AIRMOTEC AG S.A
15 Rue d'Artiguelongue
33240 SAINT-ANTOINE - FRANCE
Tel : +33 (0)557940626 Fax : +33 (0)557940620

E-mail : support@chromatotec.com

The Problem :

VOC ANALYSIS AMBIENT AIR

Ozone concentration has increased by 5 since the end of the previous century at middle latitudes of the Northern hemisphere from **10 PPB in 1874 to approximately 50 PPB today**. This represents a growth rate 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)

To stop this phenomenon, directives have been launched in particular with regard to the **reduction of ozone precursors emissions** (NOX and VOC) by stating national emission ceilings (**Directive 2000/96/EC** on **Benzene** emissions : the aim is to reduce the emissions to a lower value of **5ug/m3** annual average **by 2010** for countries in the EU) but also by the way analysis and follow-up must be directed.

As far as VOC analysis is concerned the **European directive 2002/3/CE** advises the analysis of **31 VOC**, in **continuous and 24 hours a day**. **The US Environnemental protection Agency** proposes the analysis of **56 VOC** as part of its **PAMS programme** (Photochemical Assessment Monitoring Stations), and in **Japan**, **58 VOC are concerned** (Alpha and Beta pinene). Our instruments have been developped in order to meet these requirements.

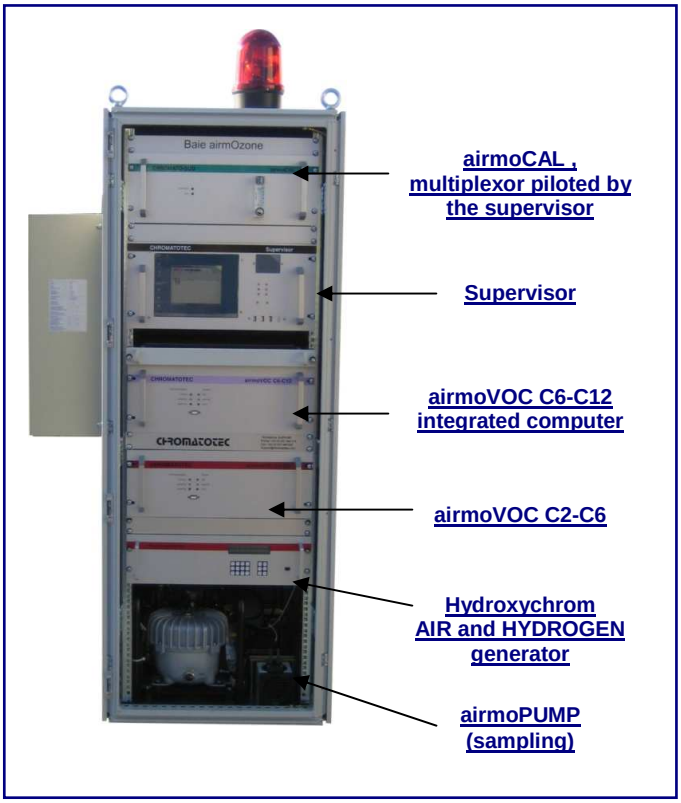
The Solution :

airmOzone cabinet

airmOzone cabinets are composed of one **airmoVOC C2-C6** and one **airmoVOC C6-C12.** The combination of these two instruments allow the analysis of light and heavy VOC compounds with an excellent quality for seperation of compounds and **high sensitivity thanks to the FID detector** (down to **few PPT**). These instruments have been calibrated with **primary standard gas mixtures certified at ±2%**.

Absolutely autonomous, our instruments are equipped with internal calibration (**airmoCAL**). The **VISTACHROM** software pilotes the analysers and can store and view chromatograms through Peak Viewer. One can transfer data to a data logger thanks to the communication protocoles MODBUS, JBUS or BAYERN HESSEN PROTOCOL.

Thanks to all these qualities the airmOzone is an adequate solution to VOC analysis in situ.



APPLICATION 31 VOC :
List of compounds (European directive 2002/3/CE) :

1	ethane
2	ethene/ethylene
3	propane
4	propene/propylene
5	isobutane (2-methyl propane)
6	n-butane
7	acetylene
8	trans-2-butène
9	1-butene
10	cis-2-butène
11	isopentane (2-methylbutane)
12	n-pentane
13	1-3 butadiene
14	1-pentene
15	trans-2-pentène
16	cis-2-pentène
17	n-hexane
18	isoprene
19	1-hexène
20	benzene
21	iso-octane
22	n-heptane
23	toluene
24	n-octane
25	ethylbenzene
26	m-xylene
27	p-xylene
28	o-xylene
29	1,3,5 trimethylbenzene
30	1,2,4 trimethylbenzene
31	1,2,3 trimethylbenzene

