ECOLE DES MINES DE DOUAI

DEPARTEMENT CHIMIE ET ENVIRONNEMENT

MESURE DU DU BENZENE

3/3 : Evaluation des analyseurs automatiques de BTEX

Convention: 000653

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Preamble

Le laboratoire Central de Surveillance de la Qualité de l'Air

The Laboratoire Central de Surveillance de la Qualité de l'Air is made up of the laboratories of the Ecole des Mines de Douai, INERIS, and LNE. Since 1991, it carries out studies and researches requested by the Ministry in charge of the environment, under technical coordination by ADEME, and in agreement with the Accredited Associations for Air Quality Surveillance. This work relating to atmospheric pollution are supported financially by the "direction of pollution prevention and risks of the ministry of ecology, development and sustainable development, re made with the constant concern to improve the quality of air surveillance in France bringing technical and scientific support to the AASQA.

The main objective of the LCSQA to participate in the improvement of the quality of the measurement done in the ambient air, from the sampling until data obtained from this measurement. This action is done within national and European regulations, but also in a prospective way in order to provide to the AASQA new tools enabling to anticipate future evolutions.

Summary

ABSTRACT

of the study conducted by Nadine LOCOGE TEL +33 3 27 71 26 19

This report presents the evaluation of analytical performances of 4 automated BTEX analyzers in place since 2007 at the various AASQA (VOC 71M Environnement SA/FID, VOC 71M Environnement SA/PID, GC 955 Synspech/PID, Chromatotec/FID), to which should be added an analyzer Perkin Elmer, more difficult to use but enabling the measurement of a larger range of VOC (Typically the 31 VOC of the list of the ozone precursors specified in the appendix VI of the directive 2003/3/CE relative to ozone in ambient air).

First of all, this study evaluates a number of performances of the analyzers and the results obtained to determine conformance to the requirements of the norm 14 662-3. The results obtained have shown significantly different results depending on the analyzer and the parameters tested.

Regarding linearity, 3 out of 4 analyzers tested (Chromatotec, VOC 71M Envt SA FID, VOC 71M Envt SA PID) meet the requirement of the performance criteria of the norm (Relative residual of the linear regression function must be below 5% for the points with concentrations 5, 15, 25, 35, 45 µg/m^3) or are slightly superior to the criteria (5.2 % for the analyzer Chromatotec for the point with concentration 5 µg/m^3). For the analyzer GC 955 Synspech, it was shown a significant difference to linearity with residuals reaching 10% for the concentration point at a concentration of 5 µg/m^3. This difference to linearity with the analyzer by Synspech explains the results obtained when analyzers are put in parallel on site and demonstrates the necessity to do an auto-linearization during calibration on site or to use a calibration mixture with a concentration close to the one measured on site. Nonetheless, it appears that the measurement of concentrations inferior to the *point of scale** will be under-evaluated and the one above the point of scale will be over-estimated.

Regarding memory effect, the analyzers by Chromatotec and Synspech measure, during a second analysis of zero air following immediately an analysis of the highest concentration of benzene, concentrations of benzene lower than 0.5 µg/m^3 and meet thus the requirement of the norm. Nonetheless, for the analyzers VOC 71M Envt SA and PID, the concentrations measured for benzene after a second analysis of zero air following the highest concentration of benzene are respectively 1.02 µg/m^3 and 0.88 µg/m^3 and thus do not meet the criteria required by the norm.

Regarding repeatability, all the analyzers have repeatability at the limited value lower than 5% and repeatability at 0.5 µg/m^3 better than 0.1 µg/m^3. Thus, they all meet the criteria of the norm.

Regarding sensitivity of the analyzers to interferences by VOC, the analyzer by Chromatotec is not sensitive to the VOC tested which is in agreement with the fact that no VOC co-elutes with benzene. For the analyzer by Envt SA, the variation in the response is in the magnitude of 100% for the analyzer equipped by a detector PID and remains limited to less than approximately 10% for the analyzer equipped with a PID detector. For the analyzer by Synspech, the response is significantly under-estimated when a mixture of organic interfering species is added by approximately 40%.

In terms of limit of detection, for all the automated analyzers of BTEX tested, the limits of detection are lower than 0.05 µg/m^3.

For the purpose of this translation, point d'échelle will be translated by point of scale

In a second phase, all the analyzers have been placed in the same study site in order to compare the behaviours and results of the analyzers tested in the real conditions of usage at an AASQA. The site of study shall be a site where the levels of benzene are above the superior level of evaluation, in other words a site where the method of surveillance of benzene required by the directive is the active method. A site near traffic must be the site chosen.

In terms of long term drift, for all the analyzers equipped with an FID detector, which are the BTEX Chromatotec and VOC 71M Envt SA/FID, it is possible to observe a very stable response of the analyzers. On the contrary, for the two analyzers equipped with PID detection, VOC 71M Envt SA/PID and GC 955 Synspech, a significant long term drift is observed with a decrease in the areas recorded for the gas standard mixture. This drift of the response of the PID detector remains, all along the period of the follow-up, inferior to the criteria of performance of 10% for the analyzer VOC 71M Envt SA/PID; It is much more variable depending on the period chosen for the analyzer by Synspech and can sometimes be above the criteria of performance of 10%

Concerning the evaluation of the concentrations along time, a homogeneous time dynamics is observed with overall two daily peaks of concentrations corresponding to the time when car traffic is maximum with nonetheless very significant differences in the amount of benzene measured.

In order to study the correlations between the various analyzers, in particular for benzene, the analyzer by Perkin Elmer was used as a reference and the levels of the other analyzers have then been compared against against the values measured by the analyzer by Perkin Elmer. It appears that the correlations are relatively good with coefficients varying between 0,87 and 0,90. Nonetheless, the slopes of the curves obtained have shown:

- Good coherence of the values of benzene measured by the analyzers by Perkin Elmer and Chromatotec
- Clear under-evaluation of the levels of benzene measured by the analyzer by Synspech which can be explained by gap to linearity observed for this analyzer
- A very sensitive over-evaluation of concentrations of benzene measured by the analyzer VOC 71M/FID Envt SA (A factor superior to 2 is obtained) which can be explained by the sensitivity of the analyzer to VOC interfering species.
- An over-estimation by as much as 25% for the levels of benzene measured by the analyzer VOC 71M/PID Envt SA compared to the analyzer by Perkin Elmer.

Complementary analysis have enabled to explain the origin of the concentrations of benzene measured with the analyzer VOC 71M/FID Envt SA (Co-elution of benzene with 3-Ethylpentane and isooctane) and have enabled to show that the procedure to "auto-linearize" of the analyzer by Synspech can make a good improvement of the results with a linear regression slope at 0,73 (instead of 0,57 obtained without auto-linearization), but the magnitude of the under-estimation is still about 25% if Perkin Elmer is used as the reference analyzer.

This report has been communicated to all the manufacturers. The company Néréïdes/Synspech has indicated several remarks which have been added to this report in appendix 2.

1 – Introduction

The objective of this study is to pursue various actions concerning the measurement of benzene by the AASQA in order to do a measurement of benzene according to the requirement of the directive. Consequently, the main actions for 2007 are the following:

- Evaluate the performances of sampling methods active or passive (trials in "test chambers" or on site)
- Evaluate the performances on the field of automated BTEX analyzers according to CEN 14 662-3
- Harmonize practices in terms of benzene measurements in france

Considering the variety of actions to be done to complete this study, we have decided to do several reports according to the themes chosen. This report is dedicated to the second subject of this study that is to say the evaluation of the performances of automated analyzers of BTEX (benzene, toluene, Ethyl-benzene, xylene).

The analytical performances of 4 automated analyzers BTEX today installed at various AASQA (VOC 71M envt SA/FID, VOC 71M Envt SA/PID, GC 955 Synspech/PID, Chromatotec/FID), to which shall be added an analyzer by Perkin Elmer, heavier to use, but enabling the measurement of a large range of VOCs (typically the 31 VOC of the list of ozone precursors specified in appendix VI of the directive 2003/3/CE relative to ozone in ambient air).

This evaluation is done in 2 steps:

- First, the evaluation of a number of performances of these analyzers, examination of the results obtained to evaluate the conformance with respect to the minimal requirement of the norm 14 662-3 (linearity, memory effect, repeatability, short term drift, drift over 7 and 14 days…)
- Then, all the analyzers have been placed on the same study site and it appears that the concentrations of benzene are above the maximum evaluation level that is to say the method of surveillance of benzene required by the directive applicable. The choice was for a site located near traffic.

2 – Presentation of the various automated analyzers tested

2.1 – The analyzer automated of VOC by Perkin Elmer

This automatic analyzer has 2 modules:

- A pre-concentration/thermo-desorption/injection unit which enables automatic sampling of a given volume (600 ml in the trials conducted), the pre-concentration of VOC in a tube containing one or several adsorbants according to target VOC (Carbopack B for this study), the thermo-desorption is done at optimized temperature according to the range of COVs (300°C during trials) and the injection via an independent chromatographic system.
- A unit of separation/detection which enables to separate target VOC and which is equipped with two columns if a large range of VOC is quantified. In our case, only

one column in the chromatograph in the gaseous phase (Column CP Sil 5 CB) which is connected to a flame ionization detector.

The air sample is sucked with an external pump at a constant flow of 20 ml/min. The flow is regulated with a mass flow meter. The measurement cycle is one hour and the air sampling lasts 30 minutes.

The gases necessary to the operation of the analyzer are helium (carrier gas to ensure elution of VOC in the chromatographic columns), hydrogen and air to ensure component detection.

This analyzer has a PC which enables programming of the various parameters of operation of the analyzer on one hand and on the other hand which enables data retrieval and archiving of results.

2.2 – The automated analyzer BTEX Chromatotec/FID

This is a compact automated analyzer ensuring pre-concentration, thermo-desorption and analysis of BTEX in a sample of air.

It is made up of a filled sorbent trap (carbotrap) suited for the measurement of BTEX which ensures the pre-concentration of compounds at ambient temperature. This trap is heated at 380°C and the VOC are injected directly in the chromatographic column. It is an a-polar column of 30 m and 0,28 mm diameter which ensures the elution of all the compounds in less than 15 minutes.

The air sample has a flow of approximately 50 ml/min which is ensured by the external pump and the flow regulation is done by a critical orifice. The cycle lasts 15 minutes and the sampling time is about 12 minutes for each cycle.

The gases necessary to the operation of the analyzer are hydrogen (carrier gas necessary for the elution of VOC in the chromatographic column and also the supply of the FID), air for the supply of the flame ionization detector.

This analyzer has a PC which allows for the programming of the various parameters of operation of the analyzer and also the retrieval and archiving of the results.

2.3 – The automatic analyzers BTEX VOC 71M Environnement SA (version FID and PID)

This is a compact automated analyzer ensuring pre-concentration, thermo-desorption and analysis of BTEX in an air sample. This analyzer is available with two versions: one version equipped with a flame ionization detector (FID) and another one equipped with a photo-ionization detector (PID).

