Ambient Air Monitoring Applications

airmOzone + DET QMS: 96 VOC from PAMS and TO14

Ozone precursors by FID from WATER or AIR
0 - 325 µg/m^3 or higher

Context & Challenges

Ozone concentration has been multiplied by 5 in the last century in the middle latitudes of the northern hemisphere from 10 ppb in 1874 to approximately 50 ppb today. This is an increase of 1.6% per year; the trend is probably higher (2.4% a year) over the last decades *(Chapter 1 of the International Geosphere-Biosphere Program - World Climate Research Program)*. In order to stop this global trend, directives have been written concerning the reduction of ozone precursors emissions (NO_x and VOC) to define national emission maxima. The Directive 2000/96/EC states that the level of Benzene shall be reduced to an annual average of 5 µg/m^3 by 2010 for EU countries (1 ppb = 3.25µg/m^3).

Regarding VOC, the European directive 2002/3/CE advises to analyse 31 VOC, continuously and 24 hours per day. US Environmental Protection Agency suggests to analyse 56 VOC which constitute the Photochemical Assessment Monitoring Stations (PAMS) program. In Japan, 58 VOC are being monitored: 56 VOC + Alpha and Beta pinene.

Specific Chromatotec instruments have been designed to meet those new requirements in compliance with EN 14 662-3, MCERT certification for Benzene and VOC on airmoVOC C6C12 in 2013.

Chromatotec® Solutions

FID + MS for 96 compounds from air or water

Chromatotec® has developed the only autoGC rack mounted system selected by the national US EPA for VOC monitoring: the airmOzone + DET QMS A52022-MS cabinet 33U (option airmoS for sulfur). It consists of an airmoVOC C2-C6 expert, an airmoVOC C6-C12 expert with FID and a DET QMS with Quadrupole Mass Spectrometer. The equipment also has TUV approval on BTEX and European MCERT certification.

By combining those tree instruments, it is possible to analyse light and heavy VOC compounds. Thanks to FID + MS detection and H_2 carrier gas, the separation, identification and sensitivity is excellent down to ppt levels.

airmOzone A52022-MS 96

Cabinet XXX041-33 U

airmoVOC C6-C12 5U : A23022

Process Quadrupole Mass Spectrometer D30022

1U rack with mouse and key board

airmoVOC C2-C6 4U: A12000

Hydroxychrom (H_2 generator) 4U: XXX916

airmoCAL MFC 4U: XXX922-MFC

WHEELS

airmoPURE (zero air generator) XXX031D

and 2 sampling pumps XXX901

Main features:

- Instruments are fully automated thanks to internal calibration (airmoCAL MFC). They are calibrated with primary gas standard certified at ±2%.
- There are no interferences of the 10 potential interfering compounds with Benzene in compliance with EN 14 662-3 list.
- The analyser is linear: range 0 to 100 ppb (0 to 325 µg/m^3) (*doc airmoBTX / airmoVOC C6-C12, Linearity and repeatability Test*).
- VistaCHROM software controls the analysers and enables storage and display of the chromatograms thanks to Peak Viewer. It is possible to transfer data to a data logger with the communication protocols MODBUS RTU, JBUS or German PROTOCOL.

Thanks to these features, the airmOzone + DET QMS is the adequate solution for in situ VOC analysis.

Technical information and results

Example from a user: Accredited Association for Air Quality Monitoring

Equipment:

A complete airmOzone + DET QMS was used. VOC concentration in ambient air was monitored in the vicinity of a megalopolis city and industrial area.

- airmoVOC C2-C6 expert
- airmoVOC C6-C12 expert
- airmoCAL MFC (multiplexer (zero/calib/ambient) + calibration oven (N-Butane/N-Hexane/Benzene/N-Decane tubes) and automatic cylinder dilution with MFC using linear sequence
- DET QMS
- airmoPURE: zero air generator for VOC
- HYDROXYCHROM: H_2 generator with on line drier
- Cabinet for perfect installation

Data transfer:

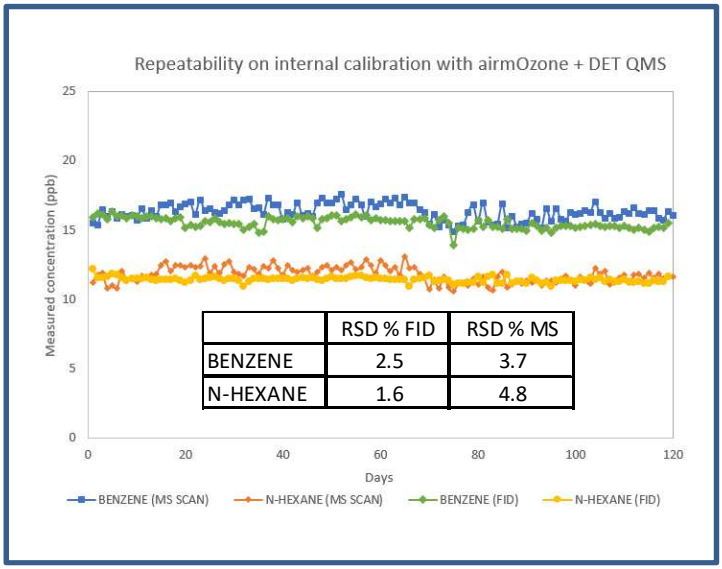
Data (substances, concentrations, methods, retention times, alarms, working parameters displayed in Vistachrom…) were transferred from our supervisor Real Time Database to a data logger by MODBUS communication protocol and the data logger transfers data to another location via a phone line.