Compounds analysed by airmoVOC C2-C6

#	Name	Rt Min	Rt Max	Alarm Min	Alarm Max	Factor
1	ETHANE	50,00	60,00	0,00	9999,00	1,00
2	ETHYLENE	72,00	82,00	0,00	9999,00	0,96
3	PROPANE	10,00	110,00	0,00	9999,00	1,00
4	PROPENE	202,00	212,00	0,00	9999,00	0,96
5	I-BUTANE	225,00	235,00	0,00	9999,00	1,00
6	N-BUTANE	242,00	252,00	0,00	9999,00	1,00
7	ACETYLENE	295,00	305,00	0,00	9999,00	0,96
8	TRANS-2-BUTENE	350,00	360,00	0,00	9999,00	0,96
9	1-BUTENE	363,00	373,00	0,00	9999,00	0,96
10	CIS-2-BUTENE	385,00	395,00	0,00	9999,00	0,96
11	I-PENTANE	395,00	405,00	0,00	9999,00	1,00
12	N-PENTANE	412,00	422,00	0,00	9999,00	1,00
13	1-3-BUTADIENE	465,00	475,00	0,00	9999,00	0,93
14	TRANS-2-PENTENE	483,00	493,00	0,00	9999,00	0,93
15	1-PENTENE	500,00	510,00	0,00	9999,00	0,93
16	CIS-2-PENTENE	515,00	525,00	0,00	9999,00	0,93
17	N-HEXANE	558,00	568,00	0,00	9999,00	1,00
18	ISOPRENE	590,00	600,00	0,00	9999,00	1,00
19	1-HEXENE	635,00	645,00	0,00	9999,00	0,97

Compounds analysed by airmoVOC C6-C12

#	Name	Rt Min	Rt Max	Alarm Min	Alarm Max	Factor
1	BENZENE	225,00	233,00	0,00	9999,00	1,00
2	CYCLOHEXANE	243,00	251,00	0,00	9999,00	1,00
3	224-TME-PENTANE	317,00	325,00	0,00	9999,00	1,00
4	N-HEPTANE	346,00	354,00	0,00	9999,00	1,14
5	TOLUENE	500,00	510,00	0,00	9999,00	1,05
6	N-OCTANE	613,00	623,00	0,00	9999,00	1,00
7	ETHYLBENZENE	703,00	713,00	0,00	9999,00	1,10
8	M&P-XYLENES	718,00	728,00	0,00	9999,00	1,10
9	STYRENE	745,00	754,00	0,00	9999,00	1,10
10	O-XYLENE	753,00	763,00	0,00	9999,00	1,10
11	N-NONANE	776,00	786,00	0,00	9999,00	1,14
12	135-TMB	852,00	862,00	0,00	9999,00	1,14
13	124-TMB	879,00	889,00	0,00	9999,00	1,14
14	N-DECANE	892,00	902,00	0,00	9999,00	1,13
15	123-TMB	907,00	917,00	0,00	9999,00	1,14

On the right : **Substance tables** programmed for the **application 31 VOC.**

- **MIN RT** and **MAX RT** : time span over which compounds appear.
- **Factor** : **Response factor** of each compound (these factors are determined values and the factor of the relative compound is 1 (BENZENE or N-BUTANE according to the analyser). During calibration a parameter (**Base Sensitivity**) is calculated for the relative compound and then applied to all other compounds.

For this application 31 COV, we propose **30-minute standard methods** to identify 31 compounds. **We voluntarily add 4 other compounds (underlined in red) which are known to be possible interfering ones (Cyclohexane with Benzene or Styrene with O-Xylene) but that we can easily separate.** We also add **Decane et** le **Nonane** present in ambiant air**.**