It is made up of 2 traps filled in with a sorbent material adapted for the measurement of BTEX which ensures the pre-concentration of compounds at room temperature. This trap is heated then to 320°C, the compounds are thermo-desorbed and transferred to a focussing trap. This trap is heated to 320°C in order to enable the injection of the BTEX in the chromatographic column. The presence of 2 traps in the analyzer enables to put a sampling trap while the other trap is in the step of desorption. Thus, the analyzer is continuously sampling ambient air which enables a continuous time sampling of 100% sample. The chromatographic column is an EPA 624 of 10 m and 0,32 mm diameter (width of the film is 1,4 um) which ensures elution of all compounds in less than 15 minutes.

The air sample has a flow of 70 ml/min which is done by an external pump and the flow regulation is done by a critical orifice. The measurement cycle is 15 minutes and the sampling time is 15 minutes.

The gases necessary to the operation of the analyzer are:

- For the PID analyzer, nitrogen as a carrier gas to ensure elution of VOC in the chromatographic column and also the additional supply to the PID detector.
- For the FID version, air and hydrogen for the supply to the flame ionization detector. Hydrogen has also the role of a carrier gas for the elution of the compounds in the chromatographic column.

This analyzer has a PC integrated which ensures retrieving and archiving of results.

2.4 – The automatic analyzers BTEX GC 955 Synspech

This automatic analyzer is compact and ensures pre-concentration, thermo-desorption and analysis of an air sample equipped with a photo-ionization detector (PID) for all analyzers currently installed in France.

It has a trap filled in with a sorbent material specially designed for the measurement of BTEX (Tenax) which ensures the pre-concentration of the compounds at ambient temperature. This trap is then heated at 180 C, the BTEX are injected in a pre-column (its role is to retain the heavier compounds, it is then back flushed), then in an analytical column type AT5. The chromatography column is 15m long and has a 0,32 mm diameter which ensures elution of all the compounds in less than 15 minutes.

The sampling of air is done is done by a sampling syringe which removes a fixed volume of gas. The volume of this syringe is small (18,5 ml), several aspirations (typically 5) are done successively which enables to reach a sampling volume of 92,5 ml. This sampling system has as a consequence an aspiration at discontinuous flow during a total time between 12 and 13 minutes. The cycle of measurement is 15 minutes.

The gas necessary for the operation of this analyzer is nitrogen as a carrier gas to ensure the elution of the VOC in the chromatographic column.

This analyzer has a PC which enables programming of the various parameters of operation of the analyzer and also retrieval and archiving of the results.

3. - TECHNICAL RECEPTION OF THE AUTOMATIC ANALYZERS IN LABORATORY

The trials which have been done in the laboratory are design to determine the performances presented in table 2 of the norm 14 662-3 in compliance (within feasible limits of the installations available at the School of Mines in Douai) with the operational methods described in the paragraph 8.5 of the norm 14 662-3.

The following parameters were recorded: gap to linearity, short term drift, repeatability at 2 concentrations levels, influence of interfering species due to addition of potential organic interfering species at the value of the point of scale. Nonetheless, considering the facilities available at the School of Mines in Douai, all the tests described in the norm 14 662-3 have not been done in particular the influence of humidity, influence of the surrounding temperature at the value of the point of scale, influence of ambient pressure at the value of the point of scale, influence of the tension at the value of the point of scale.

3.1 – Study of the linearity

3.1.1 – the norm 14 662-3 and the tests performed

The norm 14 662-3 specify that the purpose is to "determine a linear regression function with the responses of the analyzer and the level of concentrations applied corresponding. The residual at each concentration level is equal to the difference between the average response measured, expressed by concentration, and the concentration indicated by the function of linear regression".

The norm also says:"the linearity of the analyzer must be evaluated on a range between 0% and 90% of the maximum value of the range of values measured certified, using at least 6 concentrations (including the zero point). The following concentrations must be used: 0 (inferior to the detection limit); 5 µg/m^3 +/- 10%; 15 µg/m^3 +/- 10%; 25 µg/m^3+/- 10%; 35 µg/m^3+/- 10%; 45 µg/m^3+/- 10%. Evaluate the calibration function of the analyzer with a linearity test. For each concentration (zero concentration included), at least 6 independents measurements must be done. The first measurement at each level of concentration must be excluded during the analysis of the data.

The uncertainty of the dilution ratios leading to the applied concentrations applied must be below +/- 1%.

The calculation of the function of linear regression and of the residuals must be done according to appendix A.

The largest relative residual of the linear regression function must satisfy the criteria of performance indicated in table 2, which is less than 5%.

If one or several relative residuals do not satisfy the previous criteria, then the linearity test is not conclusive for the analyzer.

The biggest value $(d_r)_c$ is written X_{fit} and must be included in the calculation of the uncertainty."

The tests have been conducted with 2 different gas mixtures: one at a low concentration level with a nominal value for benzene of 5,298 ppb and the other one at a high concentration with a nominal value for benzene of 10 130 ppb. The dilutions (for which it has been it was checked that the dilution have a dilution ratio lower than 1%) chosen are at 6 different levels as specified above. To be noticed the inter-comparison exercise which had been organized by the ERLAP (European Reference Laboratory for air pollution) at ISPRA from October 10 to 14th, 2005, the test of linearity have been conducted at the zero point until a concentration of about 30 ug/m3 with five points of concentrations on the BTEX. This choice was done considering the very large range of linearity specified in the norm 14 662-1 and noticeably at the highest concentration: 45 µg/m^3.

The results obtained for all the analyzers are presented hereafter.

3.1.2 – The results obtained by the analyzer by Perkin Elmer

The figure 3.1 presents the results obtained for benzene with the analyzer by Perkin Elmer.

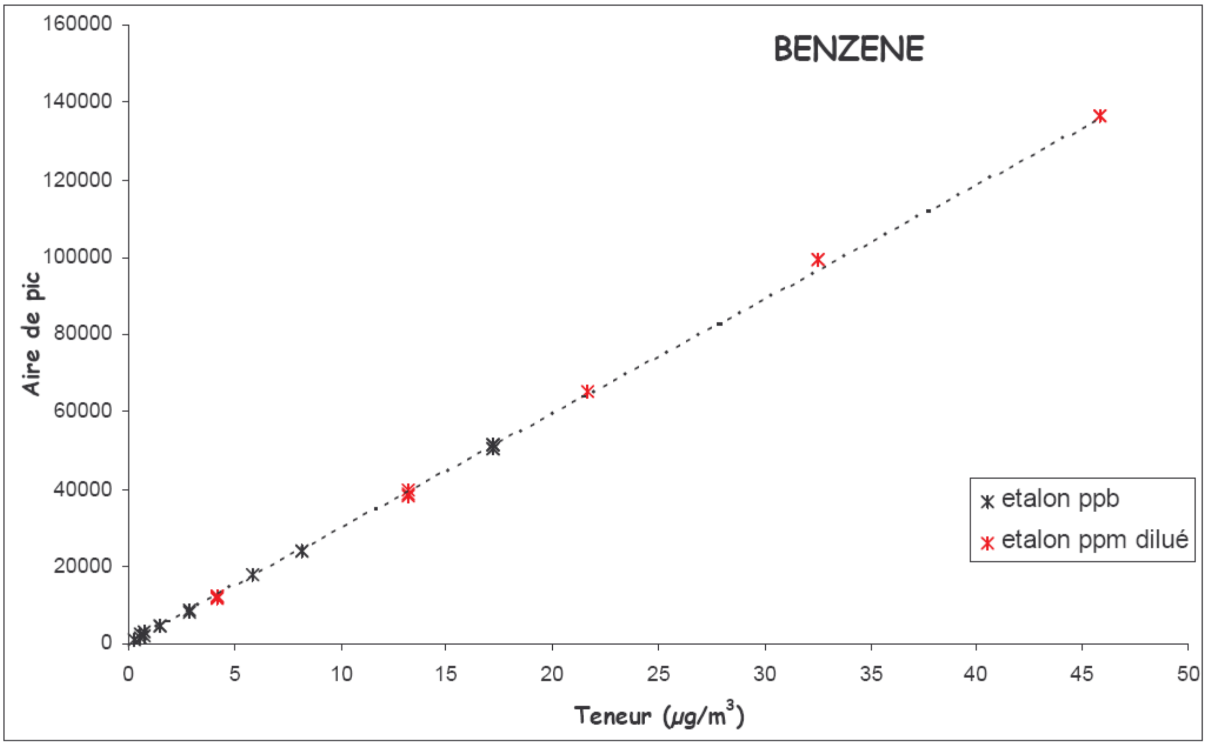

Figure 3.1: response of the analyzer Perkin Elmer according to benzene concentration in benzene

The results according to the norm 14 662-3 are presented in table 3.1.

Concentration generated(µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
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**

Table 3.1: % difference to linearity of the analyzer by Perkin Elmer according to the concentration of benzene (according to appendix A of the norm 14 662-3)

It appears that for the two levels with lowest concentrations, 1,52 µg/m^3 and 0,52 µg/m^3, the relative residuals of the linear regression function are respectively 7,6 and 41%. They are superior to 5% and do not meet the criteria of 5% required by the norm 14 662-3. Nonetheless, if we refer to the five concentrations listed in the norm 14 662-3, that is to say 45, 35, 25, 15 and 5 µg/m3; for those five levels, the difference to linearity is inferior to the criteria of 5% and consequently, meet the minimum criteria of performance.

Considering the fact that those results have been obtained after making two different gas mixtures, it was evaluated worth to conduct a second analysis of results by keeping the points corresponding to the lowest gas mixture concentration (Maximum concentration = 17,22 µg/m3) are presented in table 3.2.

Concentration generated(µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
17,22	17,23	0,05
8,22	8,13	1,0
5,82	5,96	2,4
2,86	2,75	3,7
1,52	1,54	1,5
0,79	0,79	1,1
0,52	0,62	20

Table 3.2: gap to linearity of the analyzer Perkin Elmer according to the concentration of benzene (according to appendix A of the norm 14 662-3 when using the points obtained with the lowest concentrations)

It appears that the relative residuals of the linear regression function is superior to 5% only for the level of concentrations the lowest tested (0,52 µg/m^{3}ug/m3) and it reaches 20%. This result can be explained by the fact that the nor; requires that the linear regression function calculation be done with an equation of the type: y = ax + b and consequently for the points with the lowest concentrations, the value at the origin can have a strong impact and leads to a relatively significant relative residual with respect to the linear regression function.

3.1.3 – The results obtained by the analyzer by Chromatotec

Figure 3.2 presents the results obtained for benzene for the analyzer by Chromatotec.