Sequence by day with 30-minutes cycle:

- 1 CALIB method (measurement of concentration on internal permeation tubes) : one per day
- 47 analytical methods in AMBIENT AIR

Calibration / Autocalibration: Stability

An internal calibration enabled to follow up and adjust the Base Sensitivity of the instrument which will be used to calculate the concentration of each compound. Calibration standards are permeation tubes calibrated and certified (±10%), put into the temperature controlled oven of the airmoCAL-MFC. In the range of instruments using FID MS, auto-calibration is not necessary thanks to long term stability (Figure 1).



	RSD % FID	RSD % MS
BENZENE	2.5	3.7
N-HEXANE	1.6	4.8

The fixed air quality monitoring station is installed close to an industrial area and has worked several months in total autonomy. Figure 2 shows a 5-day trend of ambient air (October 30th to 3rd of November 2017) viewed with our PeakViewer display software.

An important variation of Toluene can be observed during the night/early morning. These important peaks are confirmed by the MS in automatic quantification, as well as in unknown identification using NIST library (Figure 3).

By over-lapping follow-ups of concentrations of various compounds automatically identified by the MS over the same period of time, it is possible to identify sources of pollution by their emission profile.

Unknown compounds can be identified down to 100 ppt levels with very good match to NIST library using VistaMS software. This identification can be done either on C2C6 (Figure 4) or on C6C12 compounds (Figure 5).

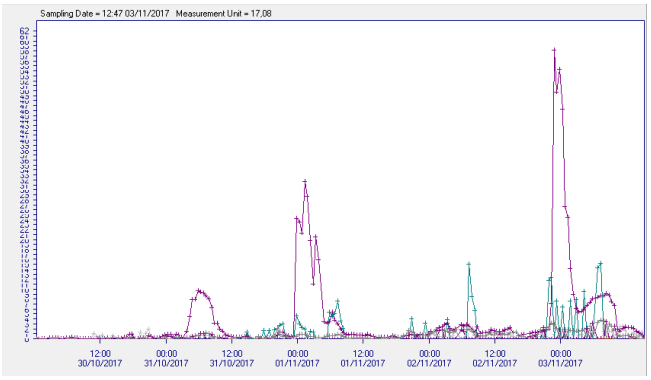


Figure 2. PeakViewer display of a 5-day trend of ambient air.

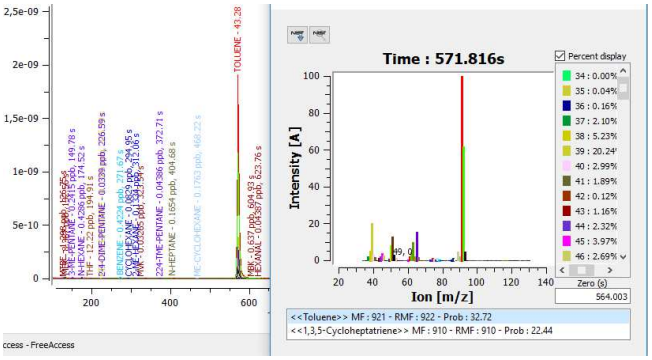


Figure 3. MS automatic quantification and unknown identification using NIST library.

Results/Validation

airmOzone + DET QMS 96 follow all kind of VOCs from PAMS and TO14 in 30 minutes which allow to identify some tracer from road traffic and/or from a different kind of industry.

The automatic identification by the MS provides an expertise and the NIST identification guarantee that the nature of the compounds is 100% sure from ppt to high ppb level.

The airmoCAL MFC with 4 internal certified permeation tubes allows an automatic validation of the data by providing a daily check of the stability for retention time, sensitivity and mass scale.

There is full traceability of the performance of the system with saving of all original data without treatment inside the supervisor. The capacity of the standard computer allows data storage for more than one year.

The capability of the airmOzone + DET QMS to analyse by MS both C2C6 and C6C12 autoGC allows a full confirmation of all VOCs in automatic mode.