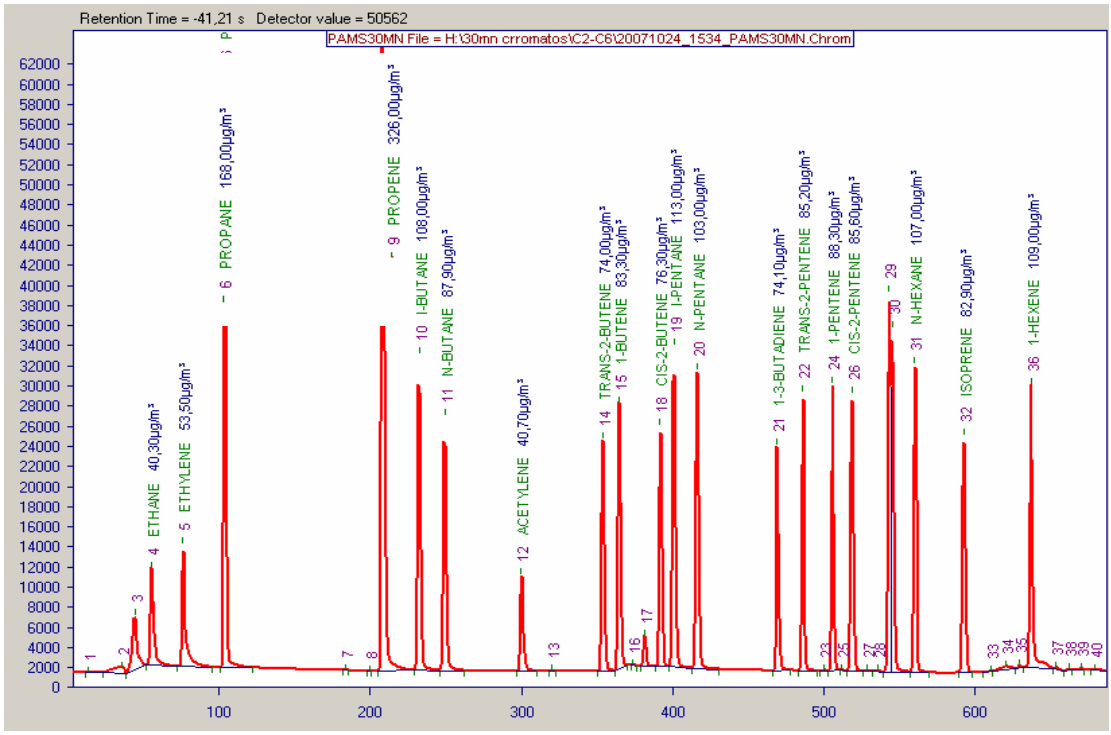
As an information, we can allot to several compounds their specific source:

- Styrene : petrochemistry

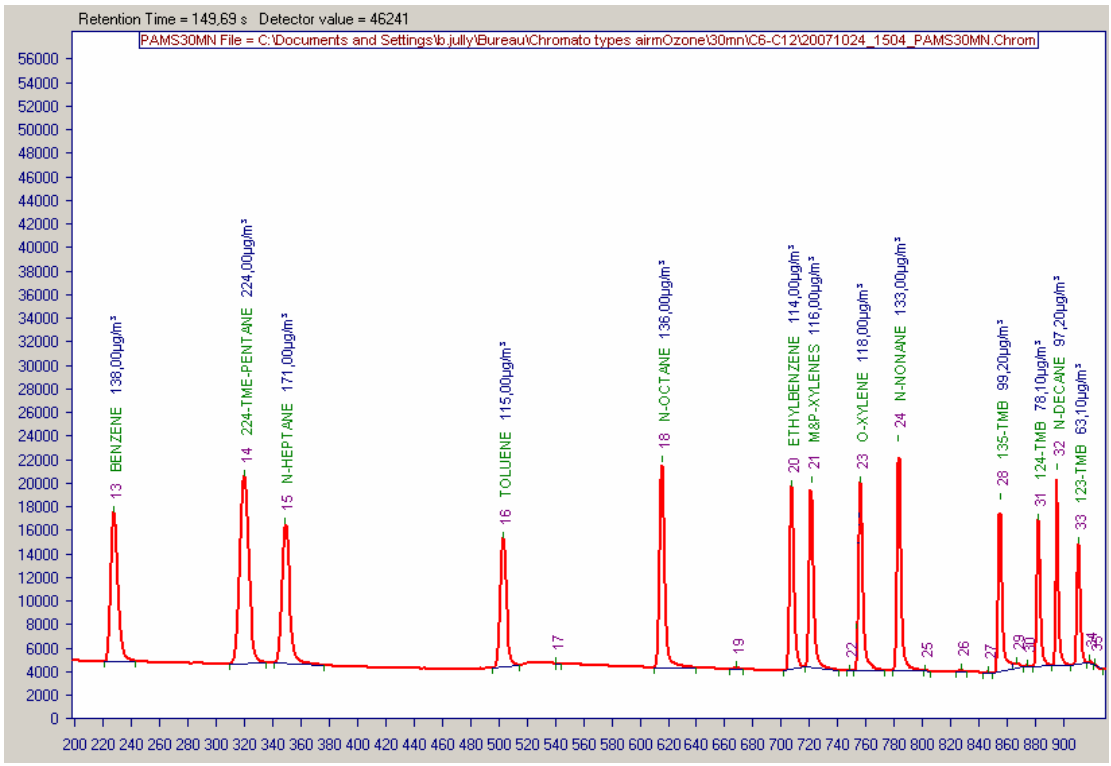
- **BTEX** : road traffic (four-stroke engine)
- **Acetylene** :road traffic
- **Cyclohexane** : solvents, two-stroke engine (mopeds,…)
- **1,3-butadiene** : chemical industry and road traffic
- **Isoprene** : plant species, biogenous origin terpene precursors (α and β pinenes, limonene…)

Chromatograms from tests realised with a cylinder with a mixture of 31 VOC : (N-Nonane, N-Décane + the 31 compounds of the European list)

airmoVOC C2-C6 :
Method 30 minutes



airmoVOC C6-C12 :
Method 30 minutes



Example from a user : Accredited Association for Air QUality Monitoring in France (AASQA).

