



Application
Note

GC–MS Air Analyser for the Determination of very low Concentrations of VOCs in Indoor and Ambient Air, Approaching method TO-17

Sjaak de Koning¹, Geert Alkema², John Maurits³

¹ ChromaVision, Veldstraat 8, 5988AK Helden, The Netherlands, info@ChromaVision.nl

² GL Sciences, Dillenburgstraat 7C, 5652 AM Eindhoven, The Netherlands

³ RUDZL, Dept. of Environmental Analysis, Nijverheidsstraat 3, 6135 KJ Sittard, The Netherlands

Key Words

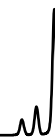
GC–MS, VOC, Air Quality , Air Analysis, Breath Analysis, Volatiles in Air, Ambient Air, Indoor Air, Airborne compounds, Volatile Organic Compounds.

Abstract

An instrument has been developed for the automated, *in situ*, determination of airborne volatile organic compounds (VOCs) using programmed temperature vaporisation injection from a sorbent tube trap. A sorbent tube placed as an injection port liner can be repeatedly used to collect samples of air, with the trapped analytes being subsequently desorbed onto a capillary gas chromatography (GC) column without the use of intermediate cryogenic refocusing. The system does not need any liquid nitrogen or CO₂, there is no need for adsorption/desorption tubes.



Graphical impression of the OPTIC – Air Analyser.



Introduction

Measurements of atmospheric concentrations of volatile organic compounds are currently required in both urban and rural environments, where their presence can be directly detrimental to health, and their ability to form photochemical oxidants in the presence of NO_x and the sunlight is important. People breathe approximately 20 000 liters of air a day, so this concern is significant. It has also been demonstrated that some hydrocarbons may contribute to global warming and stratospheric ozone depletion and may also accumulate as persistent organic pollutants in some environments. Urban concentrations of VOCs are influenced directly by the emissions from major anthropogenic sources such as vehicle emissions, solvent and petrochemical evaporative losses, gas leaks, and many other forms of emission.

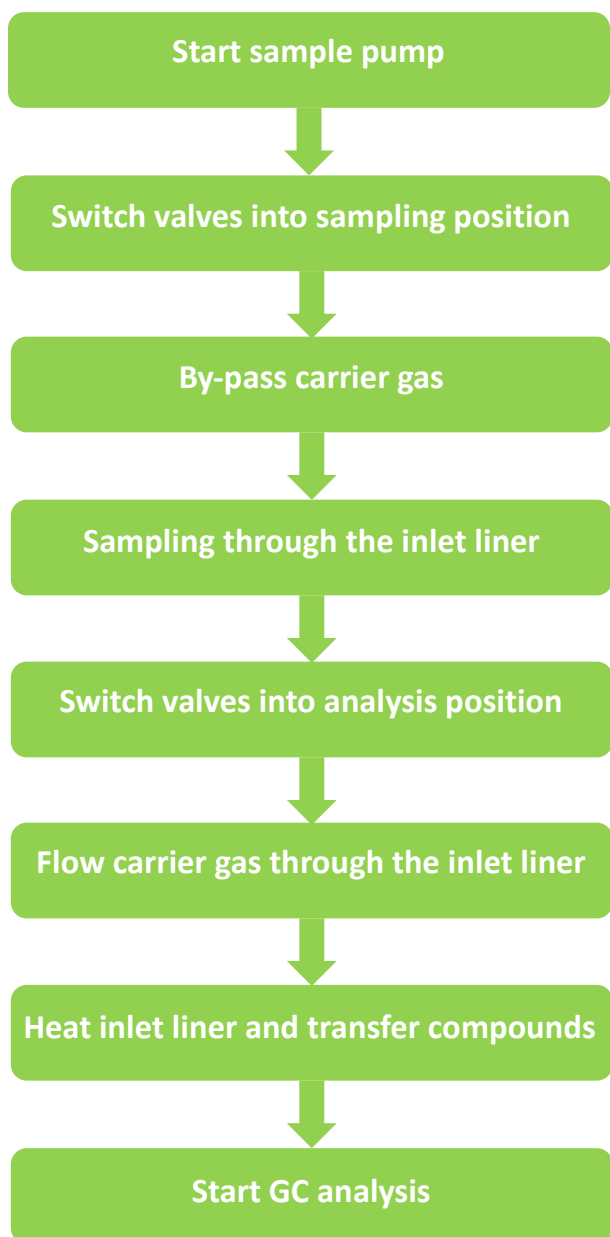
Many methods for analysing airborne VOCs have been proposed, typically using sorbent traps or evacuated canisters. Carbon molecular sieves of differing mesh sizes are particularly effective in trapping VOCs in air and are frequently incorporated into packed sorbent tubes. The analysis is usually then performed by thermally desorbing the collected sample in a stream of helium over a period of several minutes onto a cryogenically cooled intermediate trap. The sample is refocused at the intermediate trap prior to subsequent flash heating, thus introducing the collected analytes as a narrow band onto the analytical column. A method based on a thermally desorbed adsorption trap and cryogenic refocusing with liquid nitrogen (LN₂) or carbon dioxide (CO₂) uses typically 50 liters of coolant per day. Whilst methods involving the cryogenic refocusing of sample produce effective analytical separations, the equipment required is complex and has high operation costs. Also, such a device requires regular user attention to replenish cryogen supplies.