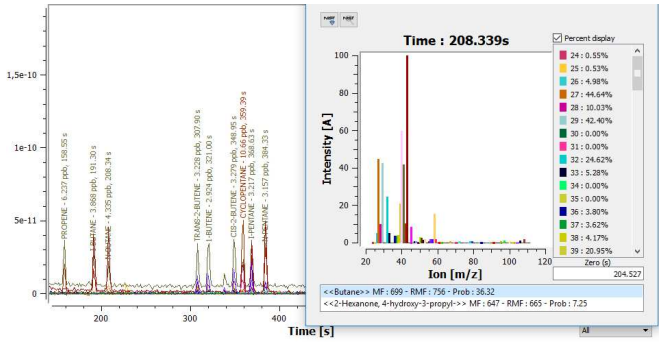


Figure 4. Chromatogram on airmoVOC C2C6 expert + DET QMS with N-Butane identified according to NIST library at 4 ppb.

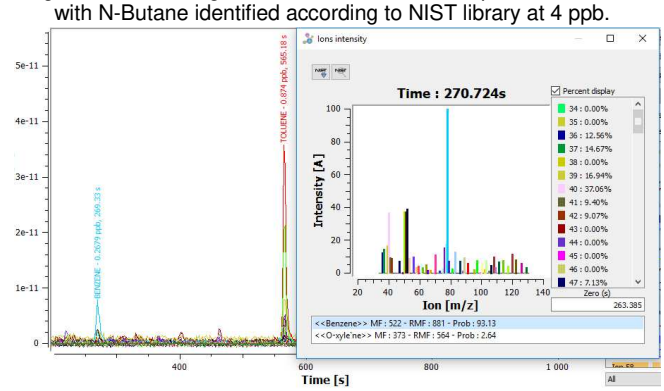


Figure 5. Ambient air chromatogram on airmoVOC C6C12 expert + DET QMS with Benzene identified according to NIST library at 267 ppt.

Applications

Application PAMS 56 VOC: 30 minutes cycle

Table 1. List of PAMS: 24 compounds analysed by airmoVOC C2C6 + DET QMS

	LOW_RETENTION_TIME	HIGH_RETENTION_TIME	RESPONSE_FACTOR	ASSOCIATED_ION
ETHANE	4	14	0.343913	26
ETHYLENE	22	32	0.21322	26
PROPANE	55	65	1.67621	41
PROPENE	153	163	0.535343	41
I-BUTANE	186	196	0.648704	41
N-BUTANE	203	213	1	41
ACETYLENE	223	233	0.22	26
TRANS-2-BUTENE	303	313	0.398145	41
1-BUTENE	316	326	0.363911	41
CIS-2-BUTENE	343	353	0.365982	41
CYCLOPENTANE	354	364	0.915151	42
I-PENTANE	363	373	0.473288	41
N-PENTANE	379	389	0.498552	41
TRANS-2-PENTENE	449	459	1.0073	55
1-PENTENE	469	479	0.702728	42
CIS-2-PENTENE	485	495	1.22599	55
ME-CYCLOPENTANE	503	513	0.447471	56
2-3-DIME-BUTANE	520	530	0.330532	42
2-ME-PENTANE	528	535	0.330532	41
3-ME-PENTANE	533	538	0.47106	56
N-HEXANE	543	553	0.43013	41
ISOPRENE	569	579	0.774378	39
2-ME-1-PENTENE	604	614	0.427009	41

Table 2. List of PAMS: 32 compounds (10 common to the TO 14 list in blue) analysed by airmoVOC C6C12 + DET QMS

2-2-DIME-BUTANE	91	101	1.4527	57
BENZENE	260	280.07	1	78
CYCLOHEXANE	287.47	297.47	2.47262	84
2-ME-HEXANE	303.33	313.33	3.39886	85
2-3-DIME-PENTANE	306.07	318.07	5.52482	71
3-ME-HEXANE	331.93	341.93	2.65564	57
224-TME-PENTANE	371	381	0.693941	57
N-HEPTANE	392	412	1.91848	41
ME-CYCLOHEXANE	467	477	1.92239	83
234-TME-PENTANE	543	557	1.58303	71
TOLUENE	560	575	0.918655	91
2-ME-HEPTANE	595	605	1.52964	41
3-ME-HEPTANE	615.53	625.53	1.34767	41
N-OCTANE	677.27	687.27	1.64129	57
ETHYLBENZENE	776.6	786.6	0.476701	91
M&P-XYLENES	790	800	0.816475	91
STYRENE	823.87	833.87	2.987	104
O-XYLENE	831.47	841.47	0.646252	91
N-NONANE	855.6	865.6	0.460238	43
I-PROPYLBENZENE	874.47	884.47	0.516704	105
N-PROPYLBENZENE	917.33	927.33	3.36765	91
M-ETHYLTOLUENE	928	934	0.57193	105
P-ETHYLTOLUENE	932	940.27	0.601904	105
135-TMB	940.47	950.47	1.00995	105
O-ETHYLTOLUENE	957	967	0.745585	105
124-TMB	969.2	979.2	1.02427	105
N-DECANE	989.93	999.93	0.582683	57
123-TMB	1013.53	1023.53	1.25822	105
M-DIETHYLBENZENE	1043.47	1053.47	1.50136	105
P-DIETHYLBENZENE	1053.13	1063.13	1.6253	105
N-UNDECANE	1120.1	1130.1	0.796797	57

Options:

- Europe: 1,3-Butadiene analysed by airmoVOC C2C6.
- Japan: 58 VOCs in total (+ 2 terpenes: alpha and beta-Pinene, analysed by airmoVOC C6C12). Limonene can also be analysed.