Matériel :

This association has a complete airmOzone and follows the VOC concentration in ambient air in a peri-urban area close to a big city.

- **airmoVOC C2-C6**
- **airmoVOC C6-C12** with integrated supervisor (computer + LCD display)
- airmoCAL (multiplexer (zero/calib/ambient) + calibration oven (**N-Butane/N-Hexane/Benzene tubes**)
- airmoPURE (zero air generator)
- **HYDROXYCHROM** (hydrogene generator)

Data transfert:

Data (substances, concentrations, kind of methods, retention times, alarms…) are transferred from our supervisor to a data logger through MODBUS communication protocole and the data logger transfers data to another site via telephone line.

Analytical mehod and sequence:

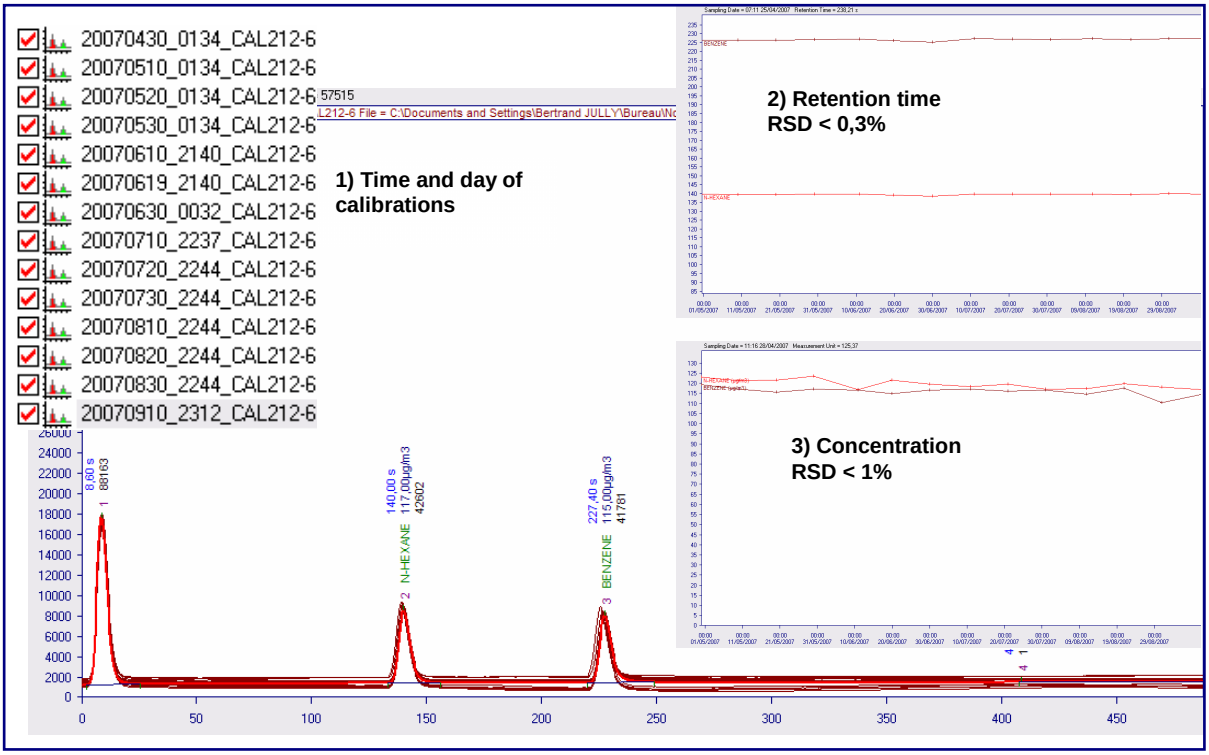
The association works with a sequence of 30-minute cycle :

- 1 CALIBRATION method (measurement of concentration on standard calibration)
- 47 analytical methods AMBIENT AIR

Calibration/Autocalibration:

