Laboratoire Central
de Surveillance de la Qualité de l'Air

Analytical characteristics for benzene and VOC automatic measuring system:

results from laboratory tests and field campaign

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Context of study

Introduction

Laboratory Tests

Field Campaign

Conclusion

- Numerous VOCs (especially in urban sites) with several sources
- Only 1 VOC under regulation; C_6H_6 vs Directive 2008/50/CE
- Reference method : pumped sampling method on sorbent cartridge + gas chromatography
- In France, 2 methods commonly used : Automated Measuring System (3 manufacturers) or active sampler (≠ origins)
- Fixed measurements complemented with passive samplers

↳ lots of comparison…

↳ Automatic instruments used as Reference Method BUT differences observed…

⇒ Are all the automatic instruments used in French Air Quality networks comparable???

Objective & technical configuration

- Introduction
- Laboratory Tests
- Field Campaign
- Conclusion

☞ The main objective of this study :

to compare results of VOC (Benzene, Toluene, Xylenes…) measured wih automatic analysers

with instruments used in the same QA/QC conditions as in the AQ networks

↳ 5 automatic instruments tested :

VOC 71M (FID) - Environnement SA

VOC 71M (PID) - Environnement SA

AirmoBTX (FID) - Chromatotec

GC 955 (PID) - Synspec

Turbo Matrix TD/Autosystem (FID) - Perkin Elmer

☞ Study organized in 2 parts:

↳ Individual metrological validation for several performance characteristics in the laboratory

↳ Field campaign of 5 weeks in a monitoring station in Paris

1st part: Laboratory tests

☞ **Determination of several performance characteristics (from EN 14662-3)**

- Repeatability
- Lack of fit
- Memory effect
- Interference from possible interfering organic compounds

Repeatability at 0,5µg/m³ and 5µg/m³

- Repeatability calculated from the standard deviation of 10 successives individual measurements at the LV / at approximately 1/10 of the LV
- Repeatility calculated according to r = t x s
- Performance Criteria : r(LV = 5µg/m³) < ± 5%, r(0,5µg/m³) < 0,3µg/m³

ANALYSER	$[C_6H_6] \approx 5\mu g/m^3$		$[C_6H_6] \approx 0,5\mu g/m^3$	
	RSD (10 successive measurements) : $s_r(5\mu g/m^3)$	Repeatability : $r(5\mu g/m3) = s_r(5\mu g/m^3) \times t$ (t=2,262)	RSD (10 successive measurements) : $s_r(0,5\mu g/m^3)$	Repeatability : $r(0,5\mu g/m3) = s_r(0,5\mu g/m^3) \times t$ (t=2,262)
Perkin Elmer	2,0%	**4,6%**	0,03µg/m³	**0,08µg/m³**
Chromatotec	1,4%	**3,1%**	0,01µg/m³	**0,02µg/m³**
Envt.SA FID	1,1%	**2,4%**	0,03µg/m³	**0,06µg/m³**
Envt.SA PID	0,77%	**1,7%**	0,01µg/m³	**0,02µg/m³**
Synspec	0,92%	**2,1%**	0,01µg/m³	**0,02µg/m³**

Lack of fit

- Introduction
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➢ Linear regression function determined from responses of the analyser and the corresponding applied concentration levels

➢ Residual at each concentration level : difference between the average response measured and the concentration given by the LR function

➢ Concentrations tested: 0-5µg/m³-15µg/m³-25µg/m³-35µg/m³-45µg/m³

➢ Performance Criteria : largest residual < ±5%

	Perkin Elmer Turbo Matrix ATD/Auto System		Chromatotec		Env.SA VOC 71M/FID		Env.SA VOC 71M/PID		GC 955/PID Synspec	
Reference Concentration (µg/m3)	Measured Concentration (µg/m3)	Residual (%)	Measured Concentration (µg/m3)	Residual (%)	Measured Concentration (µg/m3)	Residual (%)	Measured Concentration (µg/m3)	Residual (%)	Measured Concentration (µg/m3)	Residual (%)
45,86	45,61	0,54	45,31	1,2	45,61	0,53	44,72	2,5	44,52	2,9
32,52	33,16	2,0	33,5	3,0	32,42	2,8	33,21	2,1	32,74	0,69
21,63	21,73	0,46	21,77	0,67	21,06	2,7	21,29	1,1	21,21	1,9
13,21	12,96	1,9	12,95	2,0	12,77	3,3	13,05	1,2	12,07	8,7
5,82	5,98	2,7	5,82	5,2	5,58	4,2	5,68	2,5	5,21	10,5

Memory effect

- Memory effect tested at the end of the linearity test
- Analysis of zero air directly after analysis of the highest concentration of benzene required for the linearity test (45µg/m^3)
- Performance Criteria : <u>measured benzene concentration < 0,5µg/m^3</u>

	Concentrations (µg/m^3)			
	Standard Injection	Zero Air 1	Zero Air 2	Zero Air 3
Perkin Elmer	45,86	2,32	0,45	0,25
ChromatoTec	45,9	1,17	0,27	0,15
Envt. SA FID	45,9	2,01	1,02	0,41
Envt. SA PID	45,86	1,57	0,88	0,39
Synspec	45,9	0,21	0,08	0,05

Influence of interferents (from sum of possible interfering organic compounds)

- analyser response to certain interferent expected to be present in ambiant air
  - limited to the interference from specific organic compounds
- Investigation with a gas mixture of these organic compounds at a concentration of 5µg/m^3
- Possible interfering compounds :
  - methylcyclopentane
  - 2,4-dimethylpentane
  - cyclohexane
  - 2-methylhexane
  - trichloroethylene
  - (isooctane)
  - 2,2,3-trimethylpentane
  - tetrachloromethane
  - 2,3- dimethylpentane
  - 3-ethylpentane
  - n-heptane
- Influence of the interference from sum of possible interfering organic compounds tested at a benzene concentration of 5µg/m^3

Influence of interferents (from sum of possible interfering organic compounds)

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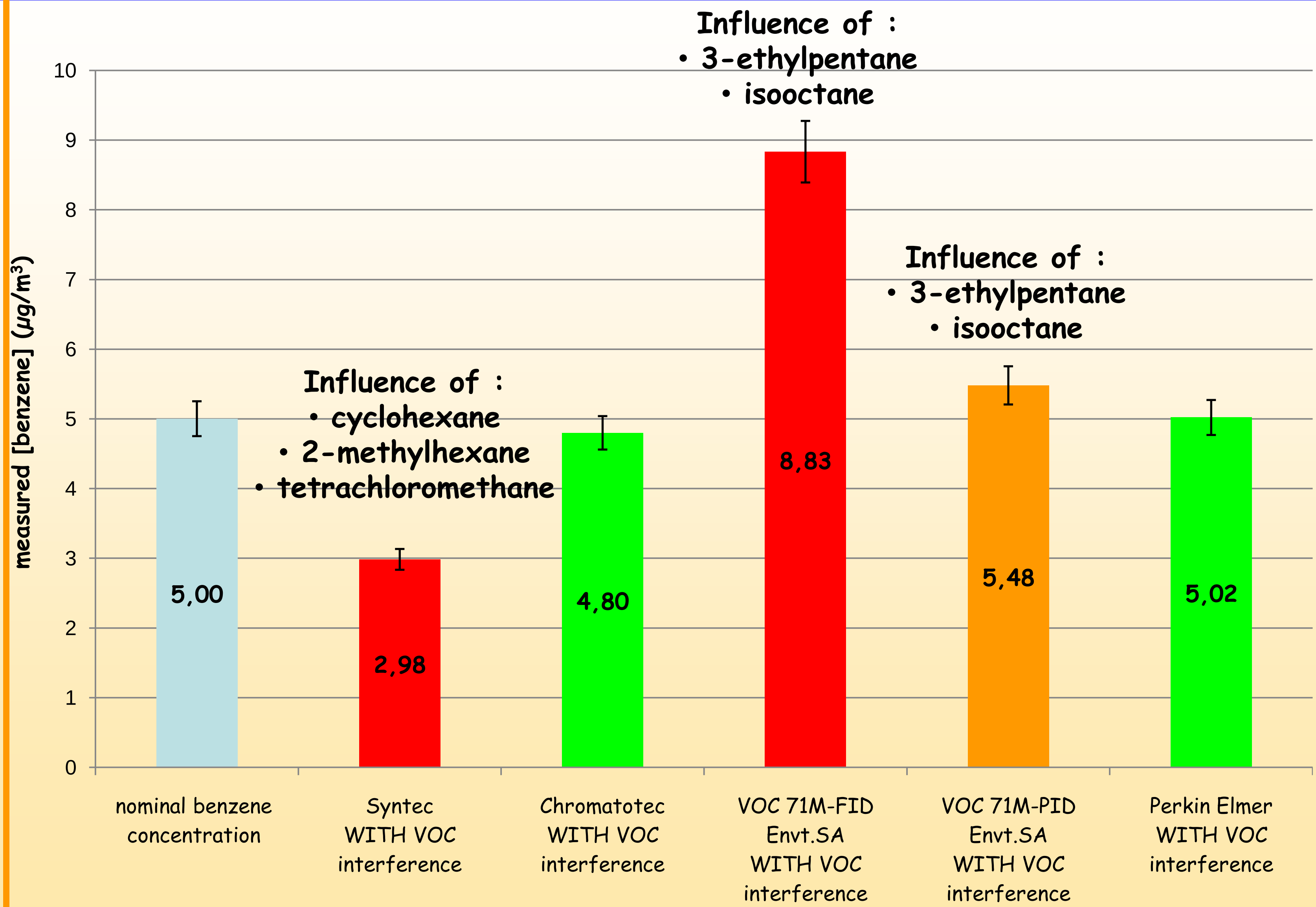
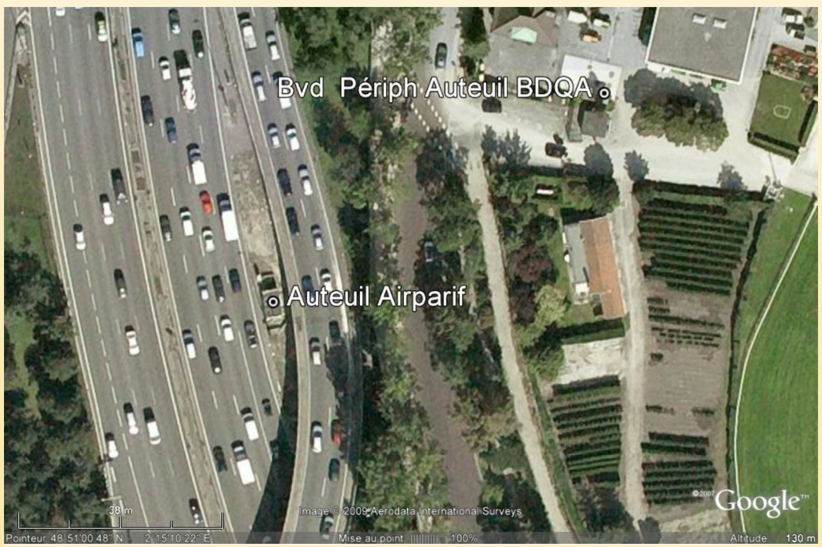