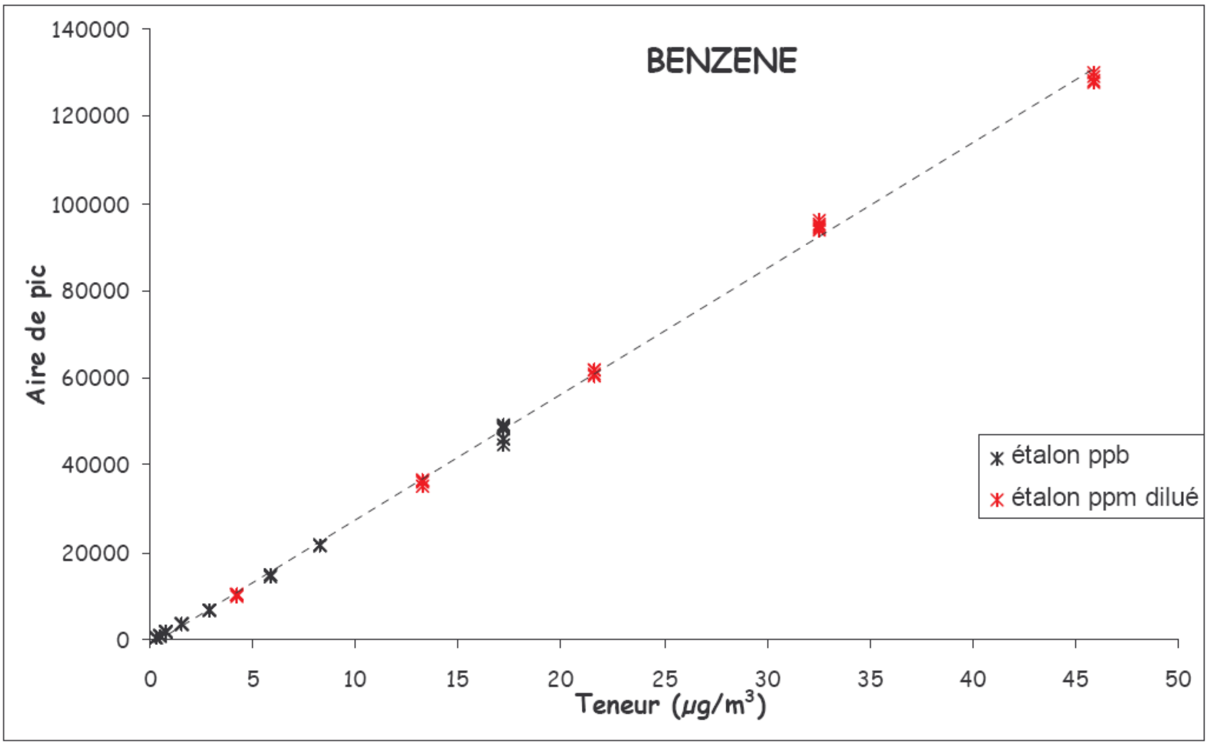

Figure 3.2: Response of the analyzer by Chromatotec according to benzene concentrations

The analysis of the results, done according to norm 14 662-3, is presented in table 3.3.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
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	1,6	**5,8**
0,52	0,69	**33**

Table 3.3: Percent difference to linearity of the analyzer Chromatotec according to benzene concentration (according to appendix A of the norm 14 662-3)

It appears thus that the 3 weaker concentrations level tested (5,82 µg/m^3, 1,52 µg/m^3, 0,52 µg/m^3), the relative residuals to the linear regression function are respectively 5,2; 5,8 and 33%. They are superior to 5% and do not meet the performance criteria of the norm 14 662-3. Nonetheless, if you consider the 5 concentration levels listed in the norm 14 662-3, which are 45, 35, 25, 15 and 5 µg/m^3, only for the concentration level lower than 5 µg/m^3, the difference to linearity remains slightly above the requirement of 5%.

As previously, a second analysis of the results was conducted, keeping only the points obtained with a low concentration gas mixture. The results obtained by analyzing data again using only the low concentrations points (Maximum concentration = 17, 22 µg/m^3) are presented in table 3.4.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
17,22	17,10	2,8
8,22	8,01	2,5
5,82	5,55	4,8
2,86	2,71	5,3
1,52	1,54	1,2
0,79	0,87	10,3
0,52	0,59	14,8

Table 3.4 – The results obtained by the analyzer VOC71M/FID Environnement SA (According to annex A of the norm 14 662-3 with only the low concentrations points)

It appears that the relative residual of the linear regression is superior to 5% for 3 concentration points:

- 2,86 µg/m^3 where the % difference to linearity is above 5% with 5,4 %

- The 2 lowest concentrations points at 0,79 and 0,52 µg/m^3 for which the difference is respectively 10,3% and 14,8%.

For the 2 lowest level, the results can be explained, as previously, by the fact that the calculation of the function of linear regression is done by an equation of the type: $y = ax + b$ and consequently for the points of lowest concentrations, the y intercept of the equation can be of great importance and lead to a large relative residual with the regression function.

3.1.4 – The results obtained by the analyzer VOC71M/FID Environnement S.A.

Figure 3.3 present the results obtained for benzene for the analyzer VOC 71M/FID Environnement SA.

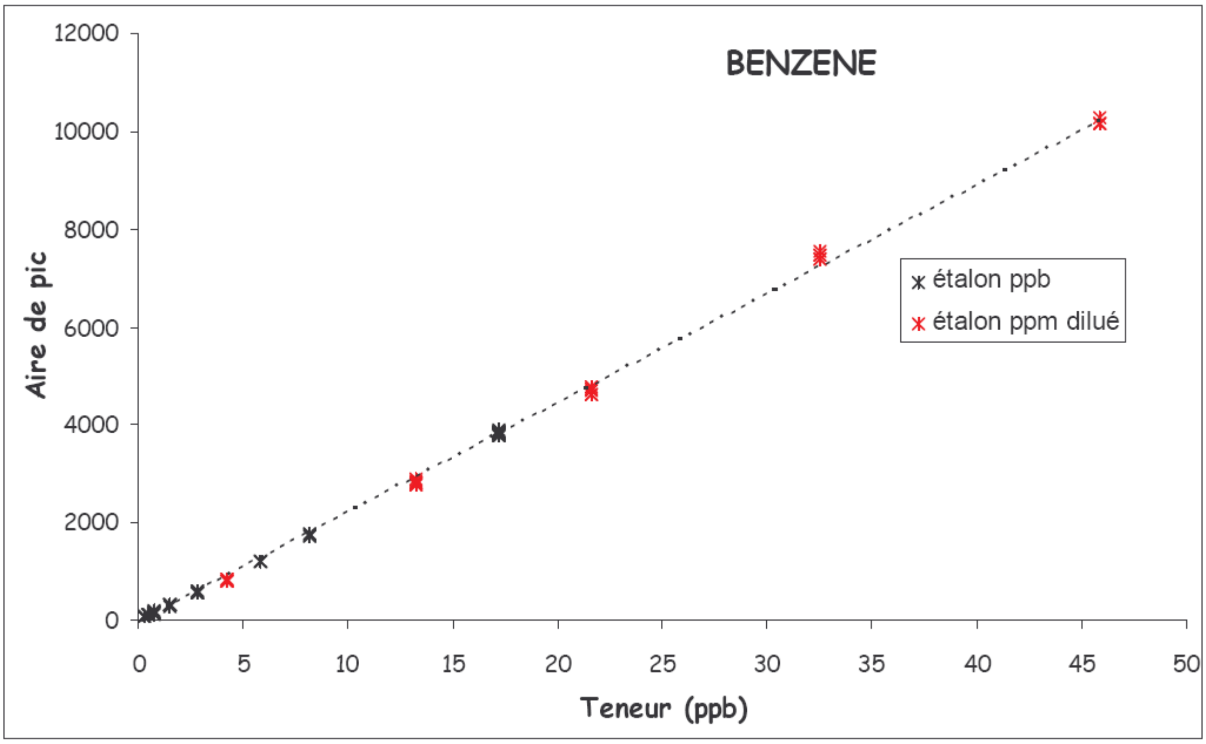

Figure 3.3.: response of the analyzer VOC 71M/FID Environnement SA according to the benzene concentration

The analysis of the results according to the norm 14 662-3 is presented in table 3.5.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
45,86	45,61	0,53
32,52	33,42	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**

Table 3.5: difference to linearity for the analyzer VOC 71M/FID by Environnement SA according to the benzene of benzene (According to appendix A of the norm 14 662-3)

It appears that for the 2 lowest concentrations levels tested, 1,52 µg/m^3 and 0,52 µg/m^3 , the relative residual of the linear regression function are respectively 6,9% and 46,5%. They are superior to 5% and do not meet the performance criteria required by the norm 14 662-3. Nonetheless, if you consider the 5 concentrations levels of the norm, that is to say, 45, 35, 25, 15 and 5 µg/m^3; for those 5 levels, the difference to linearity is below 5%.

As previously, a second analysis of the results has been done for the low concentration points. The results obtained by using the low concentration points (maximum concentration = 17,22 µg/m^3) are presented in table 3.6.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
17,22	17,42	1,2
8,22	7,96	3,1
5,82	5,50	5,6
2,86	2,72	4,8
1,52	1,50	0,88
0,79	0,83	5,3
0,52	0,63	21,9

Table 3.6: Difference to linearity for the analyzer VOC 71M/FID Environnement SA according to the concentration of benzene (according to appendix A of the norm 14 662-3 for the mixtures with low concentrations)

It appears that for the relative residuals of the linear regression function are superior to 5% for the 3 concentration points:

- 5,82 µg/m^{3}and 0,79 µg/m^3 where the difference is above 5% with respectively 5,6% and 5,3%
- The point with lowest concentration 0,52 µg/m^3 for which the difference is 21,9%.

As previously, for the lowest concentration level, the result can be explained by the fact that the norm requires the calculation of the linear regression function to be done in an equation of the type: y = ax + b and consequently for the lowest concentration points, the y intercept of this equation can be very important and have a relative residual with the linear regression function significant.

3.1.5 – The results obtained by the analyzer VOC71M/PID Environnement S.A.

The figure 3.4 presents results obtained the results obtained for benzene with the analyzer VOC 71M/PID Environnement SA.