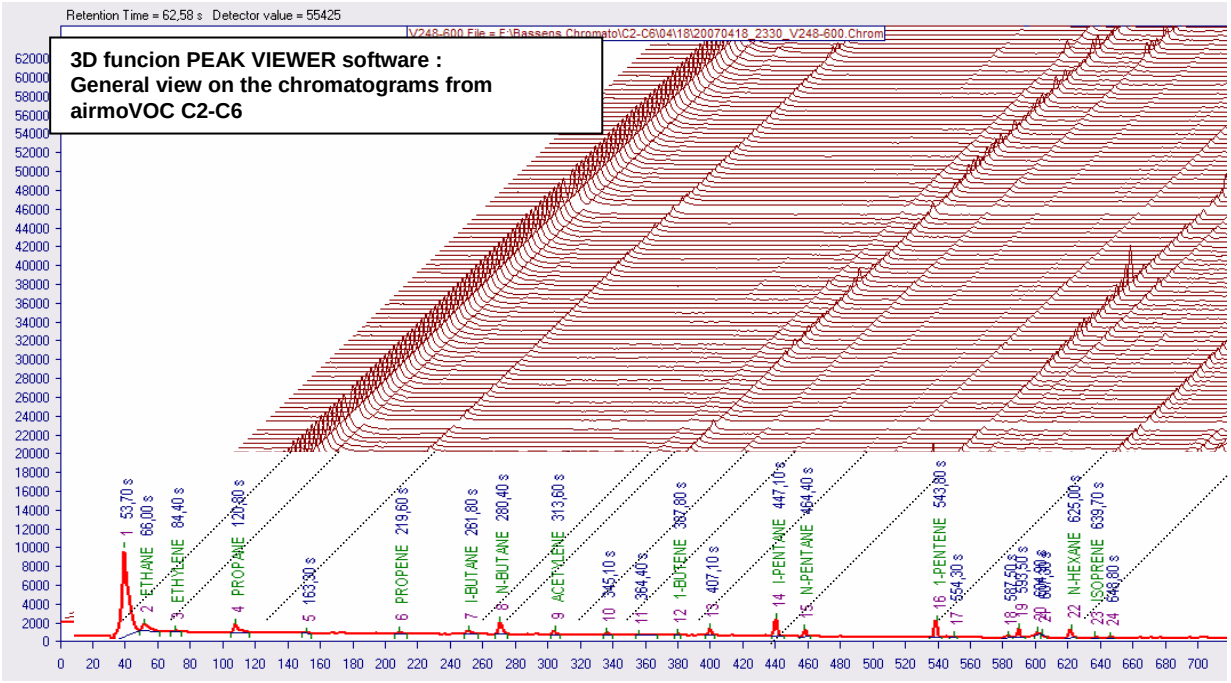
Internal calibration is used to follow-up and readjust Base Sensitivity proper to the instrument and taken into account for the calculation of the concentration of each compound.
Calibration standards are permeation tubes calibrated and certified (±10%), put into the thermostated calibration oven of the airmoCAL.
In this range of instruments with FID autocalibration is not necessary:

Underneath: the results of **5-month** calibration methods have been overlaid ((1) may to September 2007 on airmOzone C6-C12 unit). We can notice the **stability of retention times (2) and on concentrations (3) for Benzene and Hexane.**



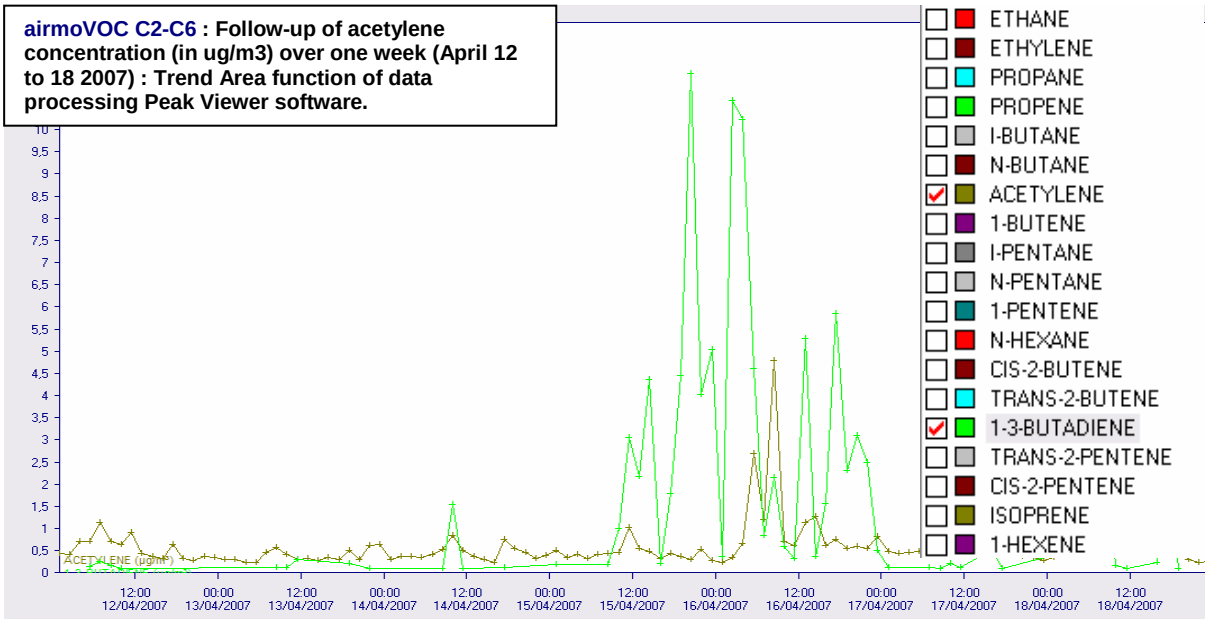
Some collected data :

