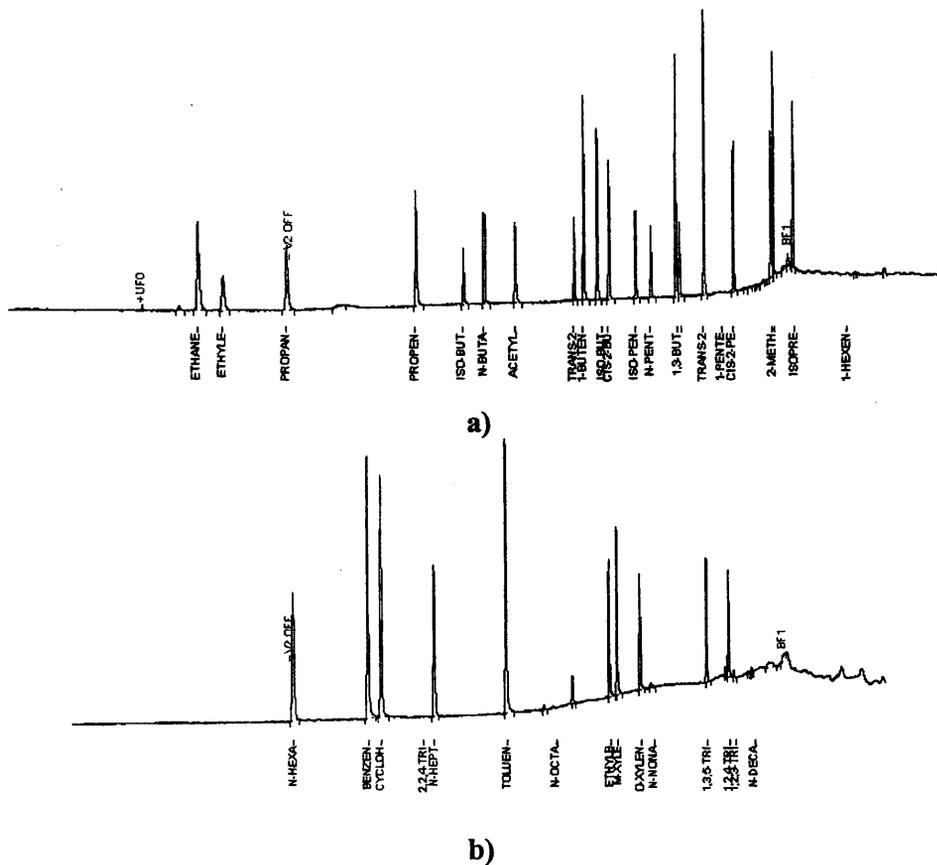
a)

b)

Figure 6 : chromatograms of 0,6 litre of NPL calibration mixture (30 VOC, concentrations from 1 to 7 ppbv) : a) light compounds, b) : heavy compounds
(Perkin Elmer ATD Turbomatrix, GC Autosystem, double column, double FID, INERIS, May 2002)

IDENTIFICATION - QUANTIFICATION

The identification and/or quantification is done at the outlet of the chromatographic column, with different types of detectors, depending on the application :

- FID : Flame ionisation detector is not specific but detects all combustible gases, is linear over a wide range of concentrations, and is very stable during the time : it is therefore well adapted for general purposes, and particularly for routine measurement of the ozone precursors. Limitations : the response factor to chlorinated hydrocarbons is smaller than

for HCs, and identification of the compounds is done only by their retention times. If compounds are co-eluted the FID response is the sum of the two signals.

- PID : Photo-ionisation detector. This detector is more specific, because only HC with multiple bonds give a response. Aromatic compounds are well measured by this type of detectors, but due to the use of a UV lamp, there is a drift in the response and this detector must be very often calibrated.

- ECD : Electron capture detector has a radioactive source of electrons. It is very sensitive to electron-acceptor compounds, like halogenated and oxygenated HC.

- MS : Mass spectrometer is more sophisticated than a simple detector like FID or PID (in particular it relies on a good vacuum system, and the coupling with the column is tricky) but is much more versatile, as it allows the identification of unknown compounds, resolution of co-elution...). It may be a little less stable than a FID, but with a good calibration quantification of the compounds is possible.

- FPD : Flame photometric detector, due to the presence of a monochromatic optical filter, responds to very few compounds but is very sensitive, and therefore useful when a single family of compounds, like sulphur, is sought.