MS Chromatograms from PAMS gas mixture cylinder: with 1-Hexene
airmOzone + DET QMS is the only online GCMS which analyse light VOCs from C2 to C6 on the MS detector.

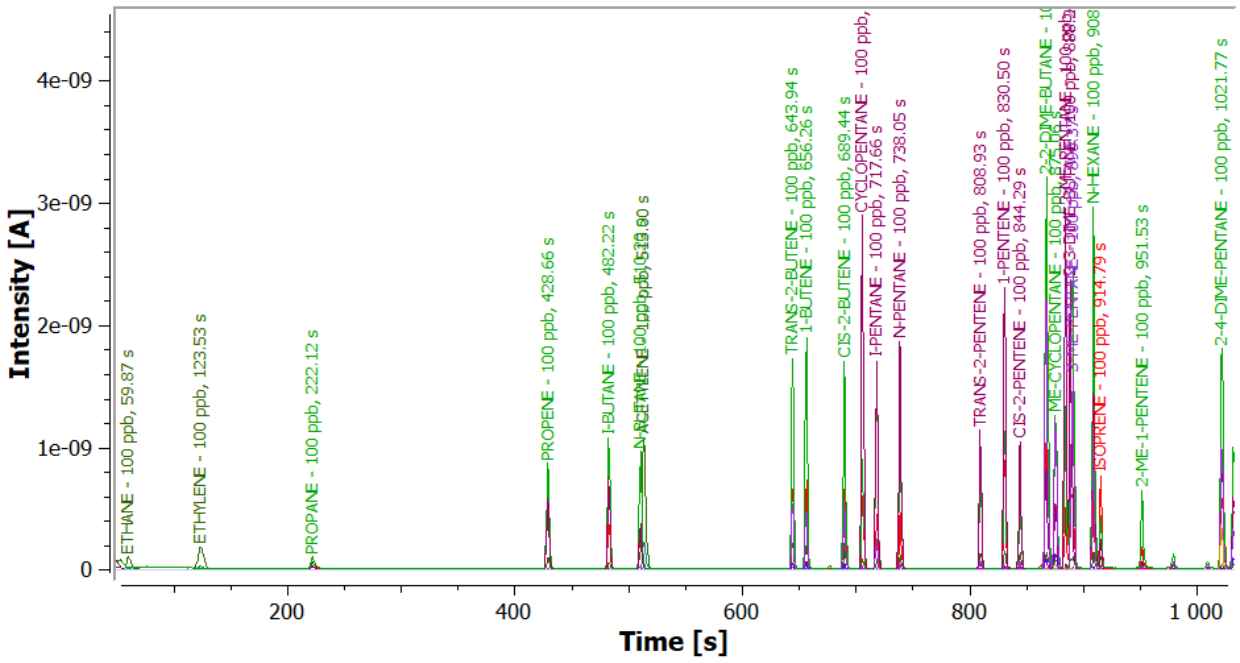