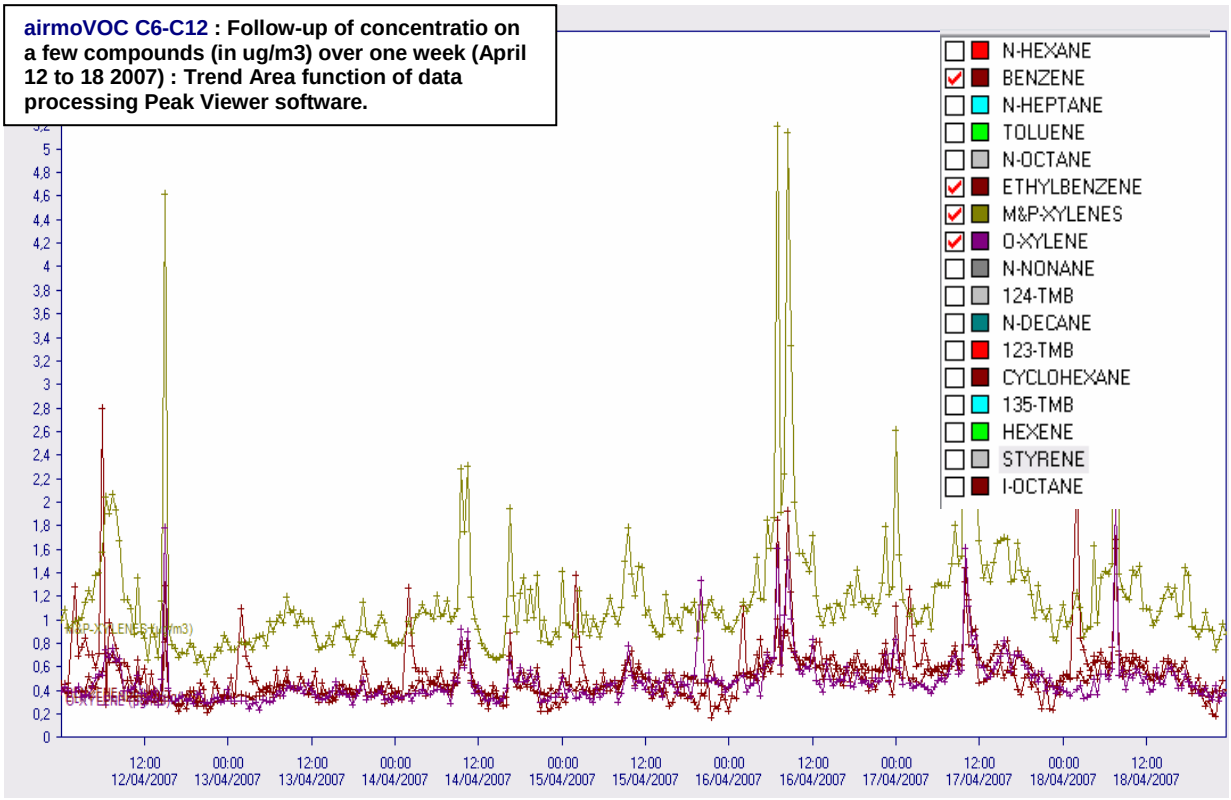
The fixed station we equipped has been running for more than six mois in total autonomy.
Here is 1-week analytical data in ambient air (april 12 to 18, 2007) viewed by our capture software PEAK VIEWER :



By superimposing follow-ups of concentrations of various compounds over the same period, one can identify sources of pollution by their profile of emission.

Follow-up of concentrations can be visible by using the Trend function Trend Result de notre Peak Viewer softa.





airmoVOC C6-C12 : Follow-up of concentratio on a few compounds (in ug/m3) over one week (April 12 to 18 2007) : Trend Area function of data processing Peak Viewer software.

Results:

Acetylene is often regarded as a **tracer of VOC emission of road traffic**. It will be noted that the concentration remains between 0,5 and 1 µg/m3 with maximum concentration in the morning around 9:00 a.m. and in the evening (rush hours of the traffic). The largest peak is observed at 9:00 a.m. on April 16 when the concentration in the air reached 5 µg/m3.

On the airmoVOC C6-C12 unit, during this week of April 12 - 18, 2007, **ethylbenzene, xylenes** variations, follow each others perfectly, this is characteristic of the emission profile one can observe for road traffic (cf :Thesis by Caroline Badol, Lille 1, 2005). This assumption is validated if one compares the evolution of the concentration of acetylene with that of the BTEX.

It will also be noted that in periurban areas, the average benzene concentration is close to 0.5 µg/m3 which remains quite lower than the annual average threshold that countries of the European Union must respect at the end of 2010.

Peaks in pollution coincide with the hours of road traffic.

