AirPass: a Cutting-edge Sampling Technology for Organic Compounds in Air

Monitoring organic compounds in air, including indoor air (domestic sampling), ambient air and exhaust gases is becoming increasingly important to properly address the impacts of biogenic and anthropogenic released species on humans and ecology. At present, our knowledge on emission and emission rates is limited. One of the main reasons is the relatively complex sampling procedure. Moreover, samples have to be taken by qualified technicians making air analysis expensive. One of the major objectives of our recent research in air monitoring was to simplify the sampling procedure such that more samples can be taken and analysed to improve our knowledge of the fate of organic carbon in the atmosphere. The sampling system AirPass is presented and its features illustrated.

> *"The robustness and reliability of the AirPass concept was tested on a real sample taken from a chemical storage room."*

Author Details:
Christophe Devos, Bart Tienpont, Karine Jacq, Frank David and Pat Sandra
Research Institute for Chromatography
Kennedypark, 26,
8500 Kortrijk, Belgium
Tel: +32-56-204031
E-mail: info@richrom.com
Web: www.richrom.com

In air monitoring, well-established methods are available for analysis of the volatile organic compounds (VOCs) or oxygenated VOCs (OVOCs). For semi-volatile solutes, including polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs, pesticides and nitrosamines, high volume samplers in combination with different traps (including; glass fiber filters, impingers, and polyurethane foam) are widely applied. These sampling devices require labour intensive and solvent consuming additional sample preparation steps before a final extract is obtained that can be analysed by gas chromatography – mass spectrometry (GC-MS).

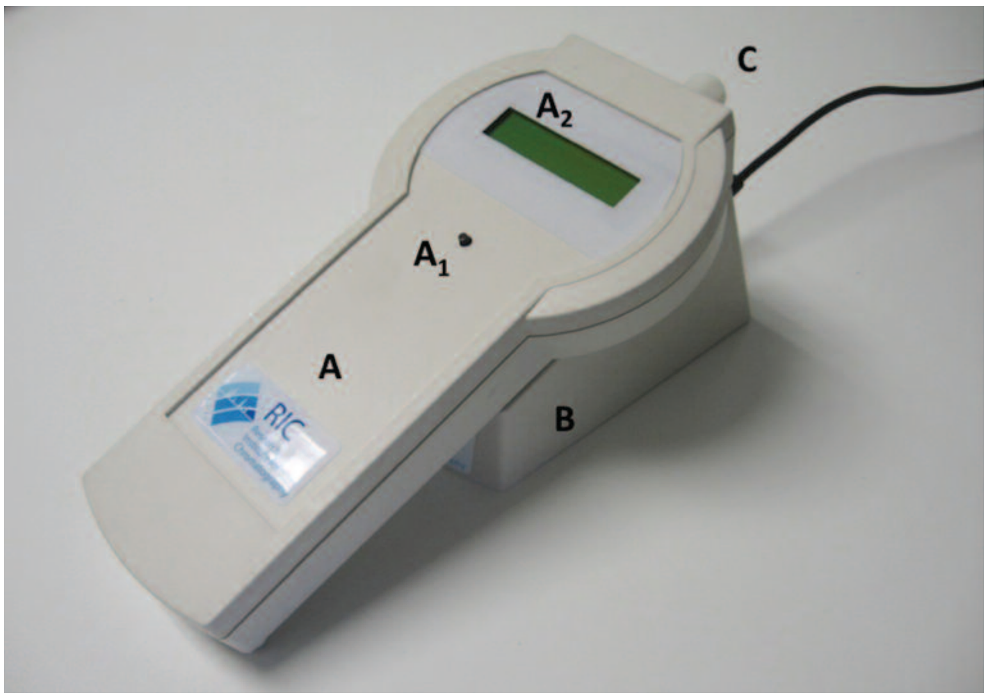

Figure 1: AirPass handheld sampler for air monitoring (A) (A1: start/stop button, A2: display), with battery charger (B) and container with (ad)sorption tube (C)