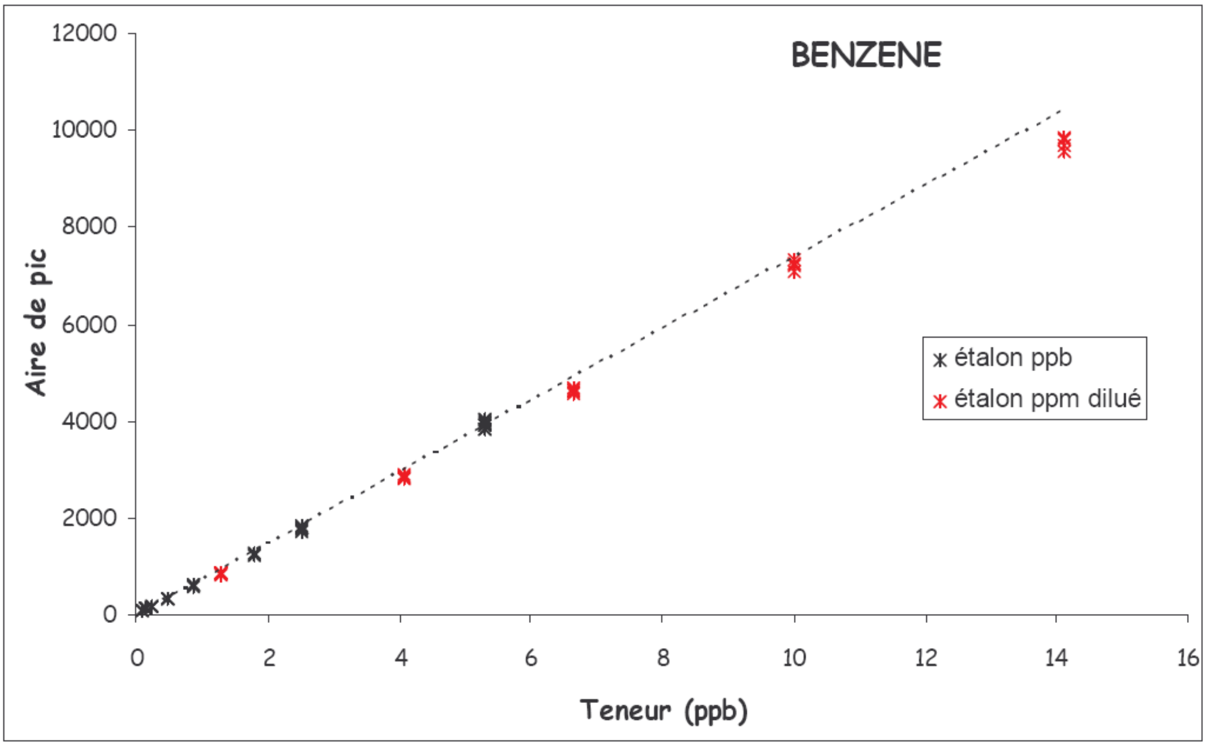

Figure 3.4: Response of the analyzer VOC 71M/PID Environnement SA according to benzene concentration

The analysis of results, according to the norm 14 662-3, is presented in table 3.7.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
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

Table 3.7: Difference to linearity for the analyzer VOC 71M/PID Environnement SA according to the concentration of benzene (according to appendix A of the norm 14 662-3)

It appears that for all concentrations levels tested, the relative residuals of the linear regression are below 5% and thus the criteria of performance of 5% of the norm 14 662-3 is met.

By concern of homogeneity with the other analyzers tested, a second analysis of the results has been done by keeping the points obtained with the lowest concentrations (Maximum concentration = 17,22 µg/m^3). The results obtained are presented in table 3.8.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
17,22	17,08	0,78
8,22	7,97	3,1
5,82	5,57	4,4
2,86	2,75	3,8
1,52	1,54	1,5
0,79	0,81	3,3
0,52	0,62	20,9

Table 3.8: Difference to linearity for the analyzer VOC 71M/PID Environnement SA according to the concentration of benzene (according to appendix A of the norm 14 662-3 for the points of the mixtures with the lowest concentrations).

It appears that the relative residual of the linear regression function is above 5% only for the point with the lowest concentration (at 0,52 µg/m^3) for which the difference to linearity is 20,9%. As discussed previously, this result can be explained by the fact that the norm requires that the calculation of the function of linear regression be done from an equation of the type: y = ax + b and consequently for the points with lowest concentrations, the y intercept has a big importance and leads to a large relative residual for the function of linear regression.

3.1.6 – The results obtained by the analyzer GC 955 Synspech/PID.

Figure 3.5 present the results obtained for benzene for the analyzer GC 955 Synspech/PID.

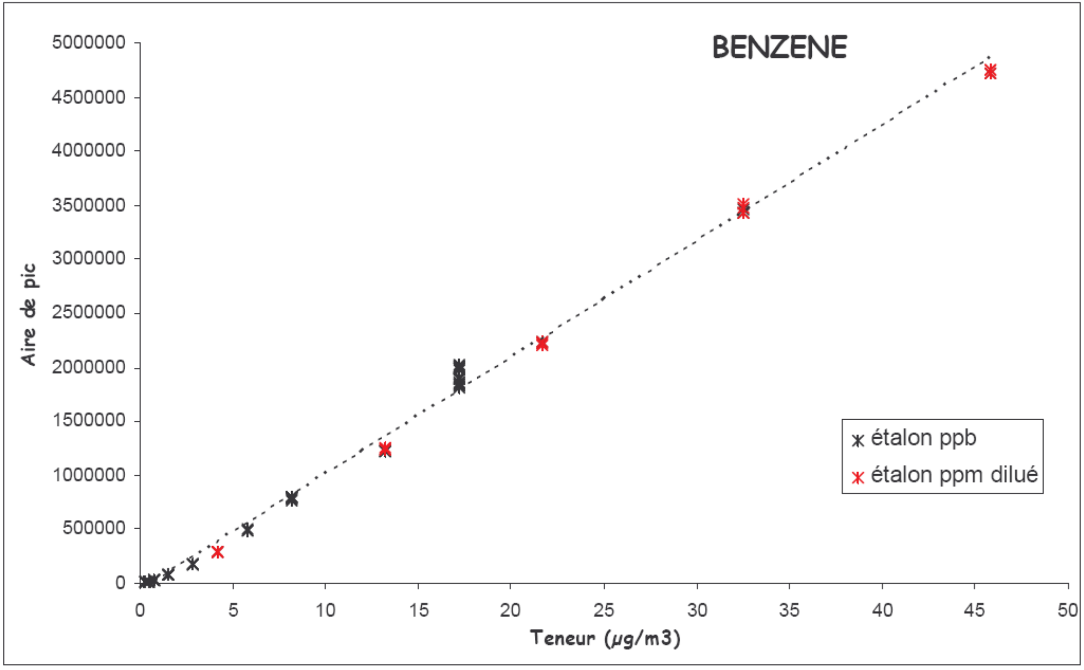

Figure 3.5.: response of the analyzer GC 955 Synspech/PID according to the benzene concentration

The analysis of results, according to the norm 14 662-3, is presented in table 3.9.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
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**

Table 3.9: Difference to linearity for the analyzer GC 955 Synspech/PID according to the concentration of benzene (according to appendix A of the norm 14 662-3)

It appears that for 4 concentrations levels out of 7 tested, the relative residuals of the linear regression function are significantly above 5% and do not meet the criteria of 5% of performance required by the norm 14 662-3. To explain this result, Figure 3.5bis presents a zoom of the responses of this analyzer according to the concentrations of benzene for the lowest concentrations. It appears clearly a large difference to linearity.

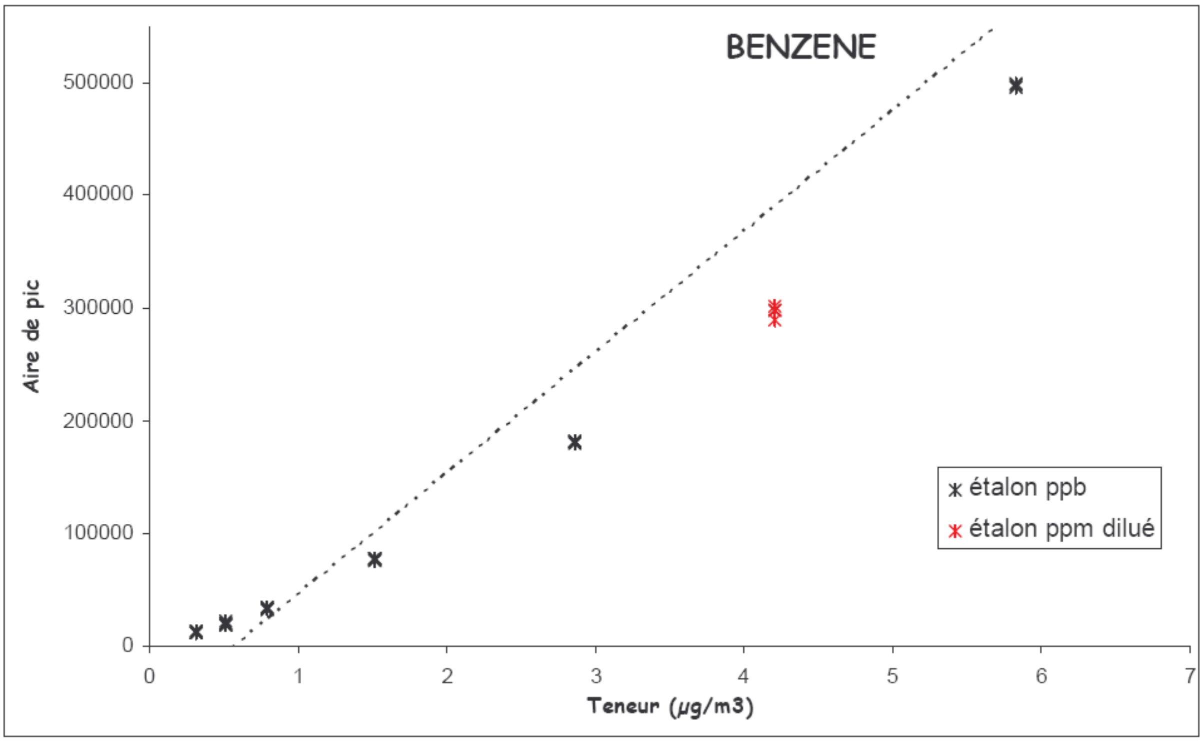

Figure 3.5bis: response of the analyzer GC 955 Synspech/PID according to the benzene concentration: ZOOM on the lowest concentrations

We notice that the curve presented in figures 3.5 and 3.5bis are the one calculated for all the points obtained during trials conducted according top the specifications of appendix A of the norm 14 662-3.

As previously, a second analysis of the results was carried out by keeping only the points obtained with the lowest gas concentration. The results obtained by analyzing the data and using only the points with lowest concentration (Maximum concentration = 17,22 µg/m^3) are presented in table 3.10. The curve of linear regression for the points with lowest concentration is presented in figure 3.6 and enables to show the difference to linearity.

Concentration generated (µg/m^3)	Concentration calculated (µg/m^3)	% difference to linearity (%)
17,22	17,38	0,96
8,22	7,57	7,8
5,82	5,03	13,58
2,86	2,29	19,9
1,52	1,38	8,4
0,79	1,01	28,6
0,52	0,89	73,0

Table 3.10: Difference to linearity for the analyzer GC955 Synspech/PID Environnement SA according to the concentration of benzene (according to appendix A of the norm 14 662-3 for the points of the mixtures with the lowest concentrations).