2nd part: Field Campaign

- the 5 automatic monitors installed in AIRPARIF AQ monitoring station « Porte d'Auteuil » (traffic-oriented site)
- Calibration with the same gas cylinder (5ppb in benzene - 16,25µg/m³) by the same operator
- Sampling on the same manifold
- Field campaign duration: from 10th of May to 19th of June 2007
- ↳ 5 weeks of validated data with these 5 analysers running in parallel
- ↳ And the results are…



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Results for ONE Week analysis

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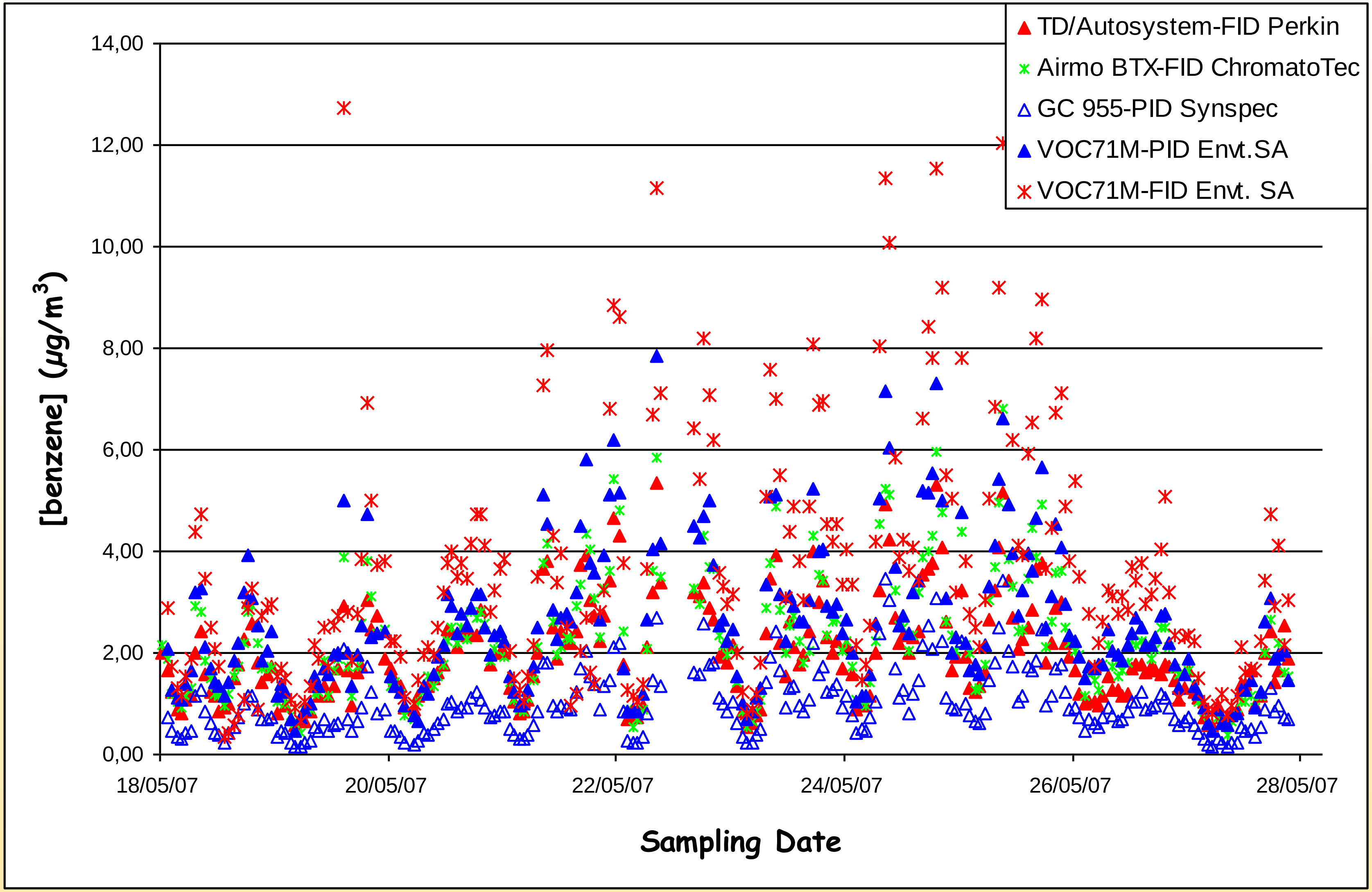

Focus on ONE Day analysis

- Introduction
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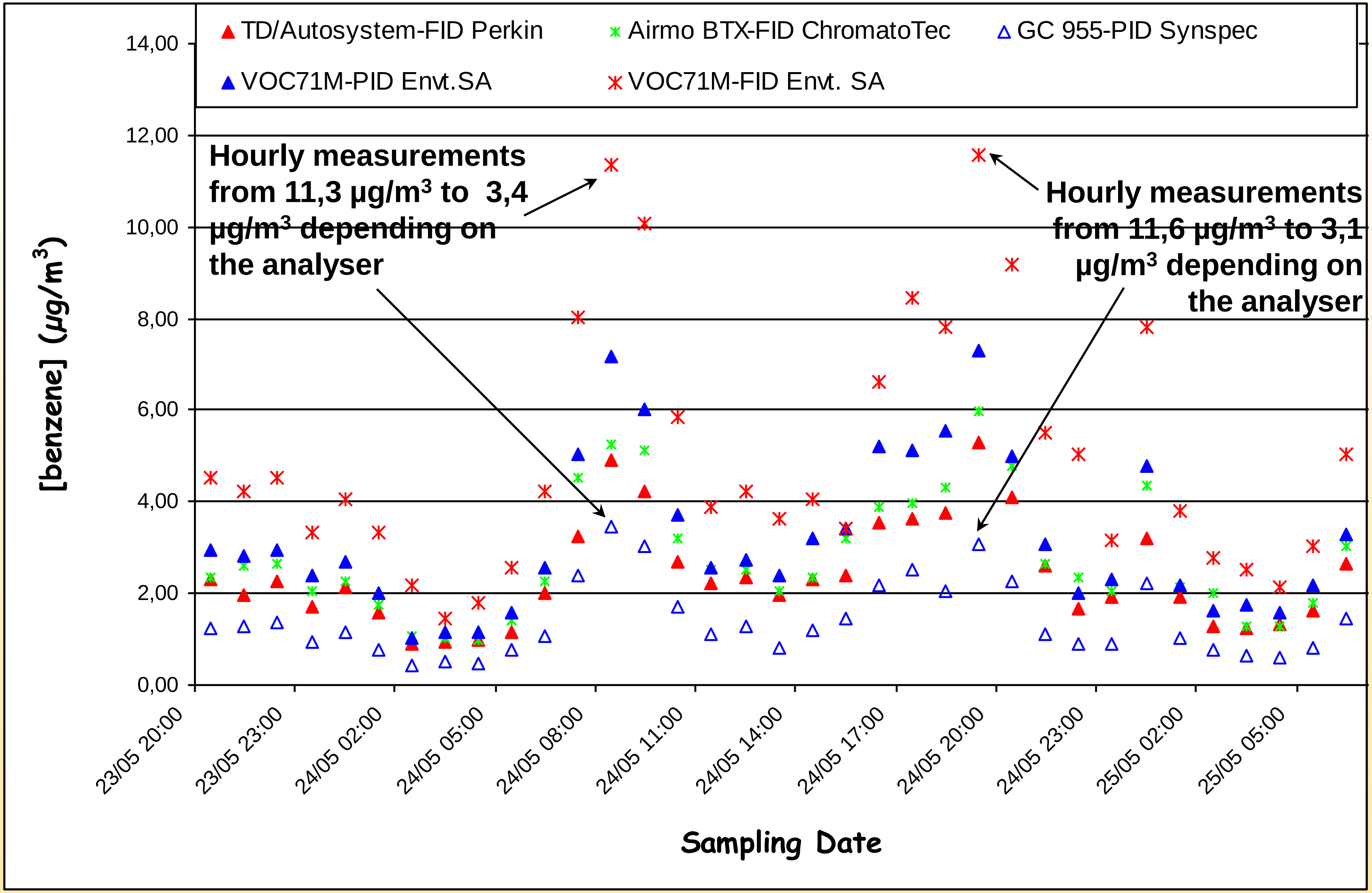
- **Field Campaign**
- Conclusion



Compiled results over all the campaign

- For Benzene :

	Perkin Elmer	ChromatoTec	Envt. SA FID	Envt. SA PID	Synspec
Availability	90,2%	92.7%	90,4%	92,0%	92,9%
Mean Concentrations (µg/m³)	1,94	2,01	**3,22**	2,80	**0,90**
Simultaneous maximum Concentration (HV) (µg/m³)	5,30	5,96	**11,60**	7,30	**3,08**
Number of exceedences (HV)> 5µg/m³	5	6	**76**	33	**0**

Mines de Douai

Conclusion

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Results

- Benzene mean levels may depend on the AMS used
- Benzene mean level may vary in a large scale
- At some sampling sites : benzene average value measured during a campaign may exceeds (or not) UAT (Directive 2008/50/EC)

↳ Depending on the system used, measurement strategy may be completely different (from fixed measurement to objective estimation)

Questions raised:

requirement of **type-approved** analysers for regulatory purpose = one of the key point for quality assurance

BUT for revision of EN 14662-3 : inclusion of additional tests? i.e. field campaign with differents models of type-approved monitors in parallel? Other interferents to be considered?