Figure 6. airmoVOC C2-C6 expert + DET QMS: 30-minutes cycle time in standard

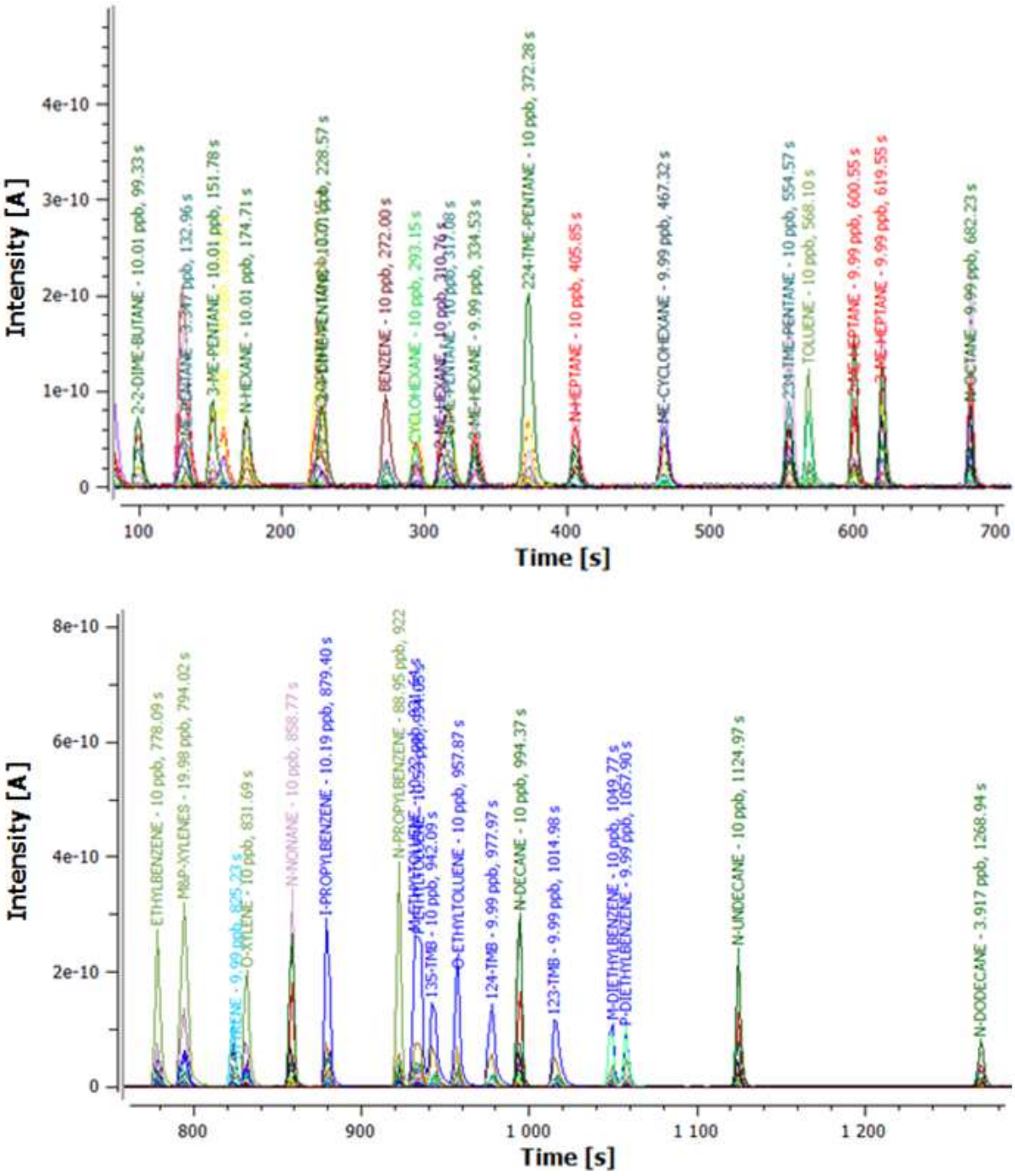


Figure 7. airmoVOC C2-C6 (top) and C6-C12 (bottom) expert + DET QMS: 30-minutes cycle time in standard with Mcerts approval for Benzene & VOC