Mobile lab for *in situ* VOC analysis.

Placing a sorbent tube as an injection port liner inside a programmed temperature vaporisation (PTV) injector allows rapid desorption of analytes directly into an analytical column. Using this method the traditional intermediate refocusing between desorption and separation is no longer required.

In this application note we describe the use of an on-line sorbent tube sample collection, with programmed temperature vaporisation (PTV) injector for the *in situ* analysis of ambient air samples. The automation of sample collection and the elimination of the intermediate refocusing step, reduces much of the necessary on-site maintenance required for continuous monitoring, and allows *in situ* analysis in locations where previously this was not possible.



Using a multi positioning valve, the system can select between standards from, *e.g.*, a Tedlar® bag or taking sample directly from the outside via, *e.g.*, a probe on the roof of a mobile lab. Via a smart flow system, a sample is pumped through the injector port liner containing a suitable trapping material in reverse flow from bottom to top trapping the analytes, while the carrier gas is re-routed to the GC capillary column by-passing the injector port. Sampling is done during a fixed time with a constant flow controlled with a mass flow controller, without the use of additional coolant as LN₂ or CO₂.

Once the sampling period is finished, the carrier gas flow via the injector port is re-established. Following this, the injection port is heated to desorb the analytes from the injection port liner for transfer to the GC capillary column. In parallel with heating the injection port liner, the GC-MS analysis is started.

Experimental

The instruments used in this application are the OPTIC Air Analyser (GL Sciences, The Netherlands), containing an OPTIC AirLiner (GL Sciences), and the QP2020 NX GC-MS (Shimadzu, Japan). Detailed analytical parameters are described in table 1. For the chromatography an Agilent PoraBOND Q capillary column (25 m x 0.25 mm x 3 µm) was used. This column was chosen because it focuses and separates the volatiles efficiently, in addition with an adequate temperature range to elute the highest boiling compounds.



Table 1: Analytical Parameters

| OPTIC Air Analyser Parameters | | GC-MS Parameters | |
|-------------------------------|------------|-------------------|------------|
| Sampling Temp | 25°C | Initial Oven Temp | 30°C |
| Sampling Flow | 75 ml/min | Initial time | 2.50 min |
| Sampling Time | 3.00 min | Rate 1 | 14°C/min |
| Desorption Temp | 270°C | Final Temp | 270°C |
| Desorption Temp Hold | 270 sec | Final Time | 5.36 min |
| Transfer Time | 220 sec | Total runtime | 25 min |
| Column Carrier gas | Helium | | |
| Column Flow | 1.6 ml/min | MS Mode | Scan / SIM |

Results

A home-made mixture of 63 compounds (comparable to the TO-17 mixture) is used for evaluation of the Air Analyser. Via a smart valving system, sample is loaded from bottom-to-top on the OPTIC Air Liner, being located inside the injection port at a temperature of 25°C. The injection port is cooled with compressed air. Sampling is done during three minutes at 75 ml/min (total sample volume = 225 ml). After sampling, the carrier gas is re-routed through the injection port from top-to-bottom. Following this, the injection port is heated to 270°C, desorbing the trapped compounds to the capillary column using splitless transfer. The resulting chromatogram starts with *n*-Propane and ends with Naphthalene. Since the sample trap is in the injection port, no additional cryogenic focusing is required at the head of the capillary column.