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Thank You for your attention…

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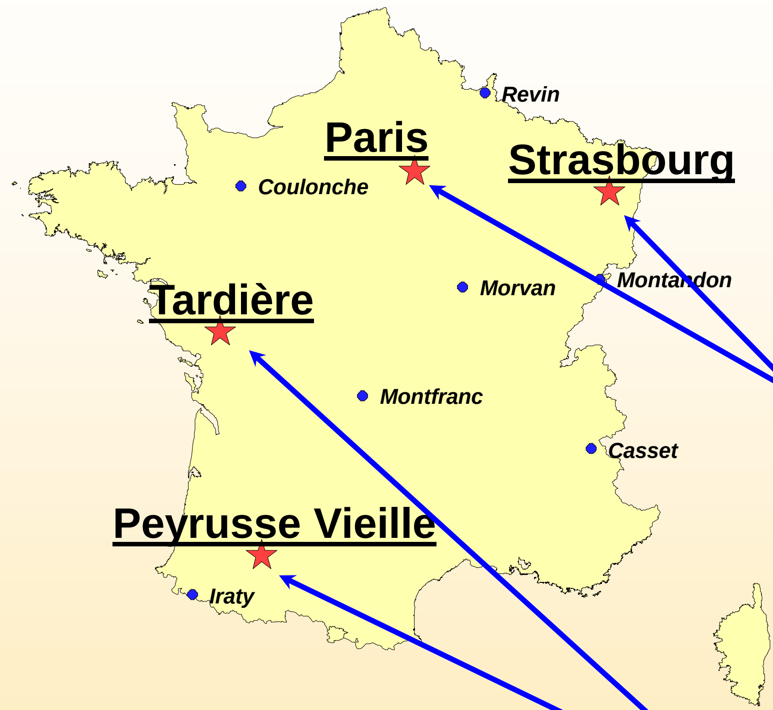
Annex…

VOC monitoring in France : MERA/EMEP observatory + Air Quality networks

- **Introduction**
- Laboratory Tests
- Field Campaign
- Conclusion



- ✓ on-line monitoring
- ✓ hourly measuring

31 HCnM :

- ✓ Strasbourg (2002-2010…)
- ✓ Paris (2003 – 2010…)

- ✓ Sampling via canisters
- ✓ 2 samplings each week

46 HCnM, Ozone, Météo :

- ✓ Peyrusse Vieille (2000-2010…)
- ✓ La Tardière (2002 – 2010…)

Laboratory Tests :Lack of fit

Turbo Matrix TD/Auto System – FID Perkin Elmer :

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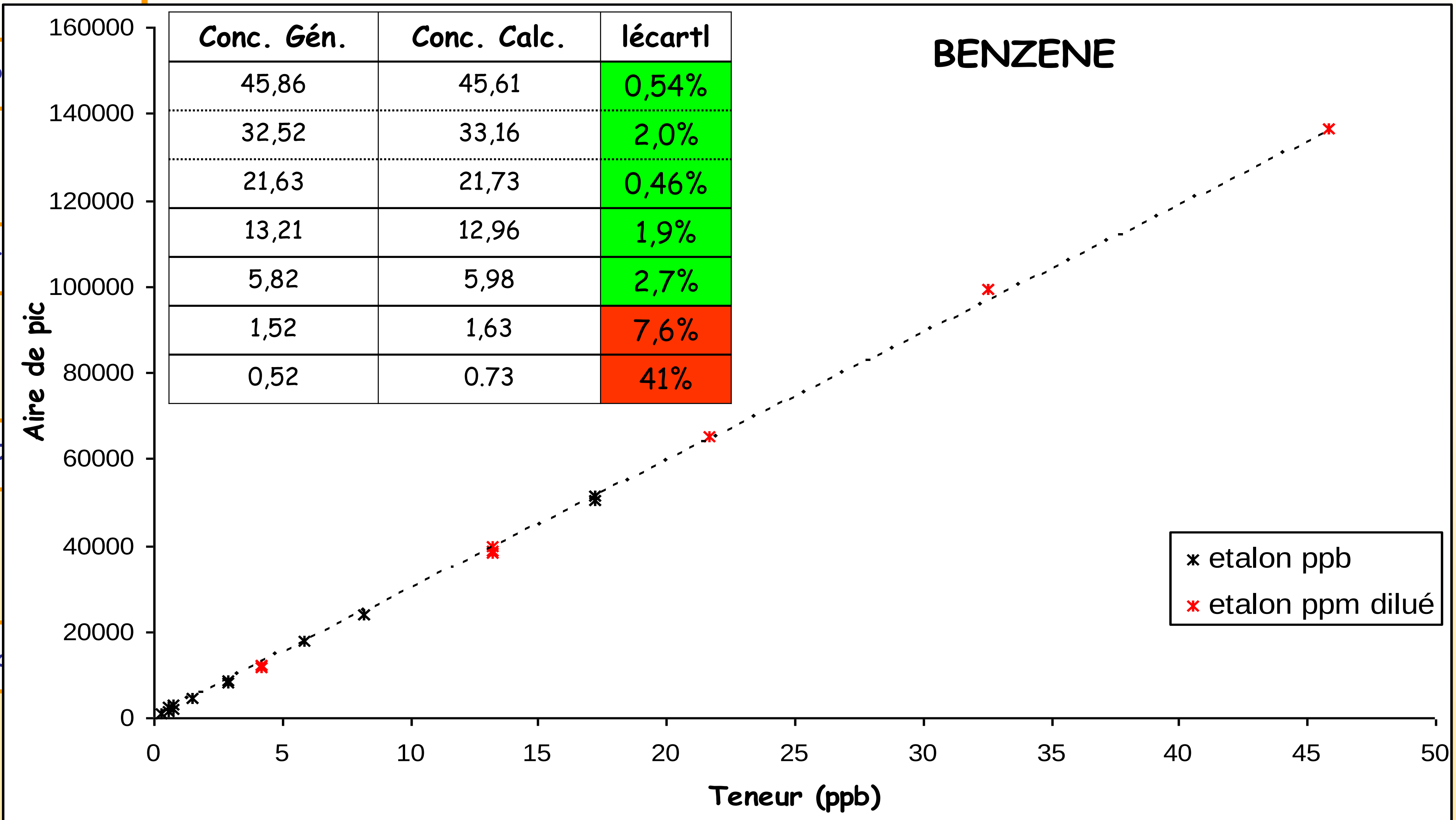
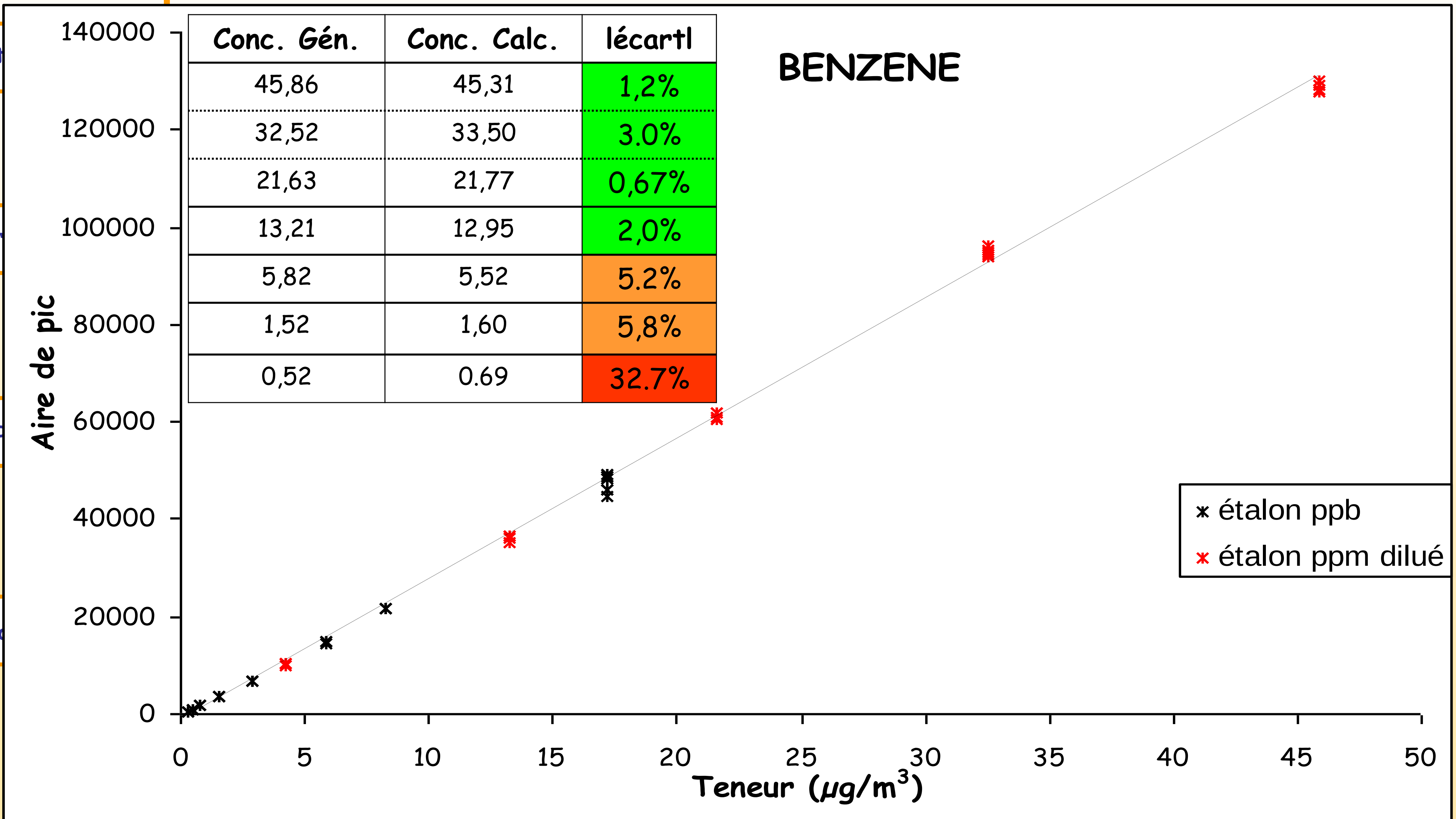
Conc. Gén.	Conc. Calc.	lécartl
45,86	45,61	0,54%
32,52	33,16	2,0%
21,63	21,73	0,46%
13,21	12,96	1,9%
5,82	5,98	2,7%
1,52	1,63	7,6%
0,52	0.73	41%



Laboratory Tests :Lack of fit

AirMo BTX FID Chromatotec:

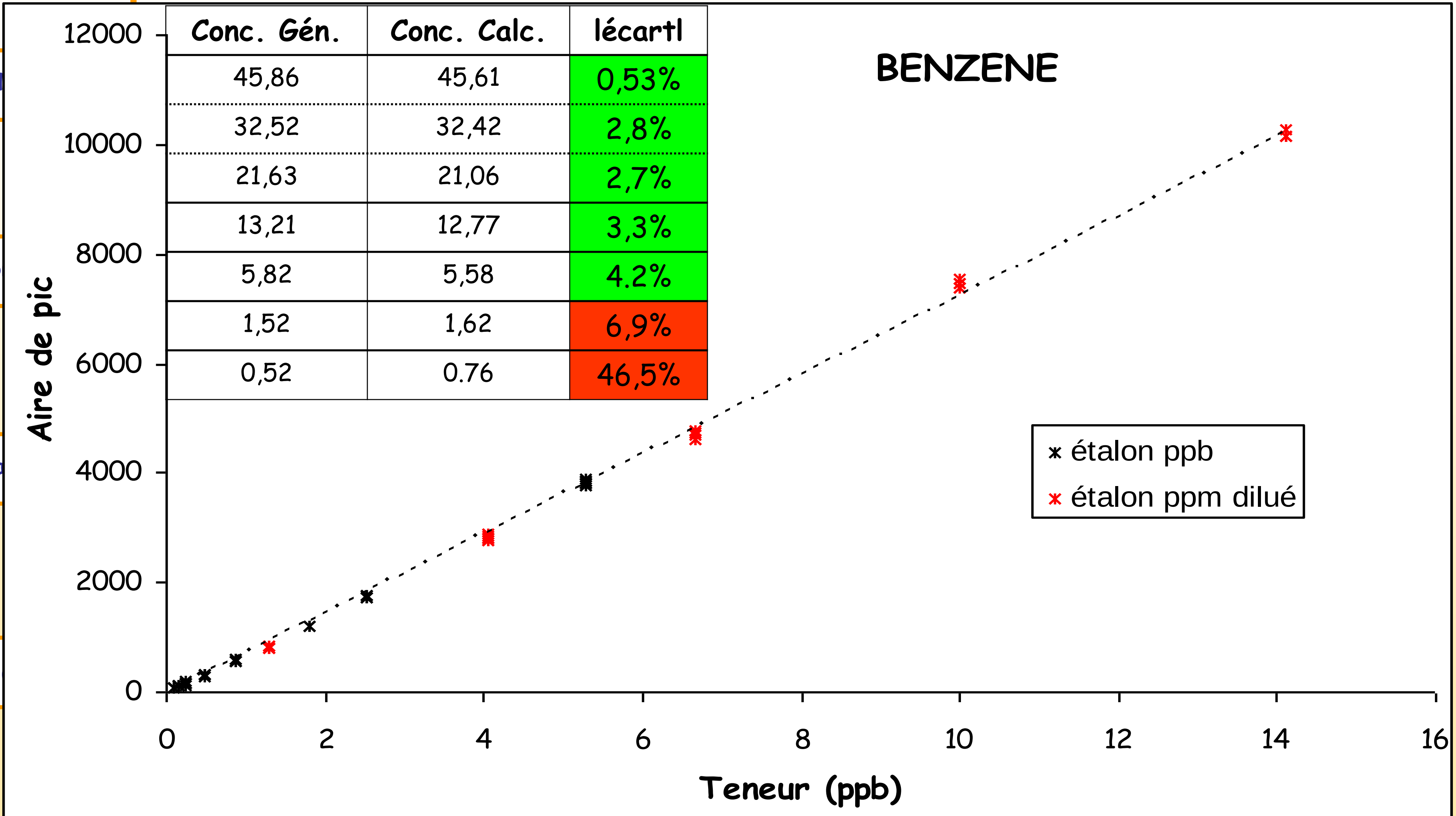


Conc. Gén.	Conc. Calc.	lécartl
45,86	45,31	1,2%
32,52	33,50	3.0%
21,63	21,77	0,67%
13,21	12,95	2,0%
5,82	5,52	5.2%
1,52	1,60	5,8%
0,52	0.69	32.7%

Laboratory Tests :Lack of fit

VOC 71 M Environnement SA FID :

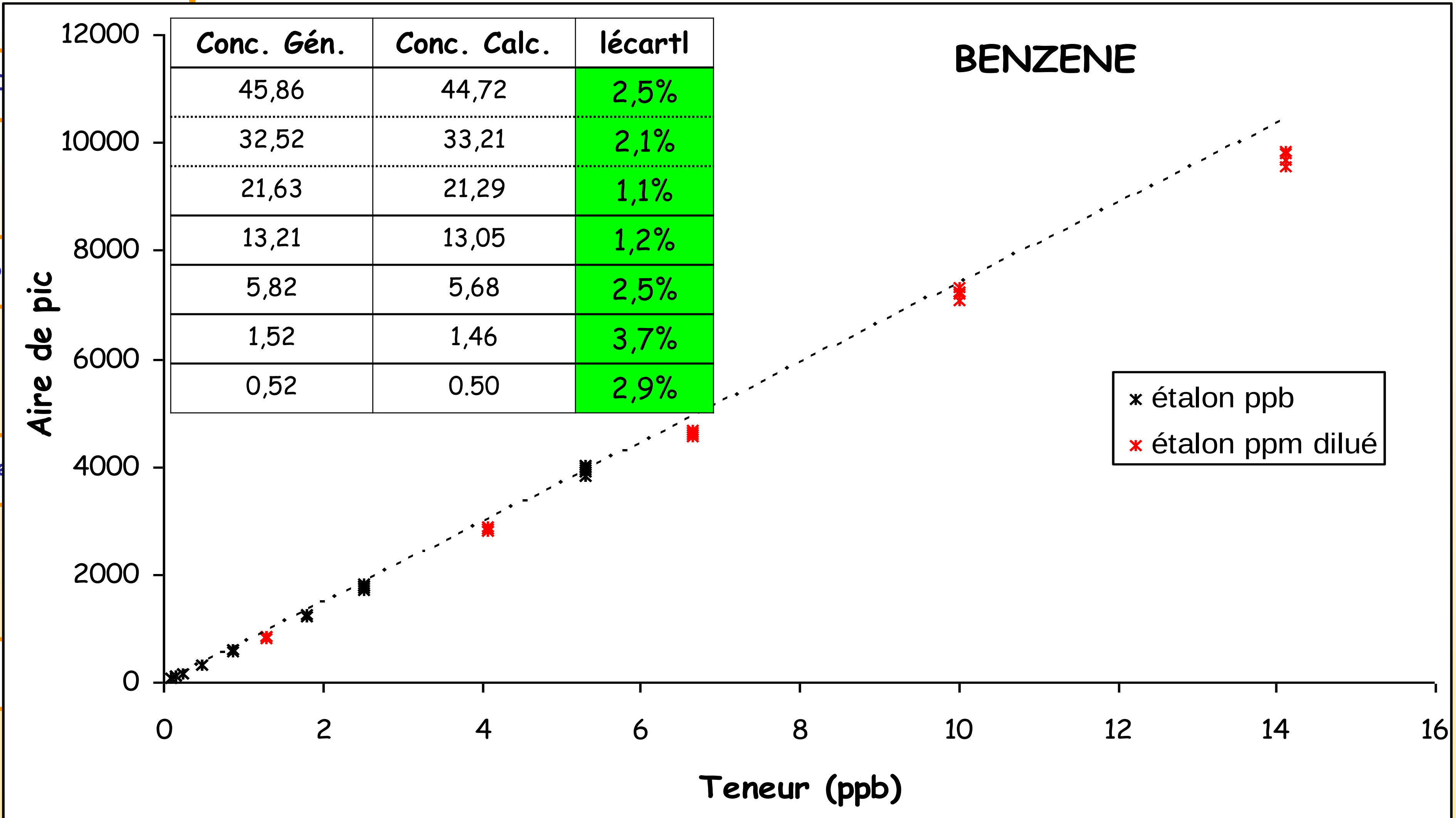
Conc. Gén.	Conc. Calc.	lécartl
45,86	45,61	0,53%
32,52	32,42	2,8%
21,63	21,06	2,7%
13,21	12,77	3,3%
5,82	5,58	4.2%
1,52	1,62	6,9%
0,52	0.76	46,5%



Laboratory Tests :Lack of fit

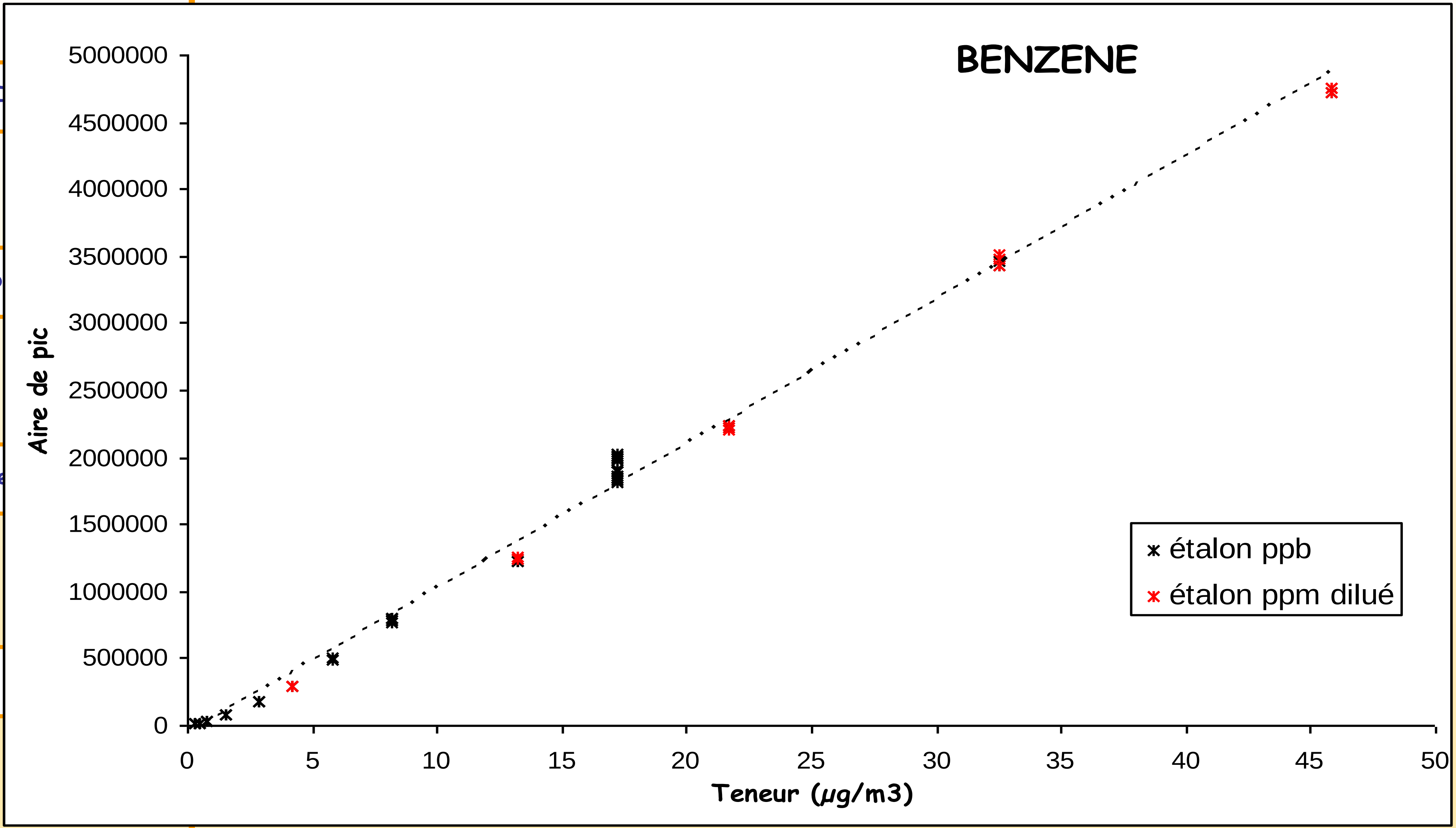
VOC 71M Environnement SA PID :

Conc. Gén.	Conc. Calc.	lécartl
45,86	44,72	2,5%
32,52	33,21	2,1%
21,63	21,29	1,1%
13,21	13,05	1,2%
5,82	5,68	2,5%
1,52	1,46	3,7%
0,52	0.50	2,9%