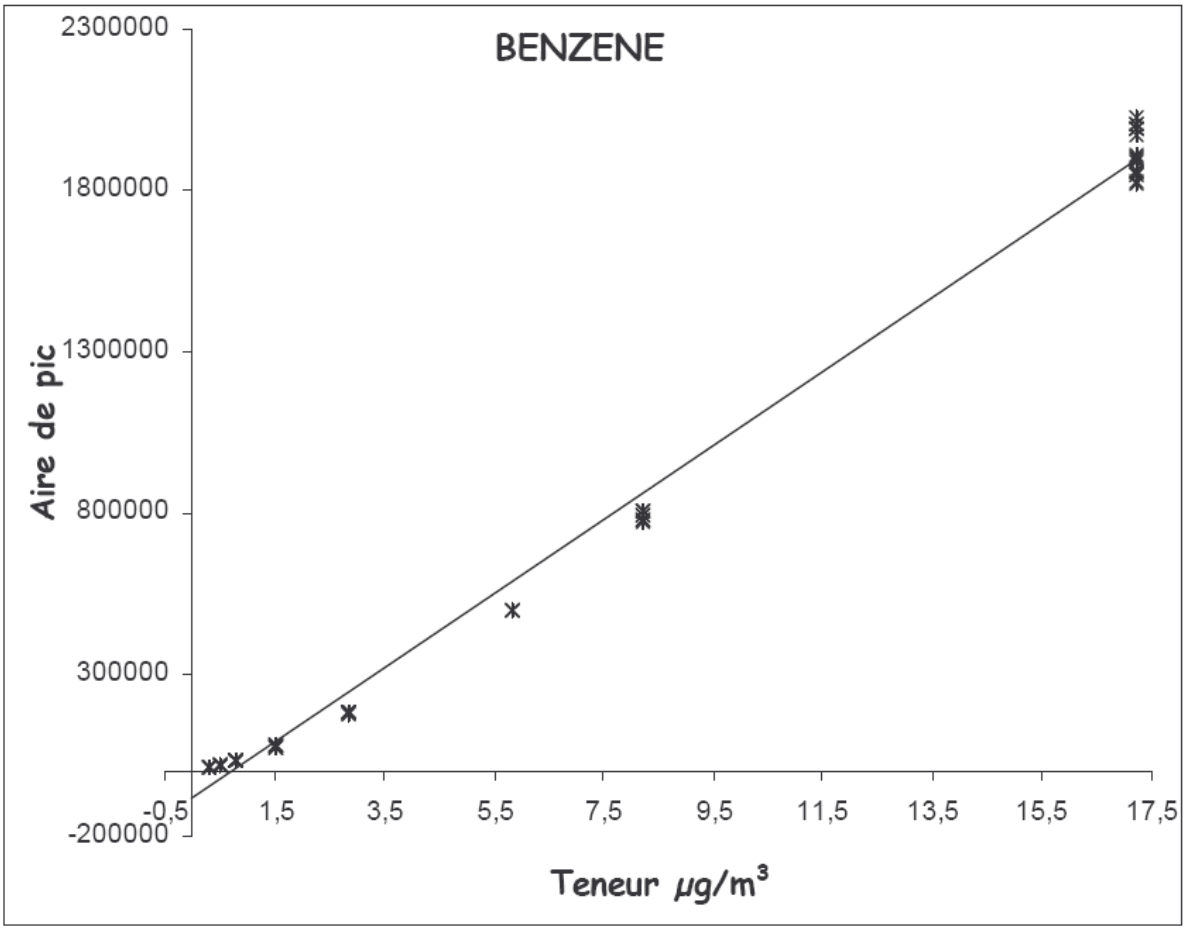

Figure 3.6: Response of the analyzer GC 955 Synspech according to the concentration of benzene (according to appendix A of the norm 14 662-3 for the points of the mixtures with the lowest concentrations).

It appears that the relative residual of the linear regression curve is above 5% for most points. Figure 3.6 shows and explains the results obtained. Concerning the results transmitted by the company Néréides (Ensuring the sales of Synspech analyzers in France), it was decided to do an "auto-linearization" of the response of the analyzer during the test period done on site. This test is presented in appendix 4.4 as well as the results obtained.

3.2 – Study of the memory effect

3.2.1 – the norm 14 662-3 and the tests performed

The norm 14 662-3 specifies: *" During the test of linearity, check the influence of the memory effect due to the retention of benzene in the measurement system because of using inappropriate materials or a large dead volume".*

The norm indicates also: "The second analysis of zero air, which follows immediately the highest concentration of benzene corresponding to 10% of the limit value (= 0,5 µg/m^3).

NOTE: It is correct that the first value of the measurements of zero air be below 20% of the limit value (=1 µg/m^3). Due to the sampling procedure, it is impossible to determine precisely the response time; according to definitions, the response time should be at least the cycle of the analysis. Consequently, the first analysis following a sudden change of concentration should not be taken into account. The evaluation of this test indicates only the capacity of the measurement system".

The analyzers must meet the requirement specified in table 2. In this case, the contribution of the uncertainty is considered as very small".

The tests are in compliance with the norm of analysis of wet zero air following the points with highest concentration (about 45 µg/m^3). All the analyzers have been calibrated in a similar way according to what is done at the AASQA (Calibration at 1 concentration point) and with a calibration mixture with a concentration of 5,298 ppb close to the concentration recommended in the "guidebook of recommendations concerning the measurement of benzene in ambient air[1]".

To be noticed that during the inter-comparison tests organized at ERLAP (European Reference Laboratory of Air Pollution) in Ispra from October 10th to 14th, 2005[2], the memory effect was not tested as described in the norm 14 662-3. As a matter of fact, in this norm, it is indicated that the memory effect is tested by the analysis of zero air just after the analysis of the highest concentration of benzene necessary for the linearity test. In fact during the inter-comparison tests, the test was not conducted during the highest level of benzene concentration (Which is about 30 µg/m^3), but after the lowest concentration of benzene (Which is about 0,5 µg/m^3). The results obtained then for each analyzer tested (VOC 71M/PID Envt SA and GC 855 Synstech) have shown that in theses conditions no memory effect was present.

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[1] Report LCSQA 2007. Measurement of benzene 2/3: Project of guideline recommendations concerning the measurement of benzene in ambient air – November 2007

[2] Report LCSQA/EMD 2005. Surveillance of benzene and VOC – November 2005

The results for all the analyzers are presented below.

3.2.2 – the results obtained during the memory effect study.

The table 3.11 has all the results obtained.

Analyzer	Concentrations (µg/m^3)			
	Injection standard Tube 2	Air Zero 1 Tube 1	Air Zero Tube 2	Air Zero 3 Tube 3
Perkin Elmer	45,9	2,32	0,45	0,25
Chromatotec	45,9	1,17	0,27	0,15
VOC 71M/FID Envt SA	45,9	2,01	**1,02**	0,41
VOC 71M/FID Envt SA	45,9	1,57	**0,88**	0,39
GC 955 Synspech	45,9	0,21	0,08	0,05

Table 3.11: Study of the memory effect (according to norm 14 662-3)

Considering the results obtained, it is possible to see that the analyzers by Perkin Elmer, Chromatotec and Synspech measure, during a second analysis of zero air immediately following the analysis of the highest concentration of benzene, concentrations of benzene below 0,5 µg/m^3 and meet the requirement of the norm. For the analyzers VOC 71M Environnement SA FID and PID, the concentrations measured during a second analysis of zero air, are respectively 1,02 µg/m^3 and 0,88 µg/m^3 and thus do not meet the requirement of the norm. This result can be explained by the fact that the analyzers by Environnement SA are equipped with two pre-concentration tubes and consequently the second analysis of zero air is like a first analysis on one of the pre-concentration tubes following the highest concentration in benzene.

3.3 – Study of the repeatability

3.3.1 – The norm 14 662-3 and the tests performed

The norm 14 662-3 specifies : " *Calculate the standard deviation of 10 measurements successive at the limit value, and at approximately 1/10 of the limit value, according to the given equation. This standard deviation is written* $s_r(c)$"

The norm says also: "*calculate the repeatability* (r_i) *according to the formula* $r_i = t_{n-1;\,0,05} \times s_i$ *where si is the standard deviation of repeatability and* $t_{n-1;\,0,05}$ *is the coefficient of Student bilateral with a confidence level of 0,05 with n-1 degree (for n= 10,* $t_{9;0,05} = 2,262$*).*

r_i *must meet the criteria of performance which is <0,3 µg/m3 for the repeatability at 0,5 µg/m3 and <+/-5% for the repeatability at the limit value*".

The tests have been carried out according to the norm with 10 analyses with gas standard mixture at the 2 concentrations indicated.

3.3.2 – Repeatability at the limit value

The table 3.12 collects the results obtained by all the analyzers at a concentration level near the limit value of 5 µg/m^3.

Analyzer	Concentrations evaluated ~ 5 µg/m^3	
	Standard deviation with 10 measurements: s_r (5 µg/m^3)	Repeatability $r_{5\ \mu g/m3}=s_{5\ \mu g/m3}$x 2,262 µg/m^3
Perkin Elmer	2,0 %	4,57%
Chromatotec	1,4 %	3,06%
VOC 71M/FID Envt SA	1,1 %	2,38%
VOC 71M/FID Envt SA	0,77 %	1,74%
GC 955 Synspech	0,92 %	2,08%

Table 3.12: repeatability at the limit value (according to norm 14 662-3)

According to the results obtained, it is possible to see that for all the analyzers, the repeatability ($r_{5\ \mu g/m3}$) is below 5% and thus all the analyzers meet the requirement of the norm.

3.3.3 – Repeatability at 0,5 µg/m^3

The table 3.13 puts together the results obtained for all the analyzers at a concentration level of about 0,5 µg/m^3.

Analyzer	Concentrations evaluated ~ 0,5 µg/m^3	
	Standard deviation with 10 measurements: s_r (0,5 µg/m^3)	Repeatability $r_{0,5\ \mu g/m3}=s_{0,5\ \mu g/m3}$x 2,262 µg/m^3
Perkin Elmer	0,034 µg/m^3	0,08 µg/m^3
Chromatotec	0,011 µg/m^3	0,02 µg/m^3
VOC 71M/FID Envt SA	0,028 µg/m^3	0,06 µg/m^3
VOC 71M/FID Envt SA	0,009 µg/m^3	0,02 µg/m^3
GC 955 Synspech	0,007 µg/m^3	0,02 µg/m^3

Table 3.13: repeatability at 0,5 µg/m^3 (according to norm 14 662-3)

Considering the results obtained, it is possible to see that for all the analyzers, the repeatability is significantly lower than 0,3 µg/m^3 since it does not go beyond 0,1 µg/m^3 for each analyzer. Consequently, all the analyzers meet the criteria of the norm.