In recent years, liquid desorption has been increasingly replaced by thermal desorption placed on-line with the GC-MS system. This offers the advantage that all solutes concentrated on a sampling tube are introduced into the analytical system increasing drastically the sensitivity compared to liquid desorption. Thermal desorption is already well established for analysis of volatiles, but extension to the analysis of semi-volatiles often encounters problems related to inefficient desorption and incomplete transfer of the solutes into the analytical system. In this respect, it is very important that desorption flow and analytical flow are independently controlled and that the flow pathways are as short as possible, thermally controlled (no cold spots) and inert. This is, for instance, the case for the Gerstel TDU thermal desorption system (Gerstel GmbH, Mülheim an der Ruhr, Germany). A short thermal desorption tube can be efficiently desorbed at relatively high flow (50-200 mL/min) and the desorbed solutes are cryo-trapped in a liner of a programmed vapourising injector (PTV) located just below the thermal desorption unit. Since there is no transfer line, efficient non-discriminating thermal desorption is realised. Cryo-focusing is then done in an inert deactivated liner during the desorption step. In the next step, the solutes are quickly injected in the GC column in a non-discriminating way using a low (capillary column) flow by flash heating the PTV inlet. This approach can be used for a very broad range of apolar and polar solutes, including; PAHs, nitro-PAHs, polychlorobiphenyls (PCBs), pesticides and flame retardants.

By using thermal desorption without splitting, very high sensitivities can be obtained. Consequently, the sample size can be reduced to a few litres. In fact, a 1 L sample is sufficient to detect levels below 1 ng/m^3 if the solutes present in the 1 L sample are quantitatively injected in the GC. State-of-the-art MS systems easily allow detection of 1 pg solute (i.e. 1 ng/m^3 = 1 pg in 1 L = 1 pg on-column). Depending on solute concentration and complexity of the matrix, either single quadrupole MS or triple quadrupole MS can be used. The single quadrupole MS performs well for general screening and target compound analysis, while the triple quadrupole MS operated in multiple reaction monitoring (MRM) mode offers enhanced selectivity for target compound analysis in the most complex matrices [1].

The small sample volumes needed when state-of-the-art instrumentation is applied, opens interesting perspectives to develop small hand held sampling devices. The sampler recently developed in our laboratory and called AirPass is shown in Figure 1. The sampler contains all parts necessary to take air samples in an accurate and reproducible way, specifically a pump, flow meter and flow controller, and sampling tube packed with (ad)sorbent. The pre-conditioned tube containing a pre-selected (ad) sorbent (such as Tenax or PDMS [2]) or a mixed bed [3] can easily be installed or removed by locking and unlocking the container body (C) in which the sampling tube is inserted, hereby avoiding external contamination. The sampling flow is fixed and calibrated at 100 mL/min while the sampling time can be varied between 10 min (1 L) and 240 min (24 L) in 10 min steps.

The robustness and reliability of the AirPass concept was tested on a real sample taken from a chemical storage room. Three different AirPass devices, each equipped with a sampling tube filled with the same amount of Tenax, a highly inert and porous polymer resin based on 2.6-diphenylene oxide, were applied at the same time to sample 2 L air. The result from this experiment is shown in Figure 2. System-to-system reliability and robustness of the design is excellent. More technical details of the AirPass can be found on our website [4].

The initial reason to develop the AirPass was domestic sampling. We receive indeed more and more requests by individuals to analyse indoor and outdoor air contaminants, pollutants, bad odours, allergens and other negative air quality parameters. Very often the bottleneck in performing such analyses is the high price which is mainly due to the costs of sampling by skilled technicians, and not at all by the costs of the analysis as such. This can be bypassed by sending by express mail an AirPass pre-adjusted to the problem at hand. The customer has only to unscrew the adsorbent container cap (C), push the button (A1), screw the cap again and send the whole unit back for analysis.