Laboratory Tests :Lack of fit

GC 955 - PID Synspec:



Laboratory Tests :Lack of fit

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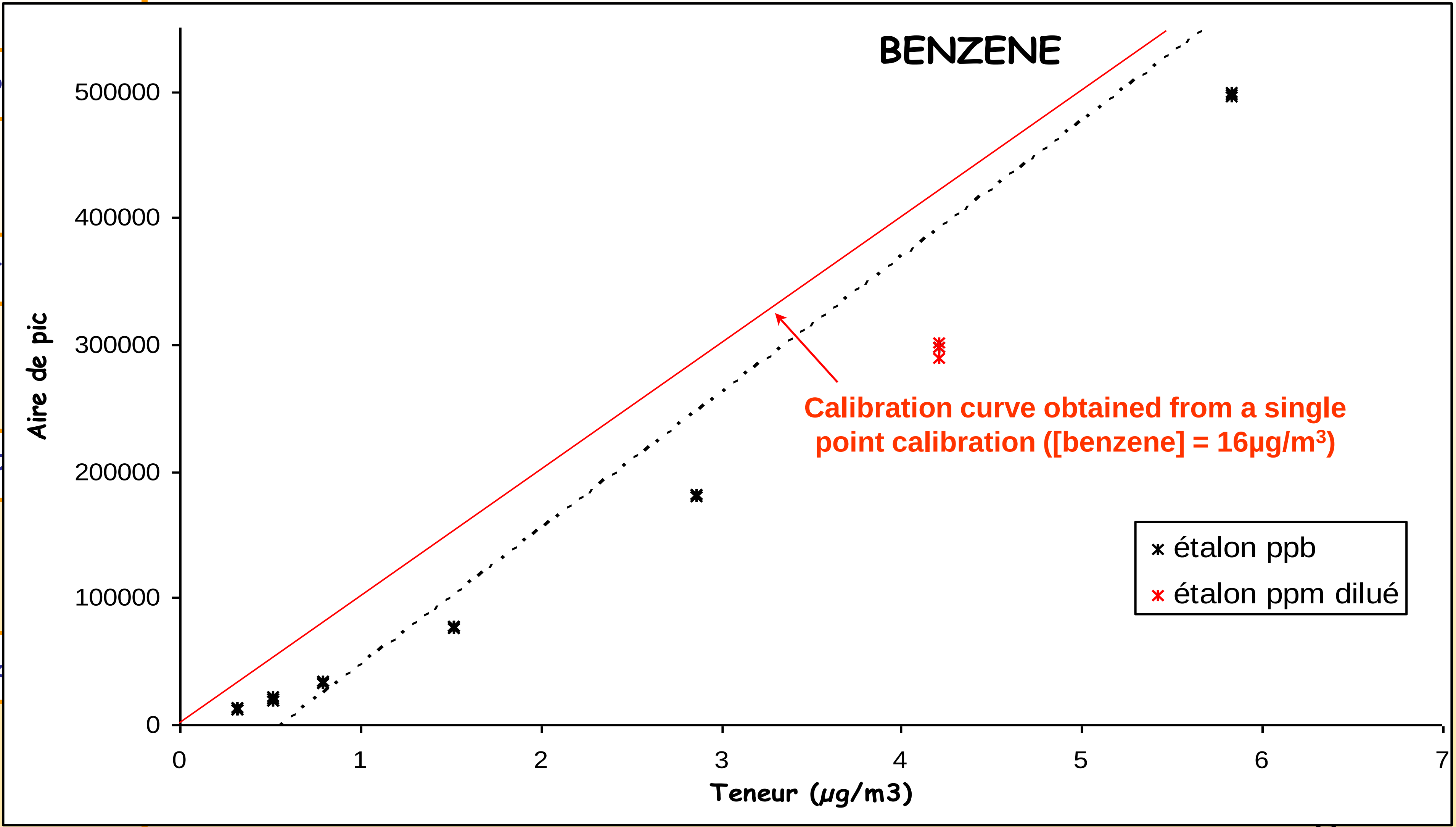
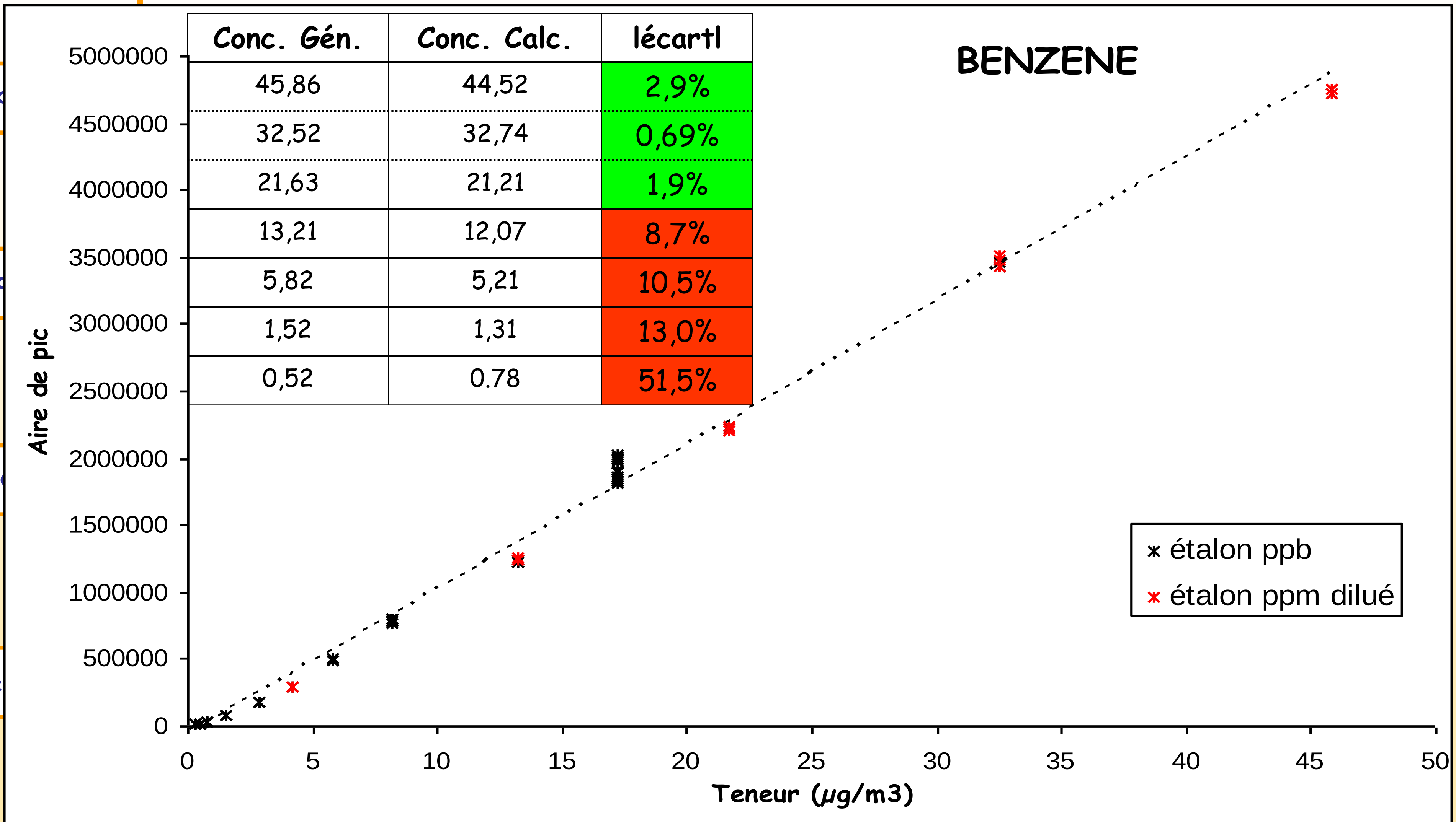
GC 955 – PID : Synspec : focus on low concentrations



Laboratory Tests :Lack of fit

GC 955 - PID Synspec:

Conc. Gén.	Conc. Calc.	lécartl
45,86	44,52	2,9%
32,52	32,74	0,69%
21,63	21,21	1,9%
13,21	12,07	8,7%
5,82	5,21	10,5%
1,52	1,31	13,0%
0,52	0.78	51,5%



Detection limits

ANALYSER	Concentrations (µg/m³)				Graphical determination
	Standard Injection	LD	Standard Injection	LD	LD (µg/m³)
Perkin Elmer	0,51	**0,070**			0,22
Chromatotec (pics assez fins)	0,34	**0,013**	0,12	**0,027**	0,03
Envt. SA FID (pics assez larges)	0,46	**0,054**	0,28	**0,031**	0,22
Envt. SA PID (pics assez fins)	0,34	**0,015**	0,25	**0,024**	0,17
Synspech (pics très fins)	0,27	**0,020**	0,13	**0,021**	0,015