APPLICATION 56 COV :

List of compounds (Programme Photochemical Assessment Monitoring Stations de l'US Environnemental Protection Agency) :

1	ethane
2	ethene / ethylene
3	propane
4	propene
5	isobutane (2-méthyl propane)
6	n-butane
7	acetylene
8	trans-2-butène
9	1-butene
10	cis-2-butène
11	cyclopentane
12	isopentane (2-methyl butane)
13	n-pentane
14	trans-2-pentene
15	1-pentene
16	cis-2-pentène
17	2,2-dimethylbutane
18	methylcyplopentane
19	2,3-dimethylbutane
20	2-methylpentane
21	3-methylpentane
22	n-hexane
23	isoprene
24	2-methyl-1-pentene
25	2,4-dimethylpentane
26	benzene
27	cychohexane
28	2-methylhexane
29	2,3-dimethylpentane
30	3-methylhexane
31	2,2,4-trimethylpentane
32	n-heptane
33	methylcyclohexane
34	2,3,4-trimethylpentane
35	toluene
36	2-methylheptane
37	3-methylheptane
38	n-octane
39	ethylbenzene
40	m-xylene
41	p-xylene
42	styrene
43	o-xylene
44	n-nonane
45	isopropylbenzene
46	n-propylbenzene
47	m-ethyltoluene
48	p-ethyltoluene
49	1,3,5 trimethylbenzene
50	o-ethyltoluene
51	1,2,4 trimethylbenzene
52	decane
53	1,2,3 trimethylbenzene
54	m-diethylbenzene
55	p-diethylbenzene
56	undecane

Compounds analysed by airmoVOC C2-C6

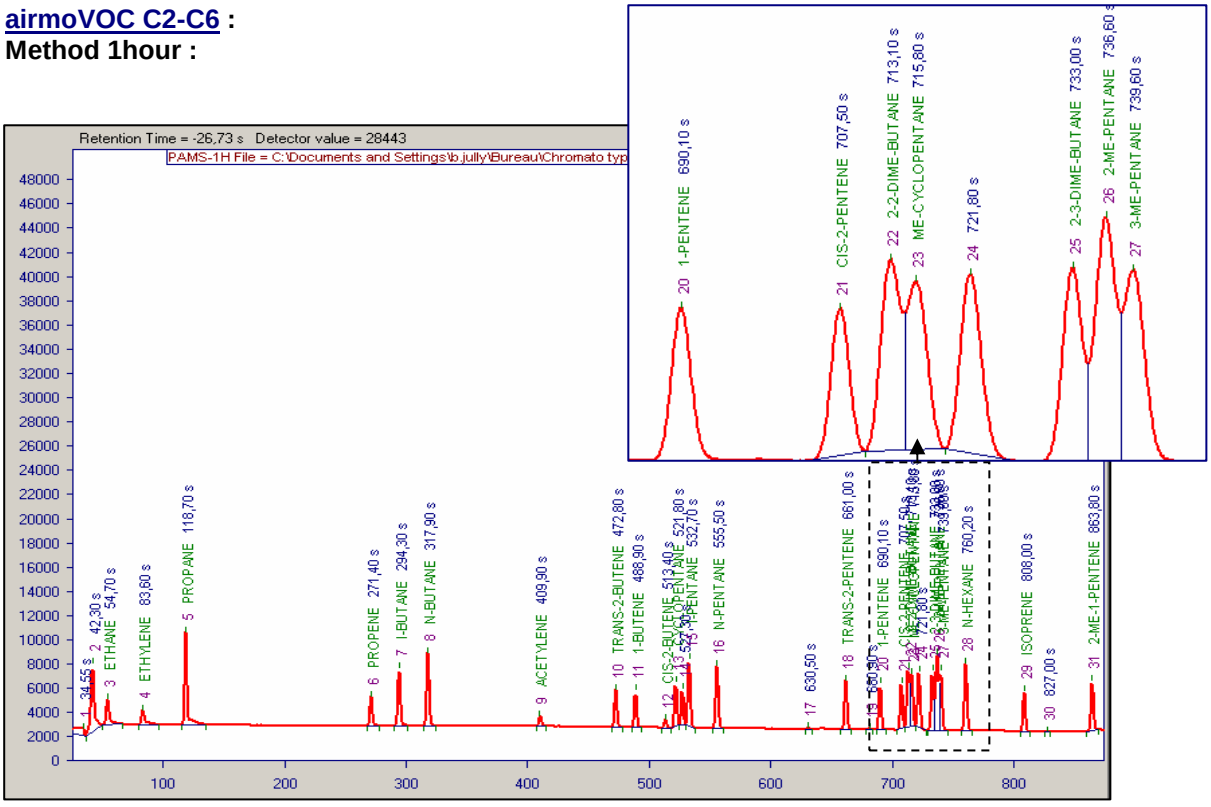
#	Name	Rt Min	Rt Max	Alarm Min	Alarm Max	Factor
1	ETHANE	51,00	61,00	0,00	9999,00	1,00
2	ETHYLENE	80,00	90,00	0,00	9999,00	0,96
3	PROPANE	115,00	125,00	0,00	9999,00	1,00
4	PROPENE	268,00	278,00	0,00	9999,00	0,96
5	I-BUTANE	290,00	300,00	0,00	9999,00	1,00
6	N-BUTANE	314,00	324,00	0,00	9999,00	1,00
7	ACETYLENE	405,00	415,00	0,00	9999,00	0,96
8	TRANS-2-BUTENE	465,00	475,00	0,00	9999,00	0,96
9	1-BUTENE	483,00	493,00	0,00	9999,00	0,96
10	CIS-2-BUTENE	508,00	518,00	0,00	9999,00	0,96
11	CYCLOPENTANE	518,00	522,00	0,00	9999,00	1,00
12	I-PENTANE	527,00	537,00	0,00	9999,00	1,00
13	N-PENTANE	550,00	560,00	0,00	9999,00	1,00
14	TRANS-2-PENTENE	653,00	663,00	0,00	9999,00	0,96
15	1-PENTENE	683,00	693,00	0,00	9999,00	0,96
16	CIS-2-PENTENE	700,00	709,00	0,00	9999,00	0,96
17	2-2-DIME-BUTANE	709,00	714,00	0,00	9999,00	1,00
18	ME-CYCLOPENTANE	714,00	718,00	0,00	9999,00	1,00
19	2-3-DIME-BUTANE	728,00	734,00	0,00	9999,00	1,00
20	2-ME-PENTANE	734,00	738,00	0,00	9999,00	1,00
21	3-ME-PENTANE	738,00	748,00	0,00	9999,00	1,00
22	N-HEXANE	755,00	765,00	0,00	9999,00	1,00
23	ISOPRENE	803,00	813,00	0,00	9999,00	1,00
24	2-ME-1-PENTENE	858,00	868,00	0,00	9999,00	1,00