3.4 – Study of interferences of VOC

3.4.1 – The norm 14 662-3 and the tests performed

The norm 14 662-3 specifies: *“The interfering species possible with organic compounds must be determined by a gas mixture made up of the following organic compounds:*

- *Methylcyclopentane*
- *2,2,3-trimethylbutane*
- *2,4 dimethylpentane*
- *tetrachloromethane*
- *cyclohexane*
- *2,3-dimethylpentane*
- *2-methylhexane*
- *3-ethylpentane*
- *trichloroethylene*
- *n-heptane*

at concentrations known of approximately $3\ \mu g/m^3$*-*$10\ \mu g/m^3$ *for each compound”.*

The norm indicates also: *“the influence* b_{org} *is calculated with the following equation:* $b_{C_{org}} = \frac{\left|\overline{C_{org}} - \overline{C}\right|}{\overline{C}}$ *with* $\overline{C_{org}}$ *, the average of the single measurements in presence of the gas mixture chosen and* $\overline{C}$ *the average of the individual concentrations measured without any interference”.*

The trials have not been carried out strictly according to the specifications of the norm 14 662-3. First of all, a qualitative analysis of the potential interfering species of the benzene has been done by adding one by one the interfering species specified by the norm and then by positioning them on the chromatogram obtained in order to show a potential co-elution with benzene. Then, several analysis of the standard gas mixture containing the BTEX mixture (with a concentration of $5\ \mu g/m^3$ for benzene) have been done and then all the components which are potential interfering species have been added simultaneously to the gas mixture; the response of the analyzer has been recorded in order to evaluate quantitatively the importance of interfering species due to the addition of the potential organic compounds interfering species.

3.4.2 – Qualitative study of interfering species due to organic compounds.

3.4.2.1 – Results obtained with the analyzer Perkin Elmer

Figure 3.7 shows the chromatogram obtained at retention times near benzene with the analyzer by Perkin Elmer.

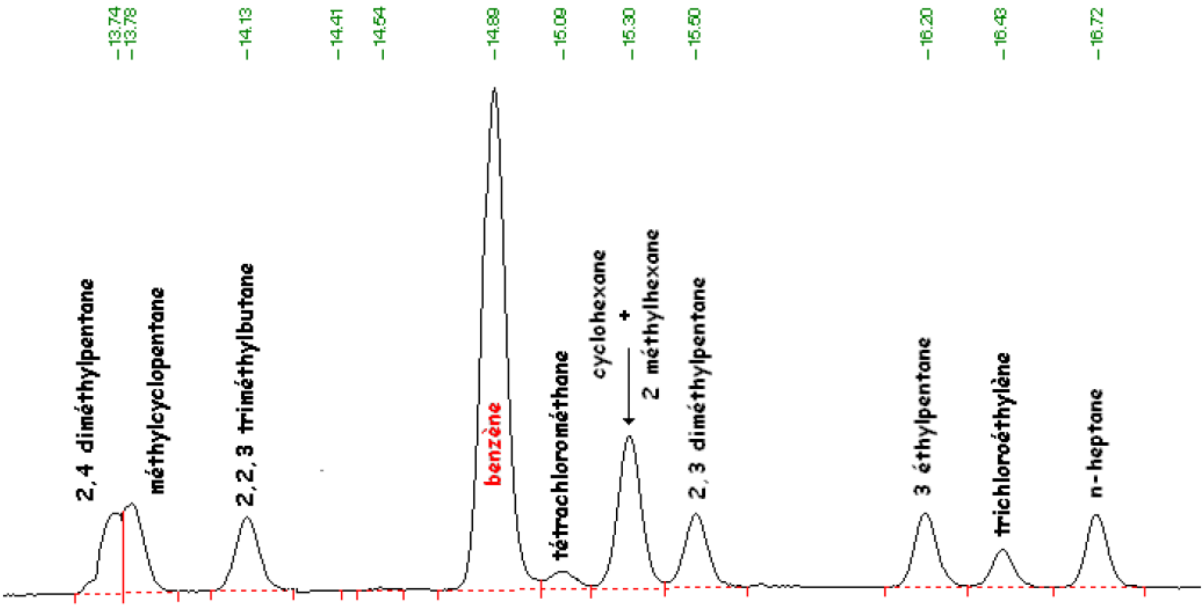

Figure 3.7: Chromatograms of organic compounds which are potential interfering species with benzene on the analyzer by Perkin Elmer.

The chromatogram shows that no VOC tested interferes with benzene.

3.4.2.2 – Results obtained with the analyzer Chromatotec

Figure 3.8 shows the chromatogram obtained at retention times near benzene with the analyzer by Chromatotec.

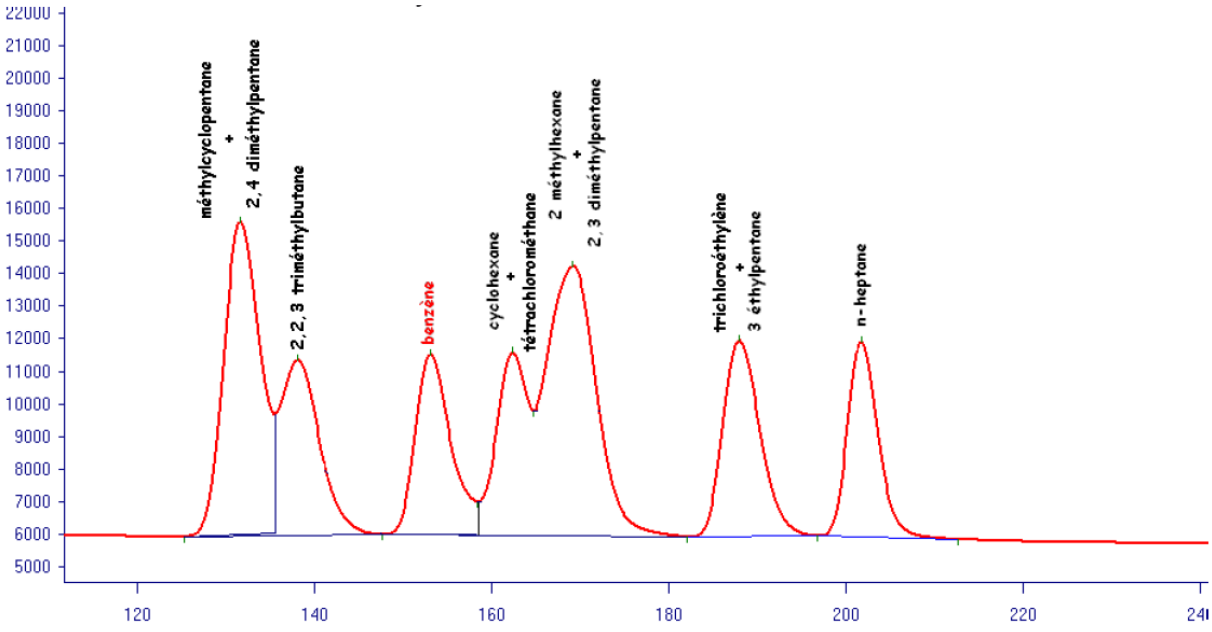

Figure 3.8: Chromatograms of organic compounds which are potential interfering species with benzene on the analyzer by Chromatotec.

The chromatogram shows that no VOC tested interferes with benzene.

3.4.2.3 – Results obtained with the analyzer VOC 71M/FID Environnement SA

Figure 3.9 presents the chromatogram obtained at retention times near benzene with the analyzer VOC 71M/FID Environnement SA.

The chromatogram shows that 3-ethylpentane co-elutes with benzene. Considering the fact that the FID is not a specific detector (On the contrary with FID), but responds globally to a mole of carbons, then we can think that with a concentration in 3-ethylpentane (with 7 carbon atoms) equivalent to that of benzene in the air analyzed, then a very sensitive over-evaluation of benzene will be obtained.

Furthermore, considering the work done at site (See 4), other organic compounds than those listed in norm 14 662-3 have been tested. This has shown that isooctane also co-elutes with benzene. Considering the fact that this compound has 8 carbon atoms, the same remark can be done that the response will be proportional to benzene at a similar concentration.

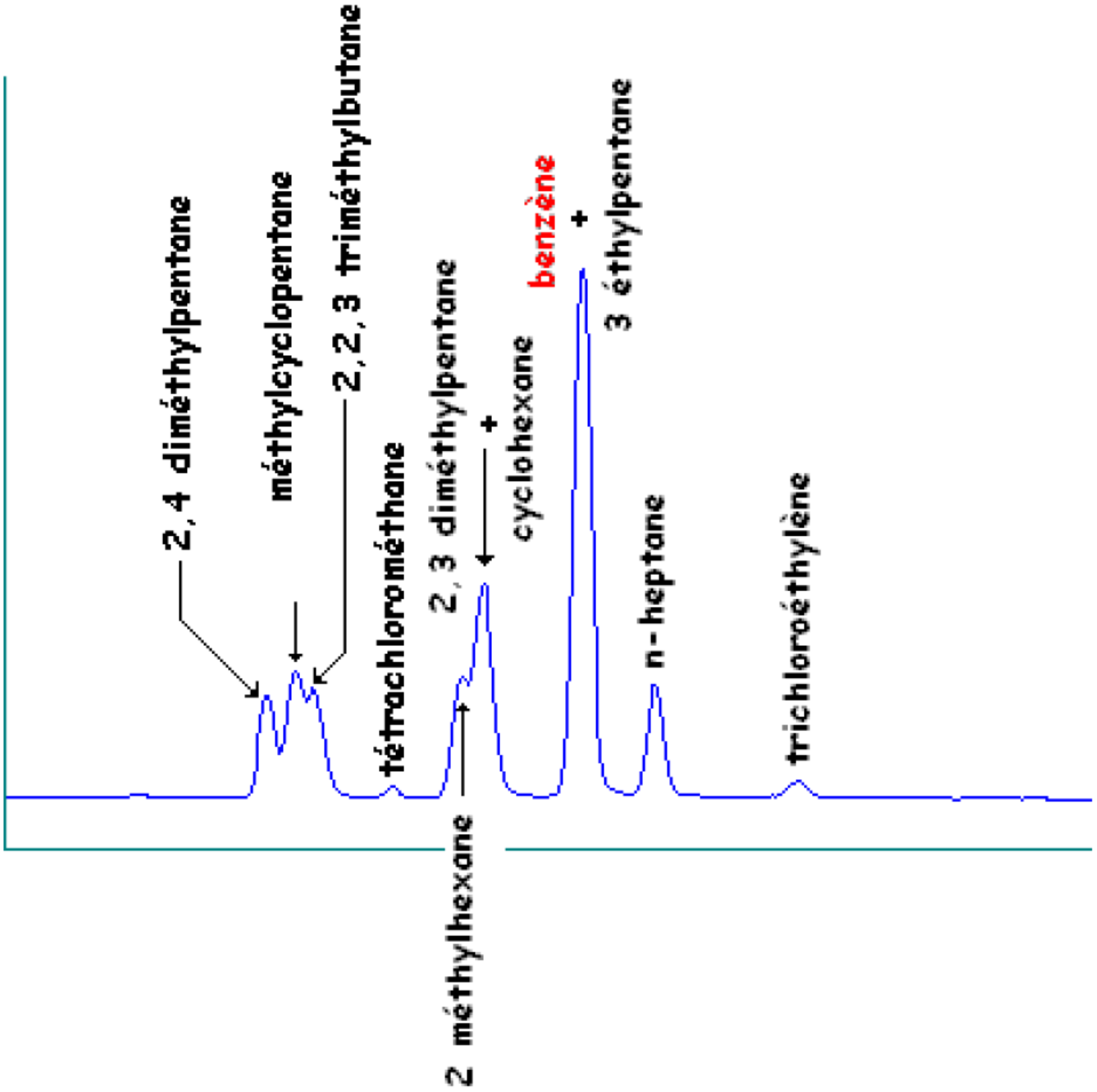

Figure 3.9: Chromatograms of organic compounds potentially interfering with benzene with the analyzer VOC 71M/FID by Environnement SA.