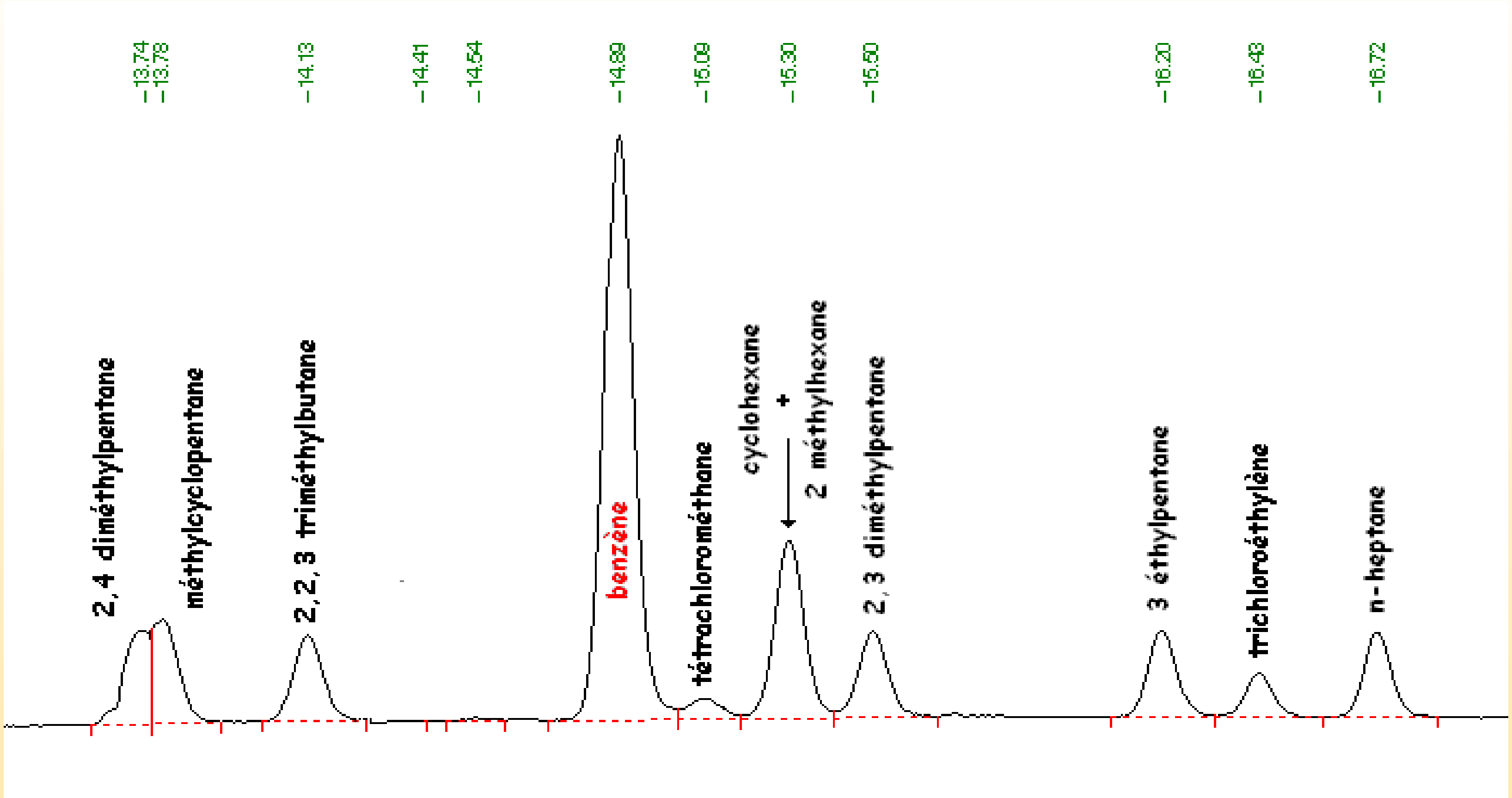
Short term drift

RESULTS for BENZENE and TOLUENE:

ANALYSER	Short term drift	
	Benzene	Toluene
Perkin Elmer	+ 3,1 %	+ 3,8%
Chromatotec	- 1,5%	+ 0,80%
Envt.SA FID	- 0,44%	-0,42%
Envt.SA PID	- 0,45%	- 0,49%
Synspech	Variable	

Influence of the interference from sum of possible interfering organic compounds

Interference from organic compounds for Perkin Elmer :



No coelution of VOC tested with benzene

Influence of the interference from sum of possible interfering organic compounds

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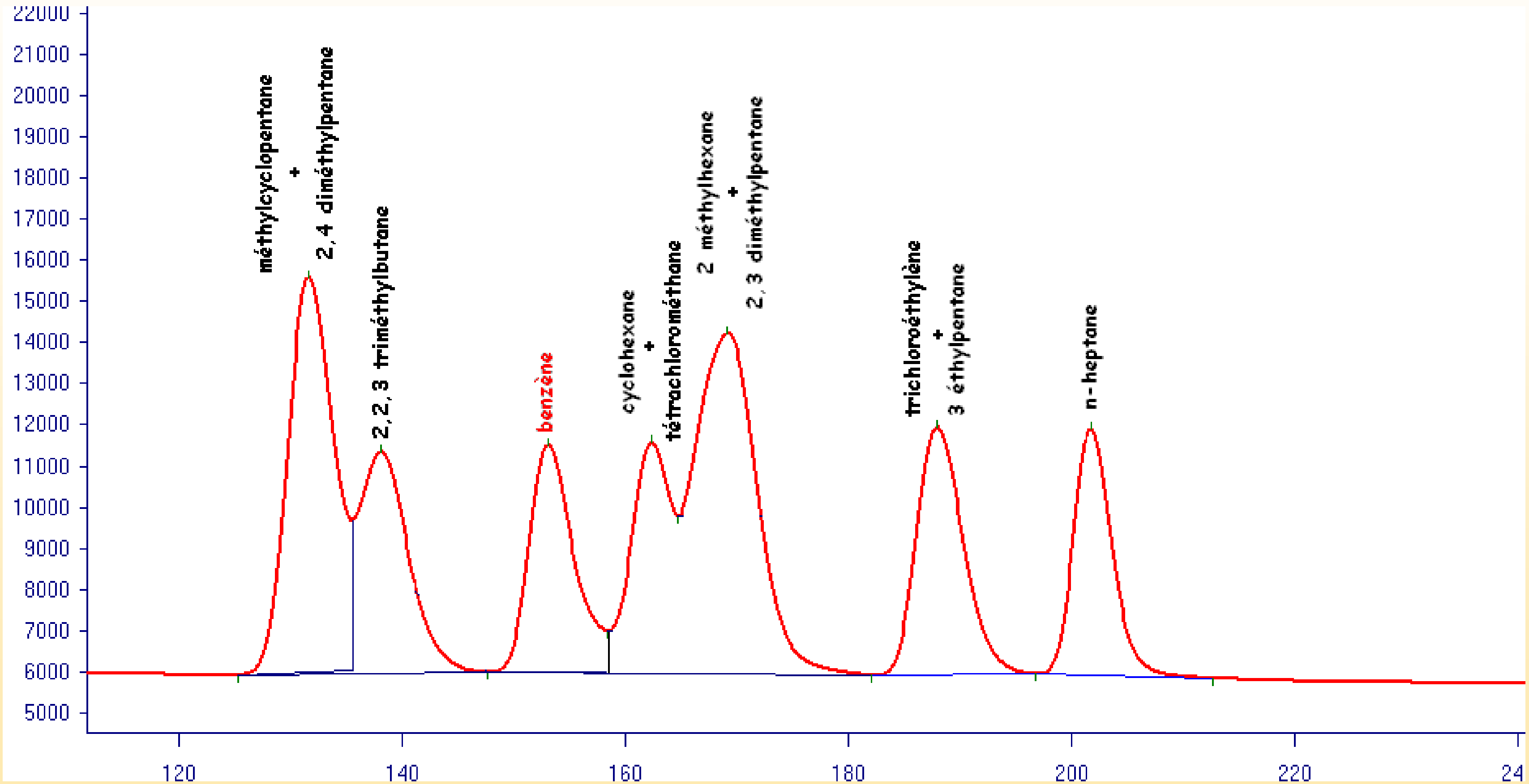
Interference from organic compounds for AirmoBTX Chromatotec :



➡ **No coelution of VOC tested with benzene**

Influence of the interference from sum of possible interfering organic compounds

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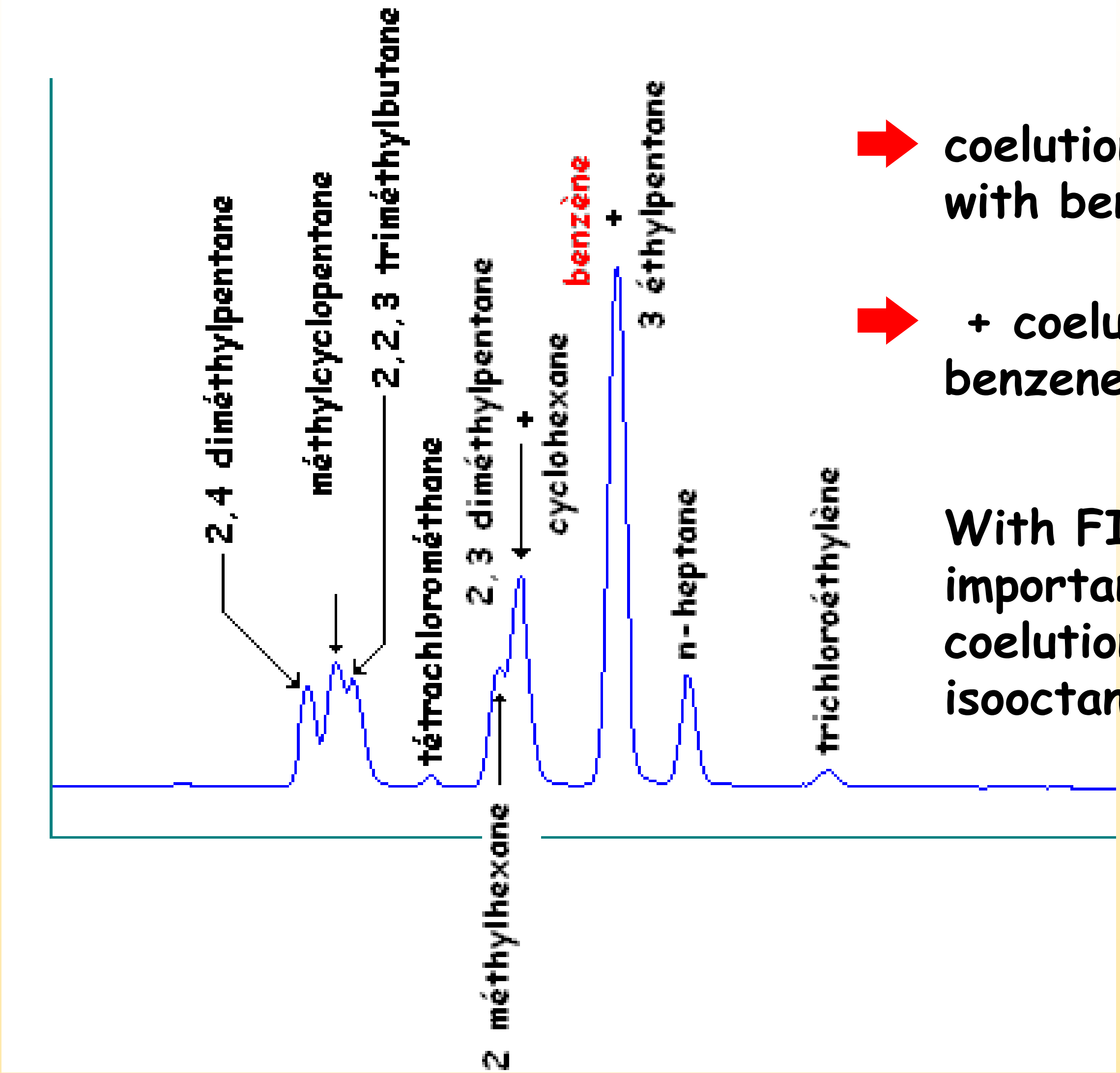
Interference from organic compounds for VOC 71M/FID Envt.SA :