Compounds analysed by airmoVOC C6-C12

#	Name	Rt Min	Rt Max	Alarm Min	Alarm Max	Factor
1	2-4-DIME-PENTANE	196,00	205,00	0,00	9999,00	1,06
2	BENZENE	238,00	248,00	0,00	9999,00	1,00
3	CYCLOHEXANE	255,00	265,00	0,00	9999,00	1,00
4	2-3-DIMEC5+2MEC6	280,00	285,00	0,00	9999,00	1,10
5	3-ME-HEXANE	297,00	307,00	0,00	9999,00	1,10
6	224-TME-PENTANE	333,00	343,00	0,00	9999,00	1,10
7	N-HEPTANE	363,00	373,00	0,00	9999,00	1,10
8	ME-CYCLOHEXANE	425,00	430,00	0,00	9999,00	1,10
9	234-TME-PENTANE	520,00	530,00	0,00	9999,00	1,10
10	TOLUENE	530,00	540,00	0,00	9999,00	1,05
11	2-ME-HEPTANE	572,00	582,00	0,00	9999,00	1,10
12	3-ME-HEPTANE	593,00	603,00	0,00	9999,00	1,10
13	N-OCTANE	660,00	670,00	0,00	9999,00	1,10
14	ETHYLBENZENE	767,00	775,00	0,00	9999,00	1,10
15	M&P-XYLENES	785,00	793,00	0,00	9999,00	1,10
16	STYRENE	817,00	826,00	0,00	9999,00	1,10
17	O-XYLENE	826,00	836,00	0,00	9999,00	1,10
18	N-NONANE	860,00	870,00	0,00	9999,00	1,10
19	I-PROPYLBENZENE	884,00	894,00	0,00	9999,00	1,09
20	N-PROPYLBENZENE	930,00	940,00	0,00	9999,00	1,08
21	M-ETHYLTOLUENE	940,00	947,00	0,00	9999,00	1,04
22	P-ETHYLTOLUENE	947,00	953,00	0,00	9999,00	1,04
23	135-TMB	955,00	965,00	0,00	9999,00	1,14
24	O-ETHYLTOLUENE	970,00	980,00	0,00	9999,00	1,06
25	124-TMB	990,00	1000,00	0,00	9999,00	1,15
26	N-DECANE	1010,00	1020,00	0,00	9999,00	1,10
27	123-TMB	1030,00	1040,00	0,00	9999,00	1,14
28	M-DIETHYLBENZENE	1060,00	1070,00	0,00	9999,00	1,17
29	P-DIETHYLBENZENE	1070,00	1080,00	0,00	9999,00	1,18
30	N-UNDECANE	1130,00	1140,00	0,00	9999,00	1,20
31	N-DODECANE	1240,00	1250,00	0,00	9999,00	1,20

Chromatograms from tests realised with a cylinder with a mixture of 56 VOC :

airmoVOC C2-C6 :
Method 1hour :



airmoVOC C6-C12 :
Method 1 hour :