A typical application using only 1 L sampling is shown in Figure 3 for the analysis of air close to a waste water treatment plant. The sludge originating from the water treatment is stored on-site causing periodical odour problems for the local residents. An AirPass, prepared with Tenax as adsorbent for sampling during 10 min at 100 mL/min, was sent to a resident. Upon return of the AirPass, the tube was removed from the unit and installed in a TDU. The solutes were desorbed at 260°C for 7 min and trapped in the PTV inlet at -100°C. The compounds were then released by heating the PTV at 12°C/s until 300°C. GC-MS analysis was performed on an Agilent 7890 GC combined with an Agilent 5975C single quadrupole MS operated in the scan mode. The profile is very complex with solutes ranging in carbon number from C_4 to C_{24}. Total profiling GC-MS easily reveals µg/m^3 amounts of organic compounds in air. As expected, most compounds are of biogenic origin (monoterpenes (II), monoterpenoids (III), sesquiterpenes (iV)) but some anthropogenic compounds with bad odour were identified in the profile such as 3-methyl butanal (peak 1), dimethyldisulphide (peak 2) and phenol (peak 3).

With state-of-the-art MS instrumentation, sub-ng/m^3 concentrations can still be measured using small sample sizes. This is illustrated with the determination of nitrosamines in the indoor air of a rubber processing plant. Nitrosamines can originate from vulcanisation initiators and are potential carcinogeneous semi-volatile compounds. Initial tests applying a 2 L air sample (20 min at 100 mL/min) and the conditions described for Figure 3 using a single quadrupole MS system operated in the selected ion monitoring mode showed a lack of selectivity in detection. The relatively low mass ions that are present in the spectra of nitrosamines indeed are not selective enough for trace analysis of a complex air sample using GC-MS in SIM mode. By using a triple quadrupole system in multiple reaction monitoring (MRM) mode, much higher selectivity, and thus sensitivity, was obtained. This is illustrated in Figure 4. Using MRM, the presence of three nitrosamines could be confirmed, namely N-nitrosodimethylamine (NDMA) at 6.80 min, N-nitrosomorpholine (NMOR) at 14.03 min and N-nitrosodibutylamine (NDBA) at 18.36 min. The measured concentrations were 0.35 ng/m^3 for NDMA, 0.01 ng/m^3 for NMOR and 0.04 ng/m3 for NDBA. These pg/m^3 levels demonstrate the extremely high sensitivities that can be obtained.

For another application, namely the elucidation of compounds responsible for a musty odour in a cellar, the sample loading was tuned to 24 L. Two samples were taken in parallel, using two AirPass systems. The first sample was analysed by GC-triple quadrupole MS in scan mode, the second sample was analysed in MRM mode. The chromatographic profile of the scan analysis (Figure 5) was very complex, but by combining with sniffing-organoleptic evaluation the elution windows of some odour compounds could be defined. The second tube was analysed in the MRM-mode and trichloroanisole (TCA) and geosmin were