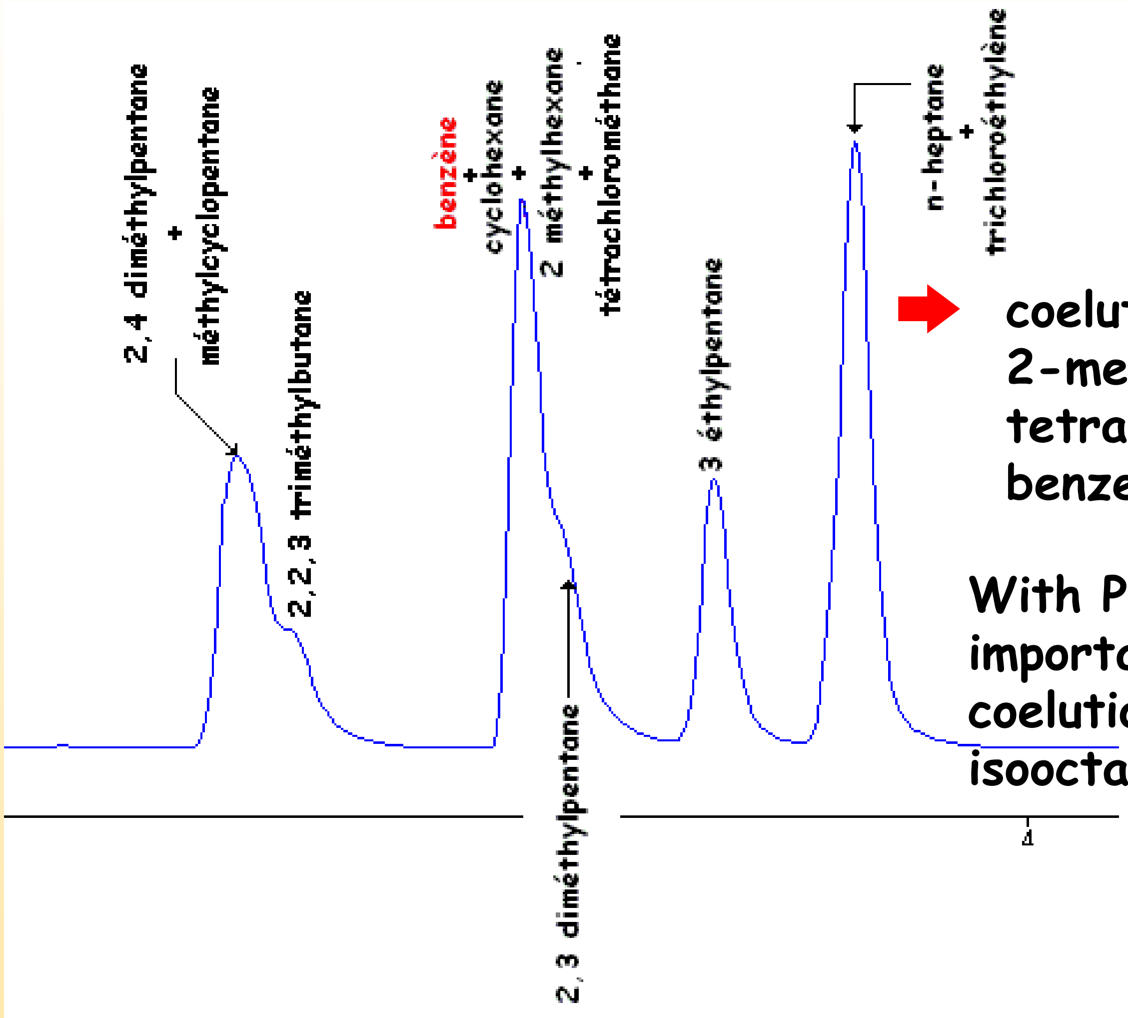


- coelution of 3-ethylpentane with benzene
- + coelution of isooctane with benzene

With FID detector : more important influence of coelution of isooctane and isooctane with benzene

Influence of the interference from sum of possible interfering organic compounds

Interference from organic compounds for GC 955-PID Synspec :



coelution of cyclohexane + 2-methylhexane+ tetrachloromethane with benzene

With PID detector : less important influence of coelution of isooctane and isooctane with benzene

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Results for ONE Week analysis

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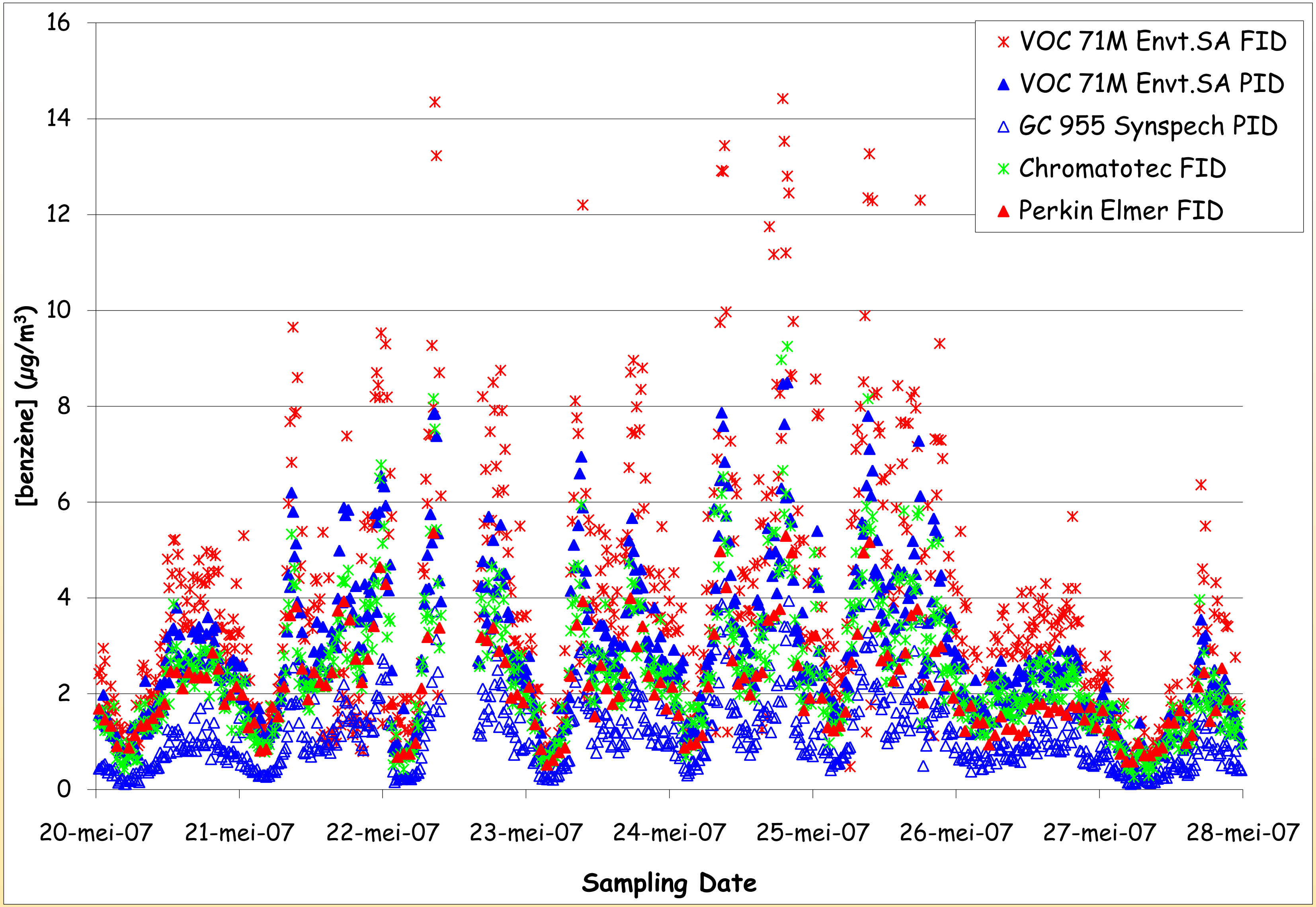