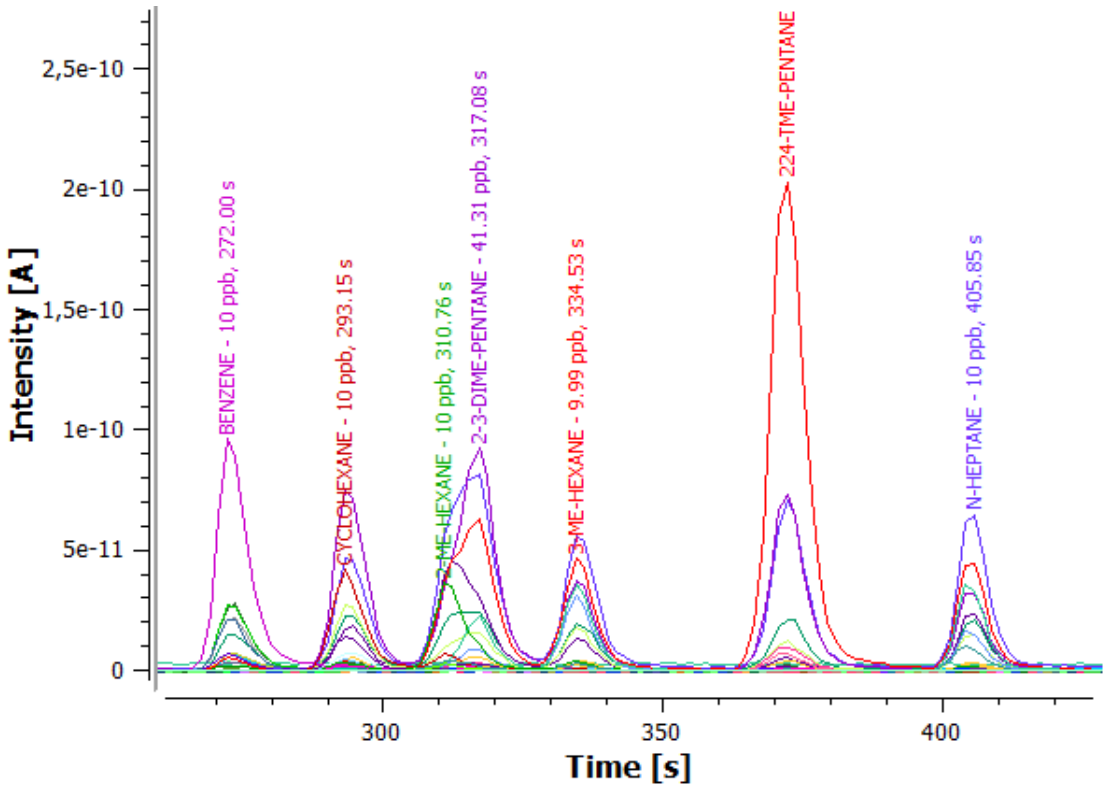


Figure 8. Quantification of partial coelution 2,3-dimethylpentane and 2-mehexane

Application TO14: 44 compounds (40 + 4 optional)

Table 3. List of TO14: 8 compounds analysed by airmoVOC C2C6 + DET QMS

	LOW_RETENTION_TIME	HIGH_RETENTION_TIME	RESPONSE_FACTOR	ASSOCIATED_ION
FREON-12	150	160	4.87424	85
FREON-114	325	345	4.51479	85
VINYLCHLORIDE	348	358	0.78437	62
FREON-11	375	396	0.890092	101
1-3-BUTADIENE	433	443	0.696459	54
1-1DICHLOROETHENE	449	459	0.565058	61
FREON-113	537	547	0.923388	101
DICHLOROMETHANE	582	592	1	49

Table 4. List of TO14 : 32 compounds analysed by airmoVOC C6C12 + DET QMS and 4 optional compounds in blue

	LOW_RETENTION_TIME	HIGH_RETENTION_TIME	RESPONSE_FACTOR	ASSOCIATED_ION
CHLOROETHANE	29	35	1	64
CHLOROMETHANE	30	40	1	50
BROMOMETHANE	40	50	33.663	94
ACRYLONITRILE	67	76	1	53
3-CHLOROPROPENE	87	95	1	78
1-1DICHLOROETHANE	120	130	15.6423	63
C-1-2-DICL-ETHENE	159	169	2.27822	61
CHLOROFORME	170.93	180.93	4.43138	83
1-2DICHLOROETHANE	216.2	226.2	30.7756	62
111-TRICL-ETHANE	231.73	241.73	62.3969	61
BENZENE	260	280.07	1	78
CCL4	277.4	287.4	45.9468	117
1-2-DICL-PROPANE	336	346	27.7673	63
TRICHLOROETHENE	360	370	16.2718	95
T-1-3-DICL-PROPEN	458	473	49.0412	75
C-1-3-DICL-PROPEN	521	534	134.337	75
112-TRICL-ETHANE	536	546	6.76837	62
TOLUENE	560	575	0.918655	91
1-2DIBROMOETHANE	633	643	68.0346	107
TETRACHLOROETHENE	684.93	694.93	5.69655	129
CHLOROBENZENE	747.2	757.2	1.96409	112
ETHYLBENZENE	776.6	786.6	0.476701	91
M&P-XYLENES	793.93	803.93	0.816475	91
STYRENE	823.87	833.87	2.987	104
O-XYLENE	831.47	841.47	0.646252	91
1122TETRACL-ETHAN	835	845	16.0558	83
P-ETHYLTOLUENE	939.27	949.27	0.601904	105
135-TMB	950.47	960.47	1.00995	105
124-TMB	981	991	1.02427	105
BENZYLCHLORIDE	988	995	1	91
1-3-DICL-BENZENE	993.33	1003.33	47.8616	111
1-4-DICL-BENZENE	998.67	1008.67	59.8467	111
1-2-DICL-BENZENE	1030	1040	35.456	111
124-TRICL-BENZENE	1285	1295	373.593	109
HEXCL-1-3BUTADIEN	1305	1360	67.1612	118