- Other types of detectors can be used, but are so specific, and restricted to peculiar applications, that they will not be described here.

SUPPLIES

Quantitative analyses of low concentrations of VOC in ambient air are performed with encumberant laboratory apparatus, situated either in the laboratory or on-site, or for limited applications, with simplified apparatus like continuous monitors for BTX. These latter systems are also generally based on the preconcentration of VOC from a volume of air, followed by a chromatographic separation and a classical detection (FID, PID). Only one system developed in France and commercialised by SERES has a preconcentration on a trap, followed by UV analysis with a spectrometer. Except this device, all systems need, in addition to electrical power, different supplies to work, which can cause difficulties for on-site installations.

- Several gases with at least a good purity are necessary : at least, a transfer and carrier gas, generally helium, with a quality of 99.999 %, but which can be replaced, in the BTX monitors for instance, by the hydrogen used for the FID. Air is often used, first for the automatic thermal desorbers, for the pneumatic controls, and in second place for the flame detectors. Hydrogen is also necessary for flame detectors. Nitrogen can be used for transfer purposes and as a make-up gas when the flowrate from the column is insufficient for the detector, like the ECD.

- A cooling system is necessary for the trap : it can be a Peltier device, which only needs electrical power. In other systems, the trap is cooled by injection of a fluid like carbon dioxide or liquid nitrogen. Cooling can also be performed by a vortex system, which needs an air compressor to work ; the latter device is heavy and noisy. With the exception of Peltier devices (when electrical consumption is not limited), coolants for the trap are heavy constraint for on-site installations.

- The use of a mass spectrometer detector implies a good vacuum, with both primary and secondary pumps, which are also to be carefully maintained in order to work properly.

- Due to the low concentrations of the target VOC, reference materials for the calibration of the analysis can be expensive and long to obtain, like calibration gas mixtures with concentrations of each compound below 10 ppbv.

–   Sampling systems like canisters, spare parts for the analytical apparatus, and maintenance are also generally very expensive and this point cannot be neglected.

SOME DIFFICULTIES

Measurements of low concentrations of VOC in ambient air, even run in routine, are subjects to a lot of difficulties which can arise one day or the other. Among them (the list is not exhaustive) :

–   Leaks can happen to any analytical apparatus, or within the transfer system from the sample to the GC. Small leaks can be very difficult to locate, and can be the source of analyte loss or miscalibration.

–   Poor blanks (of trap, canisters, tubes...) will not allow the accurate measurement of the smallest concentrations, the same as if the limits of detection are to high.

–   Samples with too high concentration levels (from very polluted areas, or industrial surroundings) will saturate the detectors, and the quantification will not be possible.

–   After injection of highly concentrated samples, the system may be contaminated and sensitivity recovery may take a very long time.

–   There may be a strong interference from water or CO_2 , particularly sensible with mass spectrometers. The volume of air sample should be limited, and use of specific procedures like "microscale purge and trap" can help to limit this problem.

–   In some cases, when sampling is done in remote locations, conservation of samples can also be critical : for example, losses in the most reactive compounds (like 1,3-butadiene) can lead to an important underestimation...

CONCLUSIONS

Depending on the application (family of VOC and expected concentrations), the different steps will be carefully chosen : type of sampling system, time period, transfer to the analytical chain, column(s), detectors, means of calibration (gas mixtures or diluted solutions)...

Accurate measurements of VOC at low concentrations in ambient air (BTX, ozone precursors...) are possible on a routine basis, provided that the persons who undertake these measurements implement high quality procedures, including systematic controls of the analytical chain, as well as controls of the sampling systems, checks of the blanks, and samples conservation. Regular calibrations, within the expected range of concentrations, are also mandatory.

All these arrangements should lead to accurate measurement of ambient, low concentrations of VOC, down to sub-ppbv.

Ozone precursors to be measured at least in one location of each member state (ref. 2) :

Ethane	trans-2-Butene	n-Hexane	m+p-Xylene
Ethene	cis-2-Butene	i-Hexane	o-Xylene
Ethyne	1,3-Butadiene	n-Heptane	1,2,4-Trimethylbenzene
Propane	n-Pentane	n-Octane	1,2,3-Trimethylbenzene
Propene	i-Pentane	i-Octane	1,3,5-Trimethylbenzene
n-Butane	1-Pentene	Benzene	
i-Butane	2-Pentene	Toluene	Formaldehyde
1-Butene	Isoprene	Ethylbenzene	NMHC