3.4.2.4 – Results obtained with the analyzer VOC 71M/PID Environnement SA

Figure 3.10 presents the chromatogram obtained at retention times near benzene with the analyzer VOC 71M/PID by Environnement SA.

The chromatogram shows that 3-Ethylpentane also co-elutes with benzene (Which is logical considering that the same column is installed on this analyzer and that the detection is done by FID or PID). Considering the fact that the PID is a more specific detector than the PID, we can think that if the concentration of 3-Ethylpentane is equivalent to that of benzene present in the air analyzed, then an over-evaluation of the concentration of benzene will be obtained, but this will be less significant than with the FID detector.

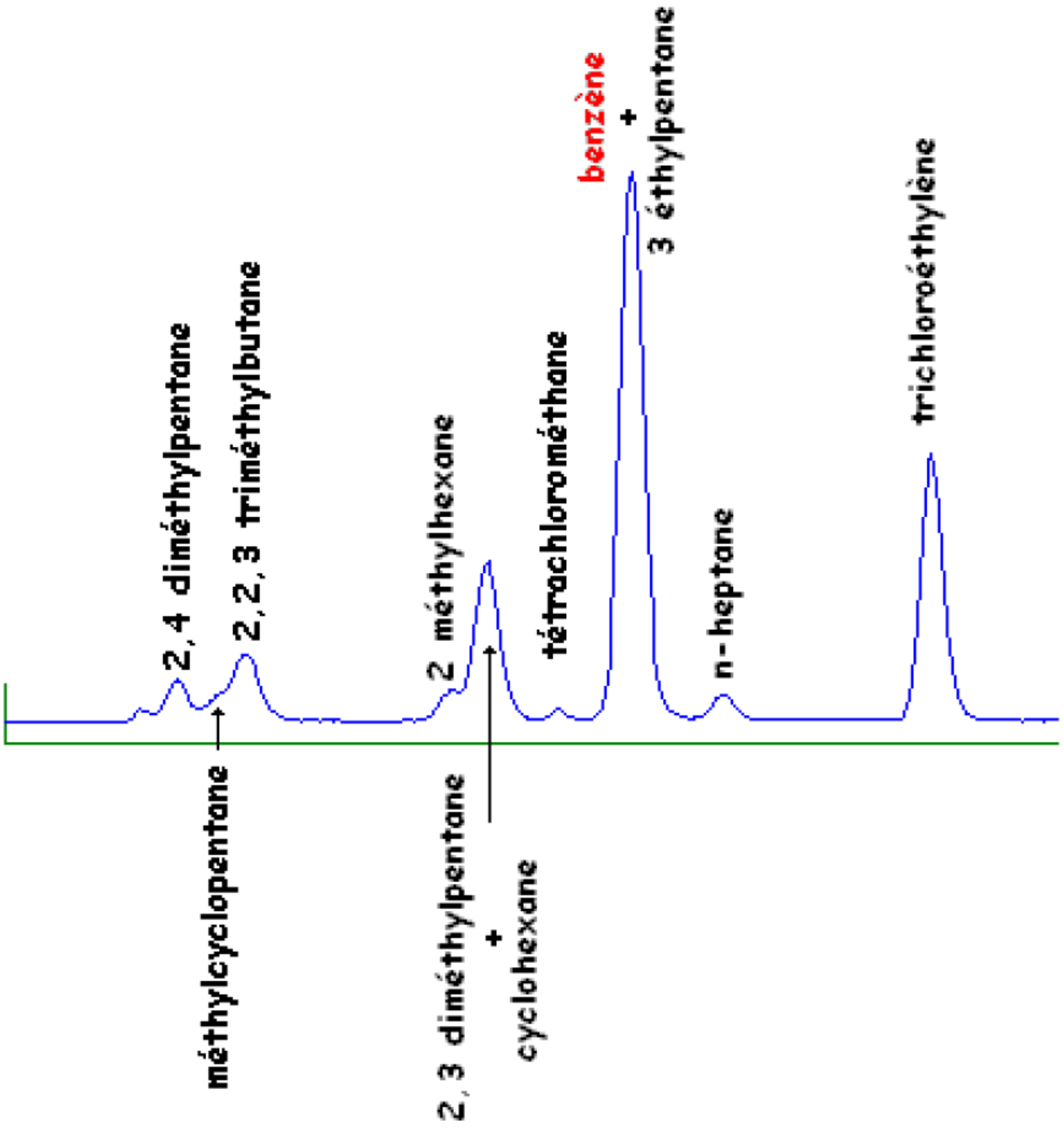

Figure 3.10: Chromatograms of organic compounds potentially interfering with benzene with the analyzer VOC 71M/PID by Environnement SA.

Following the tests carried out on the FID detector of this analyzer, other organic compounds than those specified by the norm 14 662-3 have also been tested (3-methylhexane, isooctane, 2,2,4-trimethyl-1-pentene, methylcycloheaxane). It has been shown that isooctane co-elutes with benzene. Considering the specificity of the PID detector compared to the FID detector, the same remark can be done as previously concerning the response of this compound by comparison to that of benzene.

3.4.2.5 – Results obtained with the analyzer GC 955 Synspech/PID

Figure 3.11 shows the chromatogram obtained at retention times near benzene with the analyzer GC 955 by Synspech.

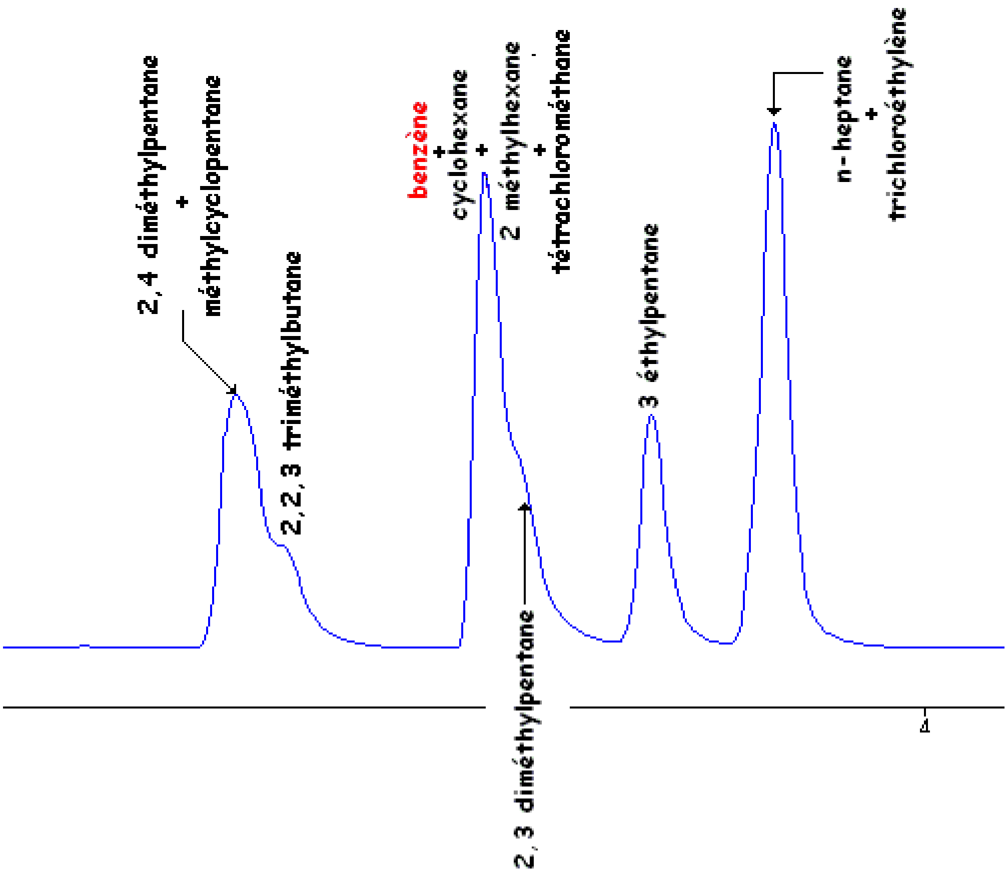

Figure 3.11: Chromatograms of organic compounds potentially interfering with benzene with the analyzer GC 955 by Synspech.

The chromatogram shows co-elution of cyclohexane, 2-methylhexane and tetrachloromethane as well as a partial separation of 2,3-dimethylpentane with benzene.

Notice that the analyzer is equipped with a PID detector and that consequently the response of hydrocarbons is lower than that of aromatic compounds with this detector.

3.4.3 – Quantitative study of interferences due to organic compounds

As indicated previously, following the qualitative study due to organic compounds, a semi-quantitative study was done by making several gas standard mixtures containing BTEX (with a concentration of about 5 µg/m^3 in benzene) and by then comparing the response obtained for benzene to that given by the analyzer if all the 8 potential interferents listed in the norm 14 662-3 are added with a concentration of about 5 µg/m^{3}are added at a concentration of about 5 µg/m^3 for each compound.

The results obtained are presented in figure 3.12.