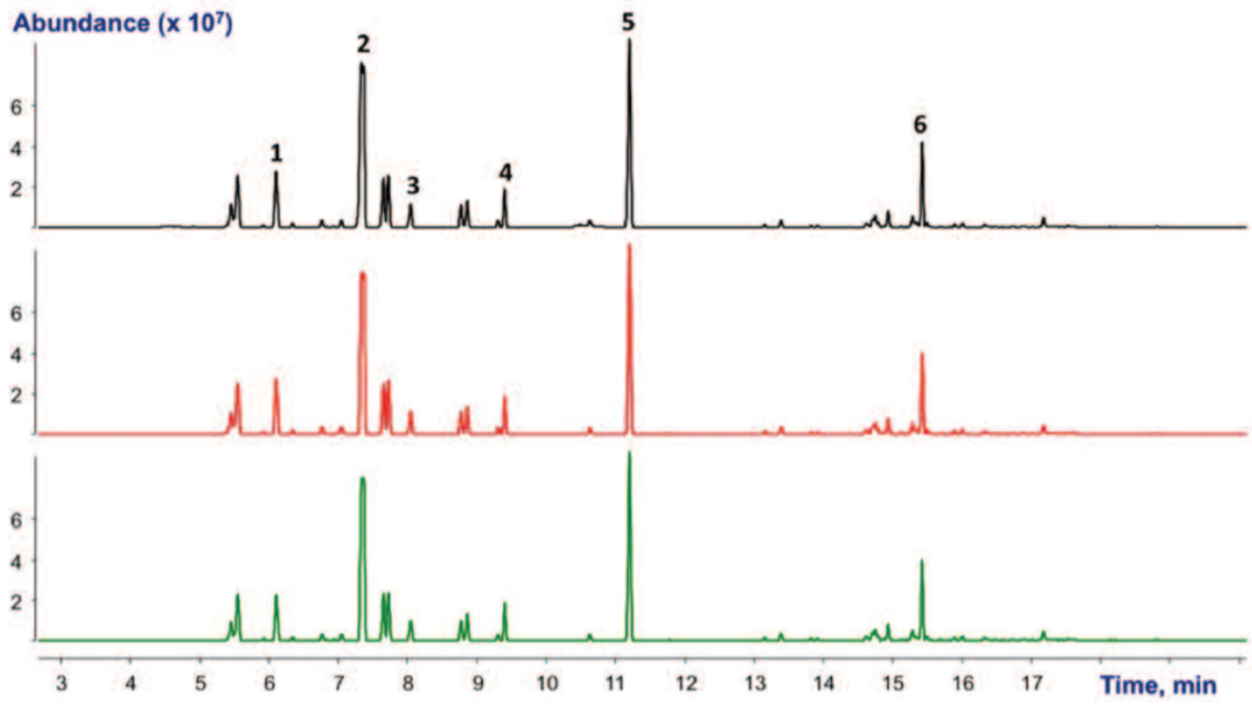

Figure 2: System-to-system reproducibility and robustness test performed on three AirPass systems. Overlaid chromatograms of three air samples (2L) taken in a chemical storage room (peak identification: 1. dichloromethane, 2. hexane, 3. tetrahydrofuran, 4. heptane, 5. toluene, 6. decane)