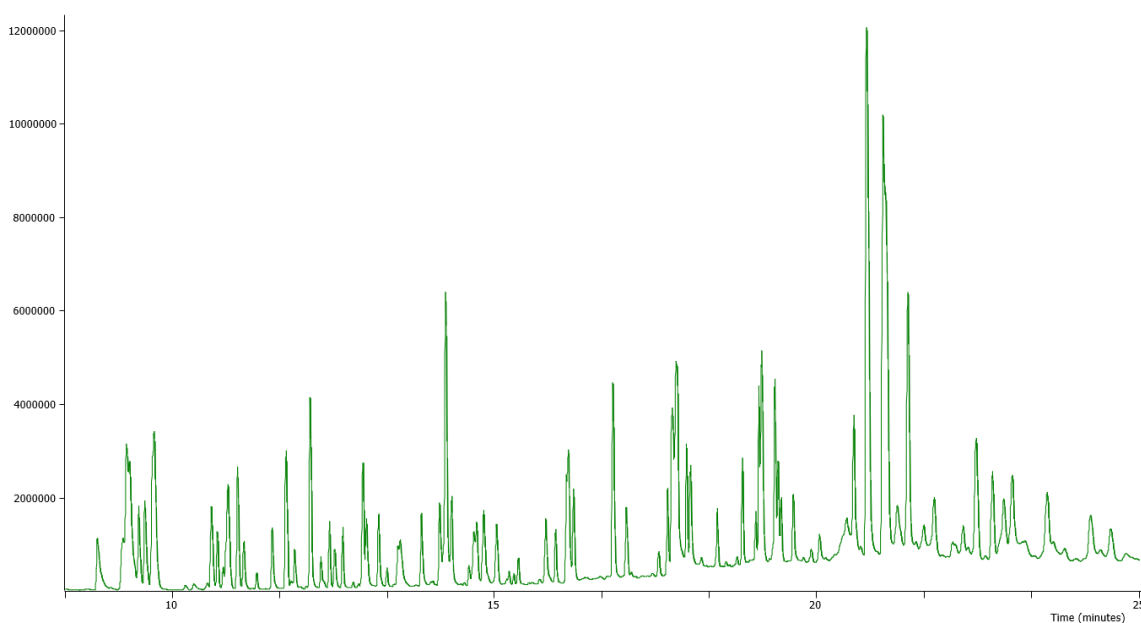


Figure 1: TIC chromatogram (scan) of a 63 compound mixture at 25 µg/m³.



The precision, linearity and instrument detection limit (IDL) is excellent for all compounds (see table 2). The precision was investigated by 10 consecutive runs of a standard with an average concentration of $0.25 \mu\text{g}/\text{m}^3$. The linearity was determined by running standards with average concentrations in the range of $0.25 - 25 \mu\text{g}/\text{m}^3$. For IDL determination, eight consecutive runs of a standard just above the limit are performed. Following the IDL is calculated using the student's t-test with a confidence level of 98% ($t=2.896$). Because of the relatively small amount of packing material in the OPTIC AirLiner, it was tested if whether the sampling conditions (3 min, 75 ml/min, 25°C) are close to the breakthrough volume. For this, sampling was done of the $2.5\text{-}\mu\text{g}/\text{m}^3$ standard for 1 – 10 minutes (75 – 750 ml). In figure 2, peak areas of some important compounds are given as a function of the sampling volume up to 750 ml. From these curves, it is clear that the breakthrough volume is over 750 ml.