Ethyl chloride = Chloro Ethane
Methyl chloride = Chloro Methane

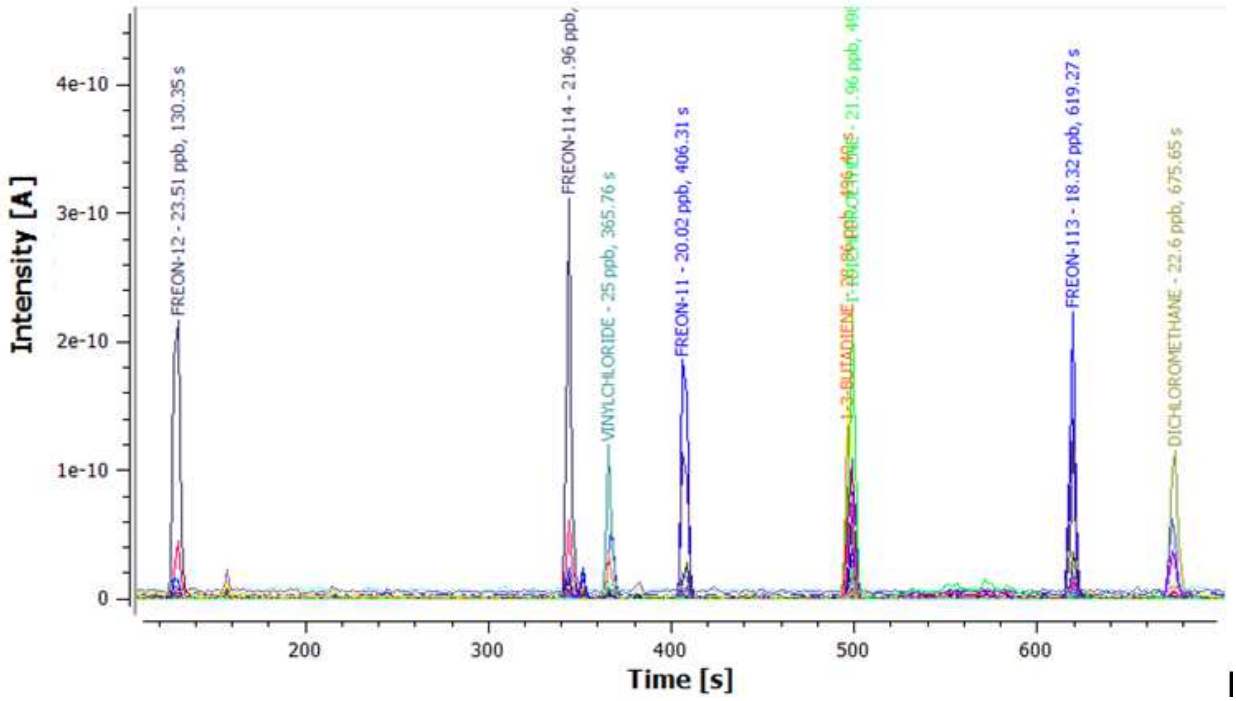


Figure 9. airmoVOC C2C6 + DET QMS cycle time 30 minutes with sample TO14 cylinder at 20 ppb

1) FREON-12 = Di chloro difluoro Methane
2) Freon-114 = 1,2-di chloro tetra fluoro ethane
3) Vinyl chloride = Chloro Ethylene = Chloro Ethene
4) FREON 11 = Tri chloro fluoro Methane
5) 1.3-Butadiene
6) 1.1-Di chloro Ethene
7) FREON 113 = Tri chloro tri fluoro ethane
8) Di Chloro Methane