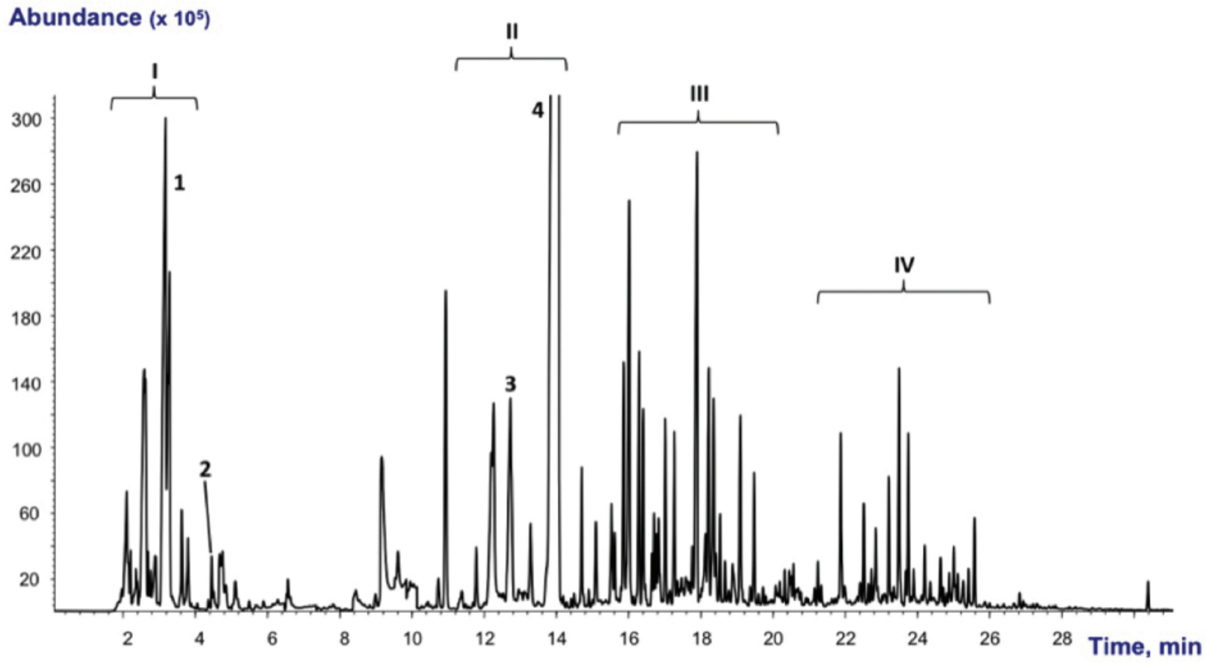

Figure 3: Total ion chromatogram of a GC-MS analysis of air sample from waste water treatment site. Sampling on Tenax, followed by thermal desorption and GC-MS analysis in scan mode. Peak group identification: I: aldehydes/ketones, II: monoterpenes, III: monoterpenoids, IV: sesquiterpenes; Peak identification: 1. 3-Me-butanal, 2. dimethyldisulphide, 3. phenol, 4. limonene

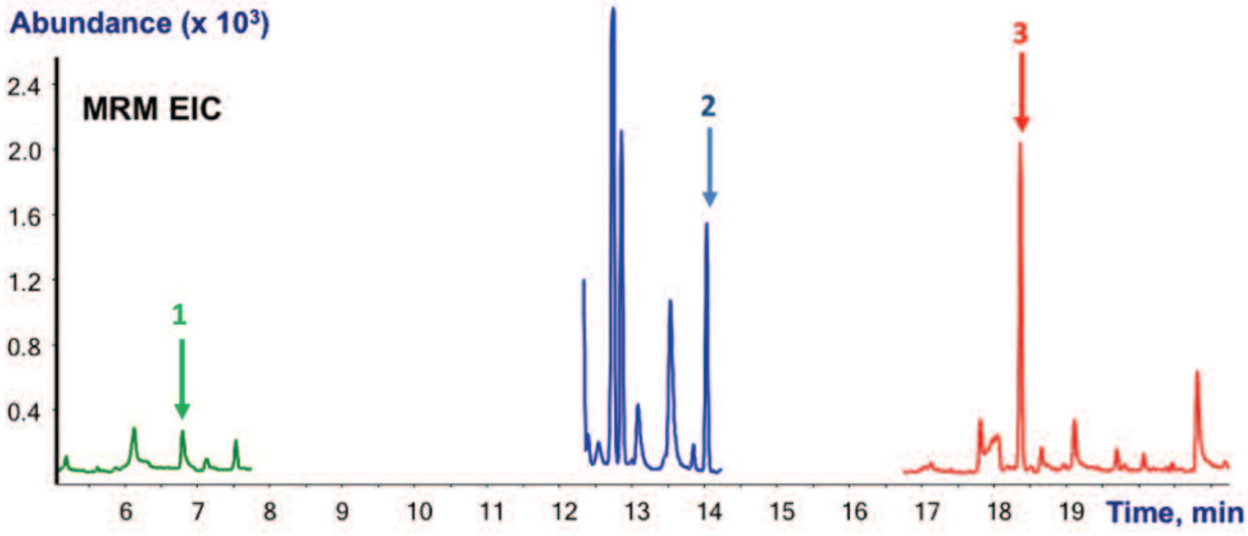

Figure 4: Extracted ion chromatograms of a GC-MS/MS analysis of air sample from rubber production site for nitrosamine monitoring. Peak identification: 1. NDMA (N-nitrosodimethylamine, MRM: 74 → 59); 2. NMOR (N-nitrosomorpholine, MRM: 116 → 86); 3. NDBA (N-nitrosodibutylamine, MRM: 116 → 99)