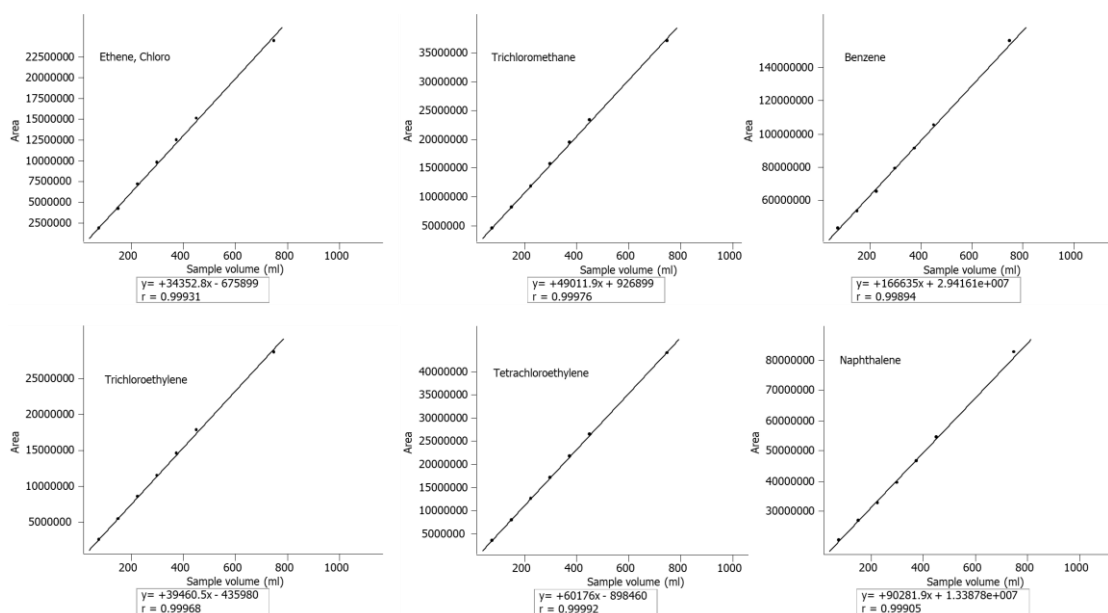


Figure 2: Sampling volumes of some important compounds.

Additional options to the system

- In case of high humidity samples, a gas dryer can get implemented in the system. Moisture will have an influence on the capacity of the trapping material in the injection port liner.
- In case of off-line loading of liners, the system can become upgraded with a manual or automatic liner exchange tool. This makes to system extremely flexible in its applicability.



Conclusions

- An analyser for *in situ* Analysis of VOCs in Urban Air has been demonstrated.
- Air samples are automatically enriched on a sorbent tube in a GC injection port and subsequently analysed by GC–MS.
- No need for LN₂ or CO₂ as trapping coolant.
- Instrument Detection Limit (IDL) is for the majority of the compounds in the range of 10 – 100 ng/m³.

Table 2: Analytical results.

| Name | t _R (min) | Quant Masses | Corr. Coeff. | IDL (ng/m ³) | %RSD* |
|-----------------------------|----------------------|--------------|--------------|--------------------------|-------|
| Propane | 5.97 | 43 | 0.996 | 72.9 | 7.8 |
| Ethene, chloro- | 7.22 | 62 | 0.997 | 36.0 | 13.6 |
| Ethanol | 8.13 | 45 | 0.862 | 27.5 | 3.7 |
| Isobutane | 8.53 | 43 | 0.992 | 39.8 | 4.2 |
| 1,3-butadiene | 8.58 | 54 | 0.945 | 42.0 | 4.8 |
| 1-Butyne | 8.77 | 54 | 1.000 | 87.4 | 9.9 |
| Butane | 8.99 | 43 | 0.841 | 67.7 | 7.1 |
| Methylene chloride | 9.99 | 84 | 0.999 | 90.8 | 12.1 |
| Propenenitrile | 10.08 | 53 | 0.992 | 12.8 | 2.9 |
| Isopropyl Alcohol | 10.14 | 45 | 0.628 | 16.8 | 7.0 |
| Carbon disulfide | 10.16 | 78 | 0.990 | 168.6 | 10.1 |
| Dimethyl sulfide | 10.31 | 62 | 0.995 | 98.7 | 7.2 |
| Ethene, 1,1-dichloro- | 10.41 | 96 | 1.000 | 20.7 | 3.0 |
| 1-Propanol | 10.85 | 59 | 0.998 | 71.5 | 9.8 |
| trans-1,2-Dichloroethylene | 11.06 | 96 | 1.000 | 30.5 | 2.1 |
| Diethyl ether | 11.08 | 74 | 1.000 | 22.5 | 3.5 |
| Isoprene | 11.20 | 67 | 0.999 | 37.0 | 9.6 |
| Pentane | 11.44 | 72 | 0.998 | 25.2 | 6.5 |
| cis-1,2-Dichloroethylene | 11.74 | 96 | 1.000 | 16.1 | 2.2 |
| Ethane, 1,1-dichloro- | 11.82 | 63 | 0.999 | 61.2 | 9.2 |
| Butanone | 12.26 | 72 | 0.989 | 57.4 | 7.9 |
| Trichloromethane | 12.26 | 83 | 0.999 | 322.8 | 38.5 |
| Tetrahydrofuran | 12.32 | 71 | 0.999 | 192.1 | 23.8 |
| 2-Butanol | 12.50 | 59 | 0.999 | 33.5 | 4.6 |
| Ethane, 1,2-dichloro- | 12.79 | 62 | 0.999 | 28.7 | 4.1 |
| Methyl t-butyl ether (MTBE) | 12.84 | 73 | 0.994 | 87.3 | 13.0 |
| 1-Butanol | 13.17 | 31 | 0.997 | 54.5 | 7.4 |
| Benzene | 13.45 | 78 | 0.994 | 16.1 | 3.2 |
| Ethane, 1,1,1-trichloro- | 13.50 | 97 | 1.000 | 20.4 | 2.7 |