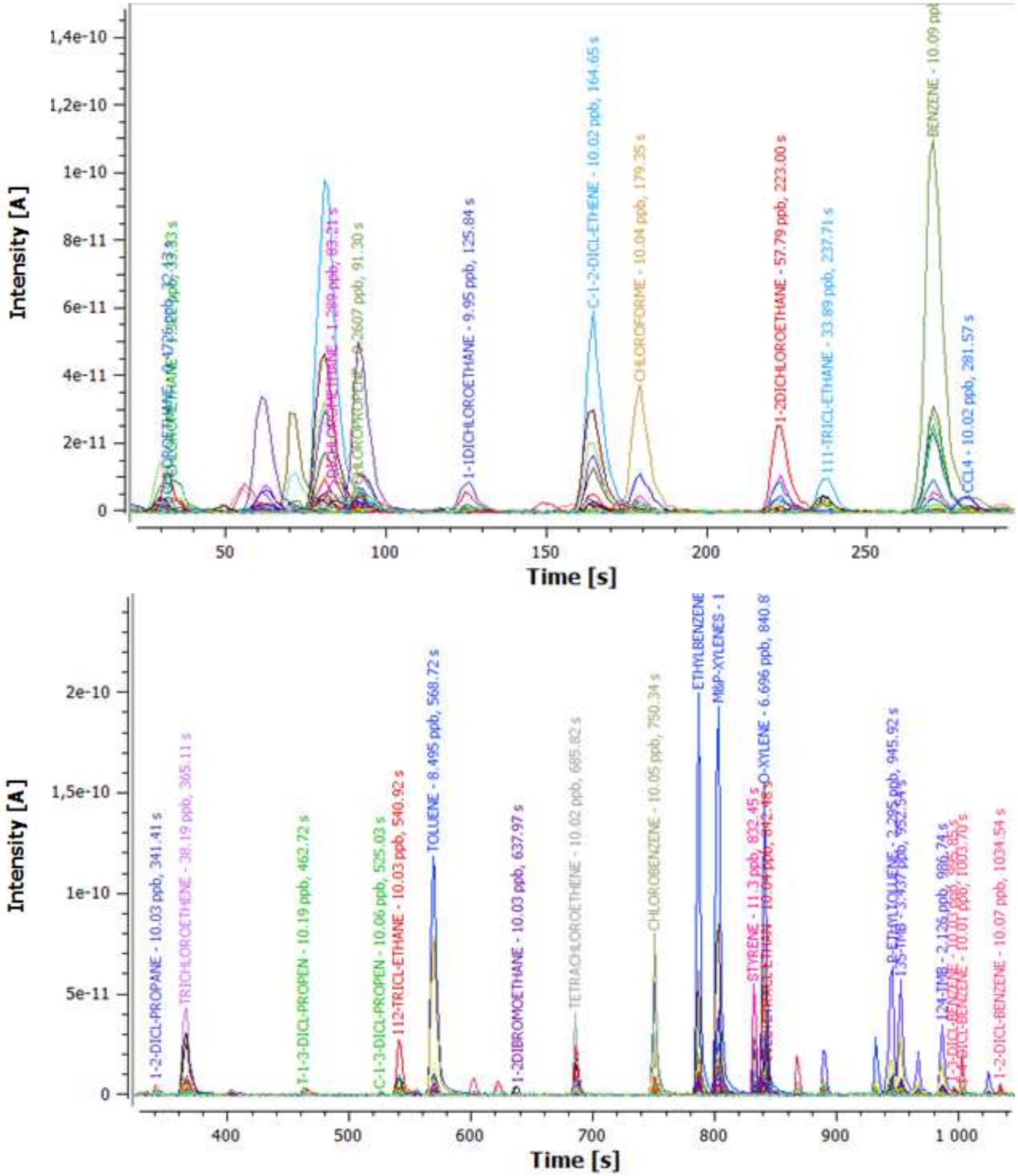


Figure 10: airmoVOC C6C12 + DET QMS sample TO14 at 10 ppb

Application 96 compounds: PAMS + TO14

- 56 from PAMS list
- 40 from TO14 list
- 10 compounds on both lists: BTEX (6) +135 TMB+ 124 TMB + STYRENE + P-Ethyl Toluene
- 10 extra compounds analysed:
  - 2 by airmoVOC C2C6: I-Butene, 1-Hexene,
  - 8 by airmoVOC C6C12:
    - Biogenic VOCs emitted by the trees:
      - α-Pinene + β-Pinene from PAMS 58 Japan List
      - Limonene + 3-Carene
    - Semi Volatile Organic Compounds:
      - Napthalene is the first gaseous PAHs
    - N-Dodecane, N-Tridecane, 1.2.3 Trichlorobenzene

(56 + 40) – 10 + 10 = 96 compounds

Conclusion:

Benefits of airmOzone A52022 + DET QMS 96:

- Fully automated system with gas generator (H2/AIR/CALIBRATION gas) and gas calibrator
- Data transfer to a data logger by modem or ethernet
- Stability and repeatability (from 0.01 to 100 ppb, areas and retention times)
- Linearity (from 0.01 to 100 ppb) (*see doc airmoBTX / airmoVOC C6-C12, Linearity and repeatability Test with Mcerts in 2013*).
- In compliance with EN 14 662-3, no interferences (see doc *List of the 10 potential interfering compounds with Benzene*)
- Approval on BTEX and other VOCs : TUV in 1996, Mcerts in 2013
- airmOzone is the only rack mounted US EPA selected autoGC system in 2014
- List of up to 96 compounds from European list and US EPA list: TO14 PAMS
- Cyclo Hexane, 22Di Methyl Butane, Methyl Cyclopentane, 2 and 3 Methyl pentane can be analysed on the two instruments
- On airmoVOC C6-C12, before 1,2-dichloro Ethane, interferences can be found (like Hexane / chloroform …)
- Identification of unknown compounds down to ppt level with NIST library
- Thanks to these features, the airmOzone + DET QMS is the online solution for in situ VOC analysis with expertise for surveillance of urban or industrial area: VOC from water, air or ground.

Additional capabilities:

- airmOzone + DET QMS for 123 compounds is also available with OVOCs from TO15 compounds
- H2S/MM/SO2/EM/DMS/DES/DMDS with TRS MEDOR range 0.1 to 100 ppb or MM/EM/DMS/DES/DMDS and CS2 with airmoS range 0.1 to 100 ppb option:
- TO14 Method 44 compounds react with FID: best sensitivity with benzene, while MS improves sensitivity with CCL4 and FREON 11 AND 113
- M&P XYLENE are co eluted with standard column; can be separated with polar column in option
- 502-2 Method: From water (striping) 60 compounds: PURGE and TRAP system airmOzone + DET QMS A52022- 502-2
- VOC extraction from ground is also possible
- airmoVOC C6C16 in option to analyze more heavy VOCs like linear alkanes up to N-Pentadecane and gaseous PAHs up to Fluorene