Focus on ONE Day analysis

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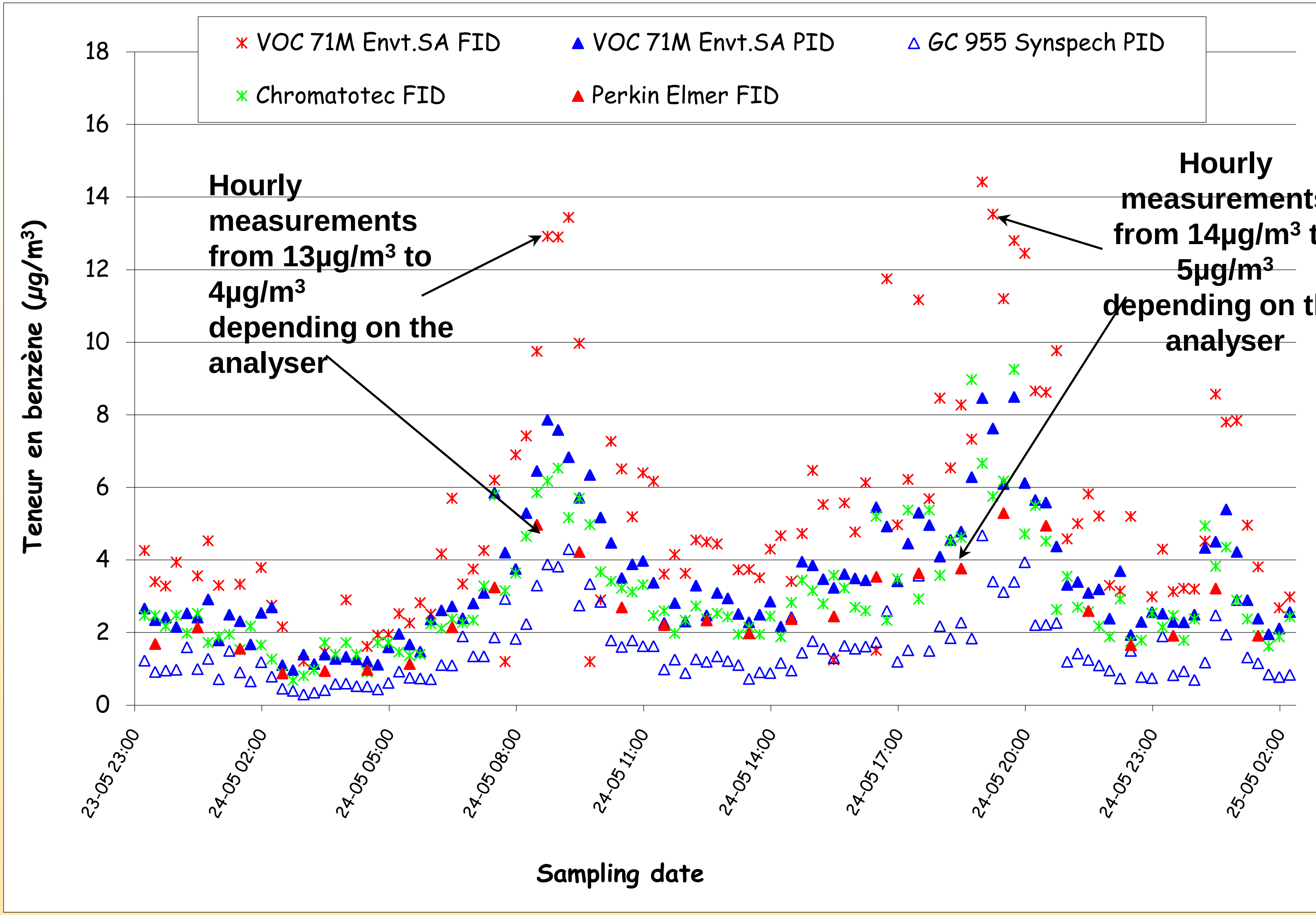
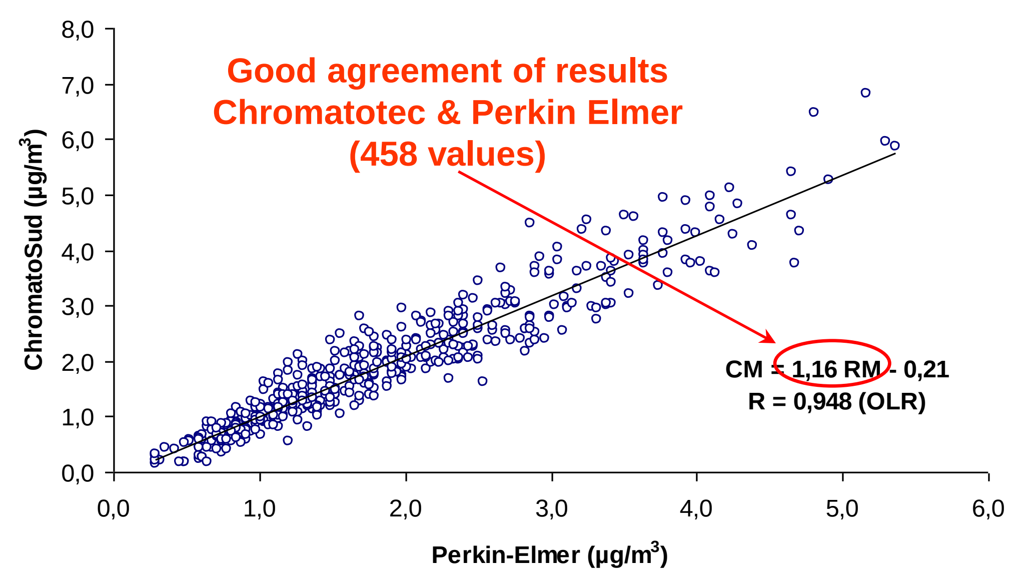
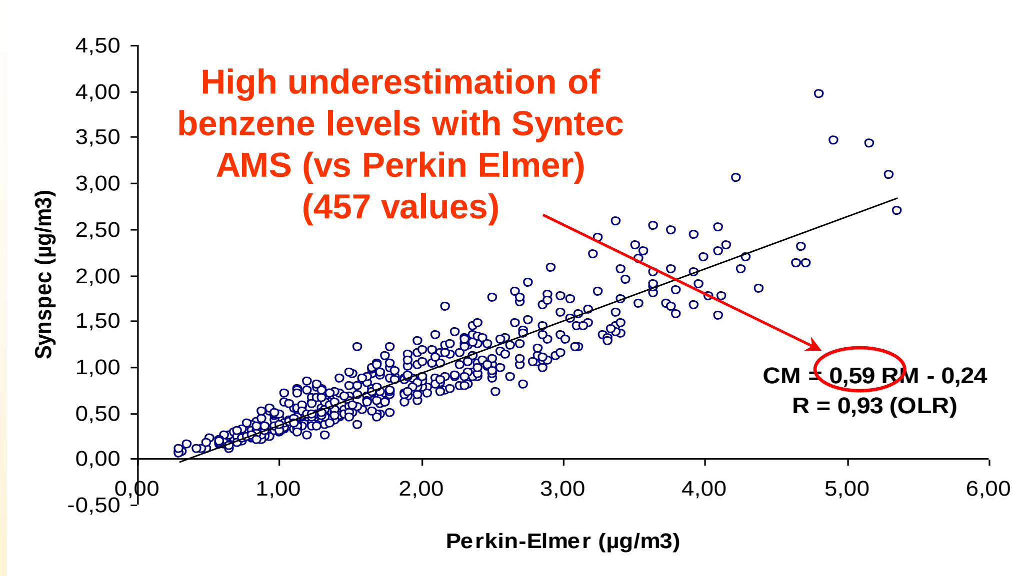
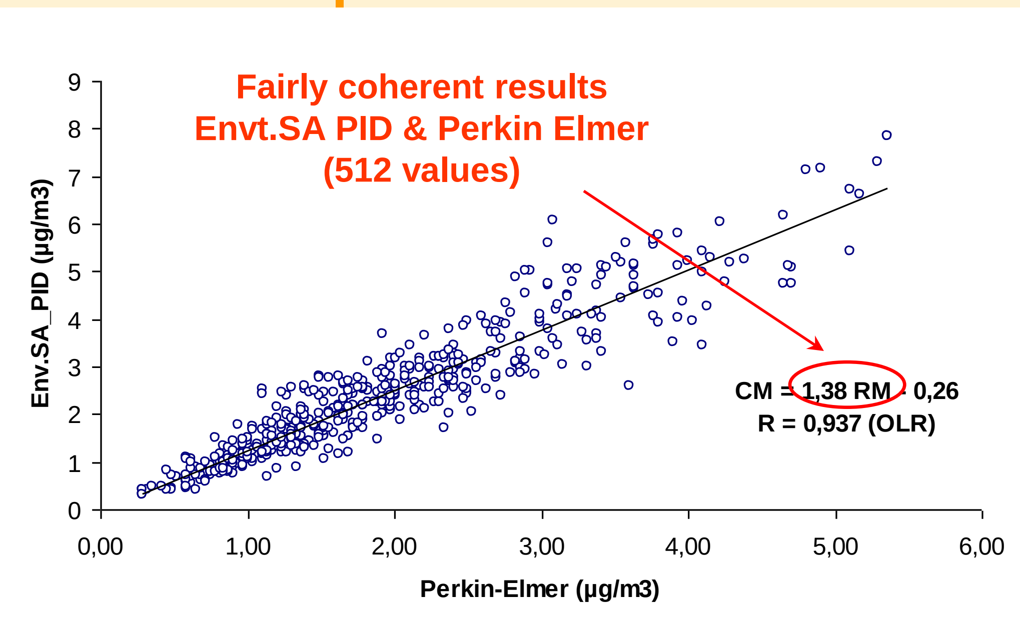
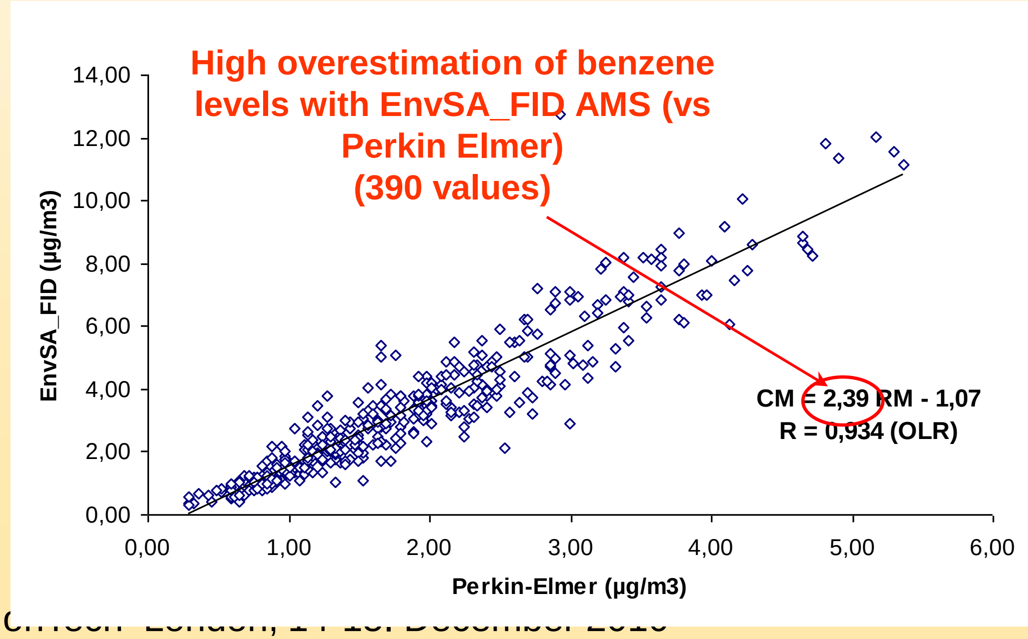


Field Campaign : results from 11/05 to 02/06









Publications : in urban zones

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- ***Atmospheric Environment 2003**, A.Borbon, H.Fontaine, N.Locoge, M.Veillerot, J.C.Galloo; « Developing receptor-oriented methods for non-methane hydrocarbon characterisation in urban air — Part I: source identification »*
- ***Atmospheric Environment 2003**, A.Borbon, H.Fontaine, N.Locoge, M.Veillerot, J.C.Galloo; « Developing receptor-oriented methods for non-methane hydrocarbon characterisation in urban air — Part II: source apportionment »*
- ***Analytical and Bioanalytical Chemistry, 2004**, C.Badol, A.Borbon, N.Locoge, T.Léonardis, J.C.Galloo; « An automated monitoring system for VOC precursors in ambient air : development, implementation and data analysis », vol. 378, pp. 1815-1824.*
- ***Pollution atmosphérique, 2005**, A.Borbon, C.Badol, N.Locoge; « Développement d'une méthodologie source récepteurs pour la caractérisation des COV dans l'air ambiant »*
- ***The Science of the Total Environment, 2007**, C.Badol, N.Locoge, T.Léonardis, J.C.Galloo; « Using a source-receptor approach to characterize VOC behaviour in a French urban area influenced by industrial emissions. Part I : Study area description, source profile establishment and qualitative data analysis of the data set »*
- ***The Science of the Total Environment, 2007**, C.Badol, N.Locoge, J.C.Galloo; « Using a source-receptor approach to characterize VOC behaviour in a French urban area influenced by industrial emissions. Part II : Source contribution assessment using the Chemical Mass Balance (CMB) model »*
- ***Pollution atmosphérique « Retour aux sources » , 2010**, S.Sauvage, C.Gaimoz, F.Troussier, V.Gros, N.Locoge; « Evaluation des contributions des différentes sources aux teneurs en Composés Organiques Volails en atmosphère urbaine par l'utilisation de deux modèles sources-récepteur (PMF et CMB) »*

Publications : in rural zones

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- *Chemosphere, 2004, A.Borbon, P.Coddeville, N.Locoge, J.C.Galloo; « Caracterising sources and sinks of rural VOC in eastern France »*
- *Atmospheric Environment 2009, S. Sauvage, H. Plaisance, N. Locoge, P. Coddeville and JC Galloo, « Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas »*
- *Edition spéciale Pollution atmosphérique « Retour aux sources », 2010, S.Sauvage, N.Locoge, H. Plaisance, P. Coddeville and JC Galloo, « Identification et contribution des sources de HCNM en zone rurale »*
- *In preparation*

« Possible source areas for HCNM in three rural sites, France »