Table 2: (Continued)

| Name | t _R (min) | Quant Masses | Corr. Coeff. | IDL (ng/m ³) | %RSD |
|-------------------------------|----------------------|--------------|--------------|--------------------------|------|
| Cyclopentane, methyl- | 13.53 | 69 | 0.999 | 37.6 | 8.9 |
| n-Hexane | 13.54 | 86 | 1.000 | 65.2 | 16.8 |
| Carbon Tetrachloride | 13.61 | 119 | 0.999 | 27.9 | 3.1 |
| Trichloroethylene | 13.63 | 95 | 0.995 | 18.7 | 2.3 |
| Cyclohexane | 13.98 | 84 | 0.999 | 228.3 | 51.8 |
| Propane, 1,1-dichloro- | 14.03 | 77 | 0.997 | 94.1 | 14.7 |
| Ethyl tert-butyl ether (ETBE) | 14.13 | 87 | 0.998 | 18.9 | 2.8 |
| Propane, 1,2-dichloro- | 14.33 | 63 | 1.000 | 56.5 | 8.6 |
| Ethane, 1,1,2-trichloro- | 15.10 | 97 | 1.000 | 46.8 | 5.8 |
| Propane, 1,3-dichloro- | 15.25 | 76 | 0.999 | 46.5 | 6.9 |
| Heptane | 15.42 | 43 | 0.998 | 46.8 | 12.1 |
| Toluene | 15.45 | 65 | 0.938 | 56.7 | 11.6 |
| Tetrachloroethylene | 15.52 | 166 | 1.000 | 55.3 | 6.0 |
| Benzene, chloro- | 16.34 | 112 | 0.999 | 12.0 | 1.9 |
| Bromoform | 16.85 | 173 | 0.994 | 209.9 | 12.8 |
| 4-Vinyl-1-cyclohexene | 16.99 | 79 | 0.999 | 52.9 | 11.2 |
| Octane | 17.05 | 57 | 0.979 | 43.0 | 10.8 |
| Ethylbenzene | 17.07 | 106 | 0.968 | 40.1 | 8.1 |
| m,p-Xylene | 17.11 | 106 | 0.776 | 140.7 | 14.4 |
| o-Xylene | 17.34 | 106 | 0.990 | 77.3 | 15.5 |
| Benzene, 1,3-dichloro- | 18.35 | 146 | 0.998 | 32.3 | 4.4 |
| Nonane | 18.40 | 57 | 0.987 | 101.2 | 24.9 |
| Benzene, 1,3,5-trimethyl | 18.43 | 92 | 0.999 | 51.3 | 10.5 |
| Benzene, 1,3,5-trimethyl | 18.43 | 105 | 0.991 | 54.0 | 11.1 |
| Benzene, 1,2-dichloro- | 18.45 | 146 | 0.998 | 18.5 | 2.5 |
| Benzene, 1,4-dichloro- | 18.65 | 146 | 0.999 | 49.2 | 8.7 |
| Benzene, 1,2,4-trimethyl- | 18.69 | 120 | 0.977 | 37.0 | 7.5 |
| Indane | 18.93 | 118 | 0.996 | 68.2 | 12.1 |
| Decane | 19.87 | 142 | 0.989 | 25.4 | 6.2 |
| Decaline | 20.54 | 96 | 0.999 | 76.7 | 15.1 |
| Benzyl methyl ketone | 20.58 | 134 | 0.705 | 39.8 | 4.4 |
| Benzene, 1,2,4-trichloro- | 20.77 | 180 | 0.994 | 24.2 | 2.9 |
| Naphthalene | 21.64 | 128 | 0.962 | 17.5 | 3.1 |
| Undecane | 22.03 | 57 | 0.815 | 11.0 | 2.6 |

* Calculation based on measurements close to the IDL level.

$$IDL = \frac{StDev}{Average\ peak\ area} * concentration * t$$