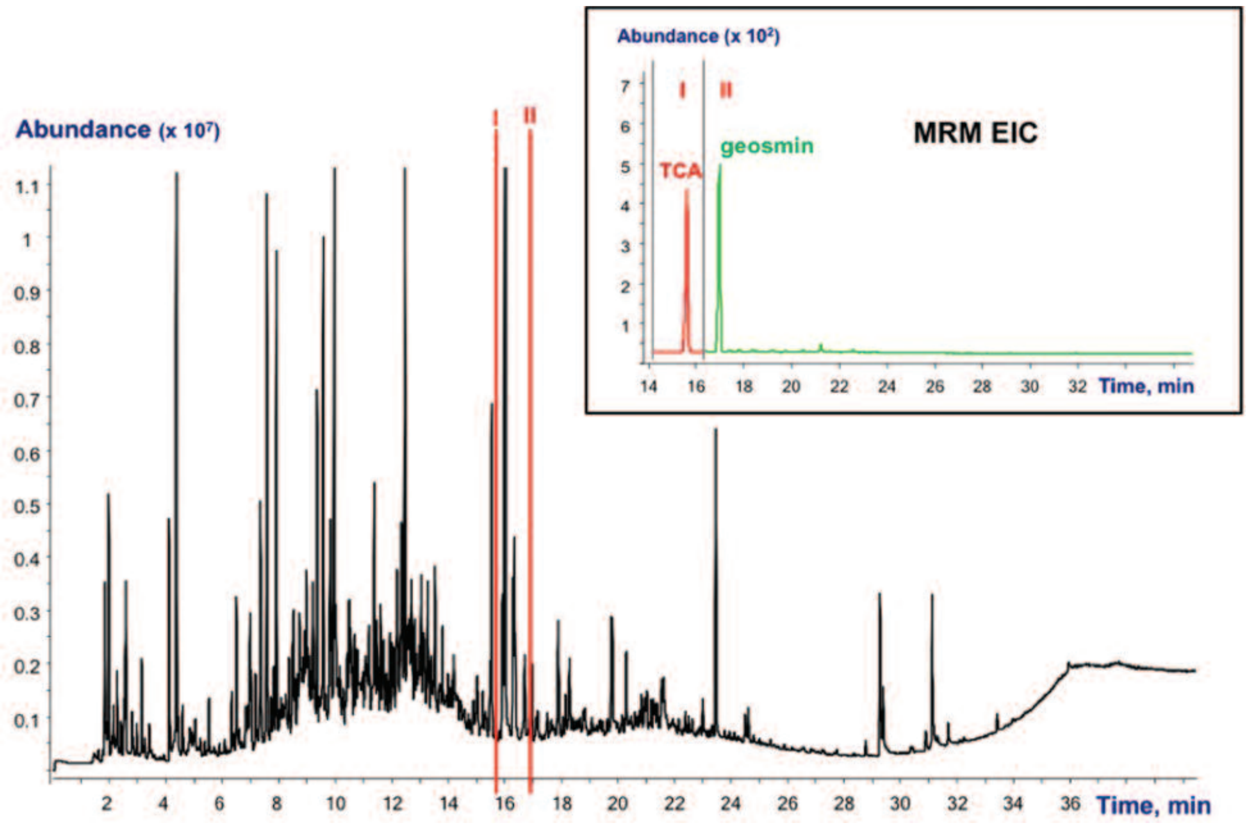

Figure 5: Total ion chromatogram of a GC-MS analysis of air sample from cellar. Odour peaks were detected around indicated zones I and II. Insert shows extracted ion chromatograms from subsequent GC-MS/MS analysis in MRM mode with identification of trichloroanisole (TCA) and geosmin.

identified and quantified (Figure 5, insert). The concentrations were 4 ng/m^3 for TCA and 40 ng/m^3 for geosmin.

In conclusion, the newly developed hand held air sampler in combination with thermal desorption (TD) and GC-MS or GC-MS/MS is an excellent tool to measure air pollution (targeted or non-targeted) on a more regular basis, whilst being cheaper than currently possible. Additionally, sampling can be performed by more inexperienced people.

References

[1] F. David and M.S. Klee, Determination of Nitro-Polycyclic Aromatic Hydrocarbons in Air Particulates using the Agilent 7000A Triple-Quadrupole GC/MS System, Agilent Technologies application note 5990-3366EN, 2008.

[2] E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos, P. Sandra, Improved accuracy in the determination of polycyclic aromatic hydrocarbons in air using 24 h sampling on a mixed bed followed by thermal desorption capillary gas chromatography-mass spectrometry, Journal of Chromatography A, 1190 (1-2) (2008), 286-293.

[3] K. Desmet, M. Schelfaut, T. Górecki, P. Sandra, Evaluation of the suitability of sampling on Tenax TA and polydimethylsiloxane for the analysis of combustion gases, Talanta, 79 (3) (2009) 967-970.

[4] www.richrom.com