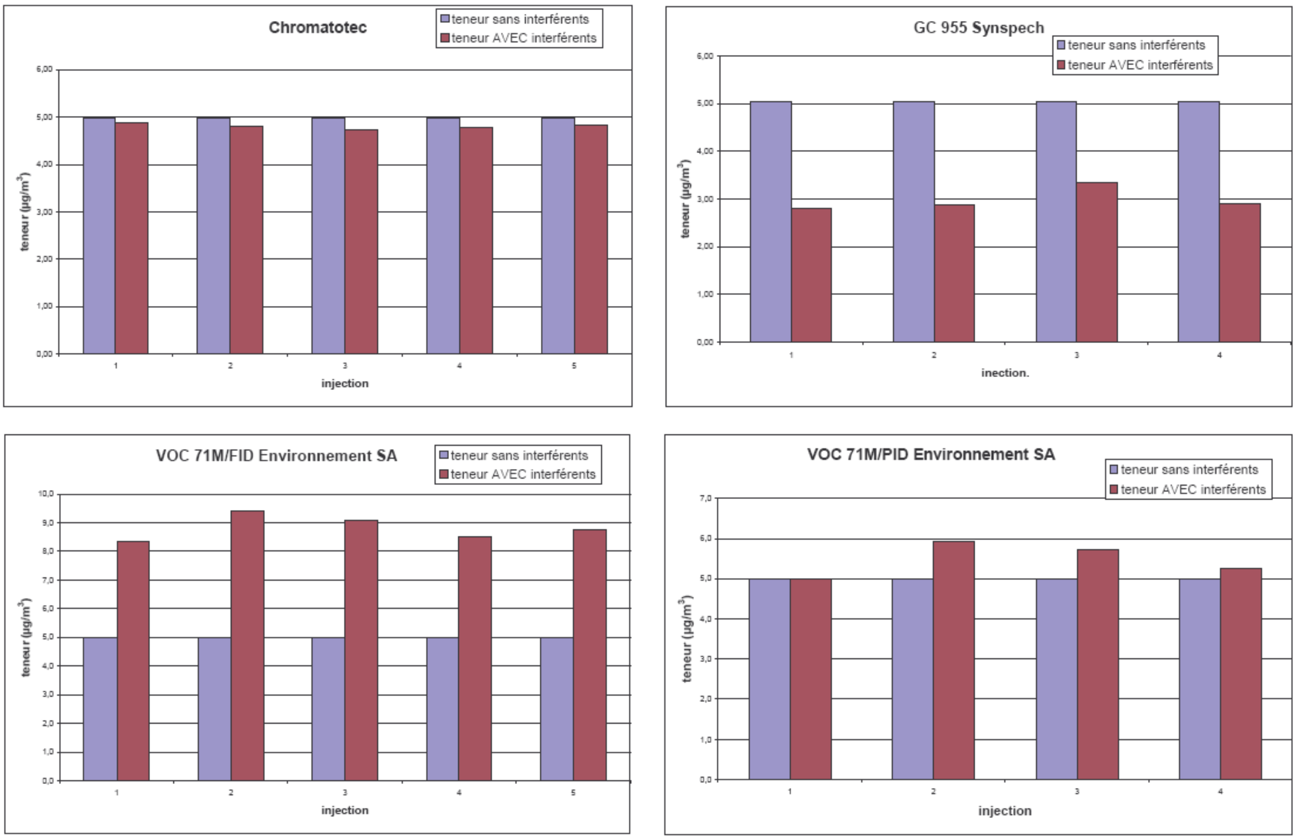

Figure 3.12: Influence on the concentration of benzene of the addition of organic compounds potentially interfering species at a value of 5 µg/m^3.

This figure shows that all the results obtained match the initial observations made during the qualitative analysis of interfering species due to VOC compounds.

As a matter of fact, for the analyzer by Chromatotec, due to the fact that none of the compounds listed in the norm 14 662-3 co-elutes with benzene, the response of the analyzer changes very slightly with or without interfering species (The variation of the response is due to the repeatability of the analyzer and to the method of preparation of the VOC interfering species generated).

For the analyzer by Environnement SA, the variation of the response is about 100% for the analyzer equipped with a FID detector and remains at about 10% for the analyzer equipped with a PID. Notice that this type of test has been carried out with an anlyzer VOC 71M/PID Environnement SA (But with a previous version) during the inter-comparison test done at Ispra[3]. Comparable results have been obtained with an influence b_{org} quantified at a maximum of 7,1% for a level of concentration in benzene of about 3 µg/m^{3}and for a high level of interfering species and limited to 2,4% for a level of concentration in benzene of about 5 µg/m^3.

For the analyzer by Synspech, the response is very under-evaluated during the addition of organic interfering species, the under-evaluation is about 40%. This under-evaluation is explained that one of the interfering species is tetra-chloromethane which is very electronegative and thus, which takes the electrons of the benzene in the PID lamp which causes a decrease of the current collected at the detector. Just like with the analyzer VOC 71M/PID by Environnement SA, this type of test has been carried out with an analyzer GC 855 Syntech (The previous version of the GC 955 tested here) during the inter-comparison tests done at Ispra[4]. Comparable results have been obtained with the comparable observation of a strong under-evaluation of the response of the analyzer with benzene in the presence of interfering species, the influence b_{org} quantified at a maximum of 73,7 % for a level of concentration of benzene of the magnitude of 10 µg/m^3 and for a strong level of interfering species and at 59,4% for a level of concentration of benzene of about 5 µg/m^3.

3.5 – Detection limit

3.5.1 – The norm 14 662-3 and the tests performed

The norm 14 662-3 (§ 9.3.6) specifies: “ The limit of detection is determined with 10 analysis at a nominal value of about 0,1 x limit value (=5 µg/m^3) and is calculated in the following manner: L = ($t_{n-1;\,0,95}$ x $s_{x0,5}$)/B where $s_{x0,5}$ is the standard deviation for 5 µg/m^3, B is the slope of the calibration function and $t_{n-1;\,0,95}$ x $s_{x0,5}$ is the Student coefficient for a bilateral confidence level at 95%.

The tests have been done according to the norm with 10 analysis with a gas standard mixture and, for the automatic analyzers of BTEX, 2 levels of concentration different have been tested in order to ensure the coherence of the results. It has been thought interesting to compare the detection limits obtained with the repeatability of the measurement at low concentrations of the standard gas mixture at the limits of detection of the graphics (LD corresponds to a concentration for which Signal >3 x noise).

3.5.2 – The results obtained when determining the limits of detection

The table 3.14 has all the results obtained.

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[3] Report LCSQA/EMD 2005. Surveillance of benzene and VOC – November 2005

[4] Report LCSQA/EMD 2005. Surveillance of benzene and VOC – November 2005

Analyzer	Limits of detection (µg/m^3)		
	With 10 gas analysis of a gas at conc. inj. About 0,5 µg/m^3	With 10 gas analysis of a gas at conc. inj. about 0,25 µg/m^3	With ratio S/B>=3
Perkin Elmer	0,070[5]		0,22
Chromatotec (fine peaks)	0,013	0,027	0,03
VOC 71M/FID Envt SA (Wide peaks)	0,054	0,031	0,22
VOC 71M/PID Envt SA (Fine peaks)	0,015	0,024	0,17
GC 955 Synspech (Very fine peaks)	0,020	0,021	0,015

Table 3.14: limits of detection

Considering the results obtained, it is possible to see that for all the analyzers, the limits of detection established with measurement repeatability do not exceed 0,1 µg/m^3 and that for all the automatic BTEX analyzers, they do not exceed 0,05 µg/m^3. The limits of detection established with the ratio signal/noise are usually slightly above that obtained thanks to the graphics method except for the analyzer by Synspech for which there is good coherence.

4 – MEASUREMENT IN PARALLEL OF AUTOMATIC ANALYSERS ON SITE

The trials on site had an objective to compare the behaviours and results of 5 analyzers tested in real conditions of usage by the AASQA, but their goal was not to determine the characteristics of performance during trials on site as described in the norm 14 662-3 because those are heavy to carry out. As a matter of fact, the norm 14 662-3 specifies *"during the tests on sit, the availability, the maintenance intervals, the reproducibility and the long term drift of the analyzers should be tested for a 3 months period. Two analyzers must be put in parallel and have a common sampling in a measurement station chosen for its particular conditions of ambient air".*

The tests have been done on a site near traffic of the AASQA AIRPARIF located near "porte d'Auteuil" on the Parisian loop.

The analyzers have been placed on site on May 10th 2007 and remained in place until June 19th 2007. As a result, 5 weeks of data on parallel measurements with five analyzers have been collected.

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[5] The limit of detection which is superior to what is normally obtained with Perkin Elmer (0,04 g/m3) is due to the fact that the analyzer was not used in its optimal configuration, but was utilized in a configuration which enables to work with a frequency of sampling of 30 minutes.

The five analyzers have been connected to the same sampling line equipped with a 5 µm stainless steel sampling stick and that they are all calibrated simultaneously with the same standard gas mixture containing BTEX and at a concentration in benzene of 5,019 ppb (Which is 16,31 µg/m^3). The concentrations of the other compounds are specified in table 4.1. It is necessary to change the standard gas mixture during the trials carried out during the technical reception of the automatic analyzers at the laboratory and for the trials on site.

Compounds	Nominal concentrations (ppb)	Certified concentrations by LNE(ppb)
Benzene	5,00	5,019
Toluene	10,00	10,139
Ethylbenzene	5,00	
Para+meta-xylene	5,00	
Ortho-xylene	5,00	4,767

Table 4.1: composition of a standard gas mixture used during the campaign on site

4.4 – Long term drift at the point of scale

4.1.1 The norm 14 662-3 and the tests performed

The norm 14 662-3 specifies: “*Evaluate the long term drift with the average of 4 independents measurements at the concentration of the point of scale, thanks to different measurement done at intervals of 2 weeks.*

Calculate the long term drift at the level of the point of scale the following way:

$$d_{14d} = \frac{\left|\overline{C_n} - \overline{C_{n-1}}\right|}{\overline{C_n}} \times 100\%$$

where d_{14d} *is the drift in concentration at the point of scale,* $\overline{C_n}$ *is the average of the 4 analysis at the beginning of the drift period,* $\overline{C_{n-1}}$ *is the average of the 4 analysis at the end of the drift period (14 days)”.*

The norm says also:” *the biggest value obtained during the trial period must meet the criteria of performance of 10%”.*

Considering that the trial period on site is short (less than 2 months), the follow up of the response of all the analyzers has been done on all the period during which the trials were conducted (technical reception of the analyzers in the laboratory and trials on site).

4.1.2 Long term drift of the automatic analyzers

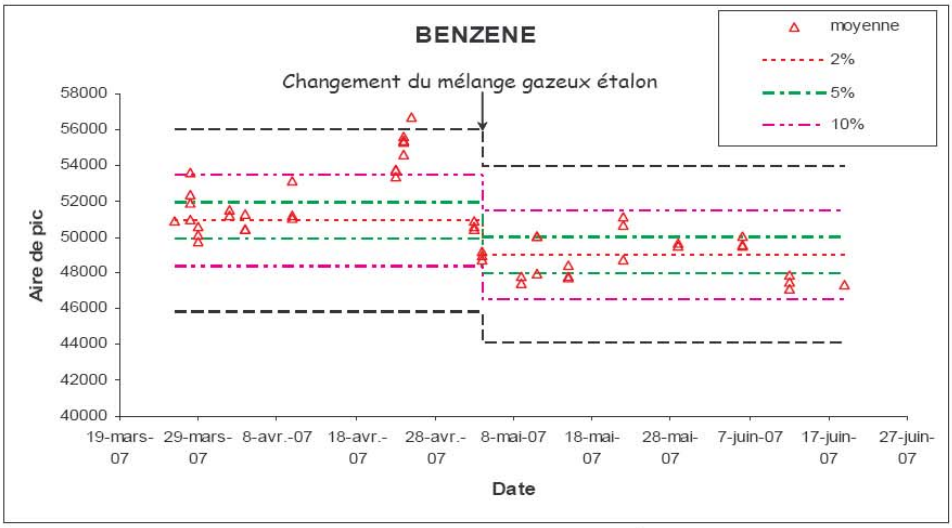
Figure 4.1 presents the follow-up of responses of the various analyzers with the area of the chromatogram peaks along the time during various analyses of the gas standard mixtures.

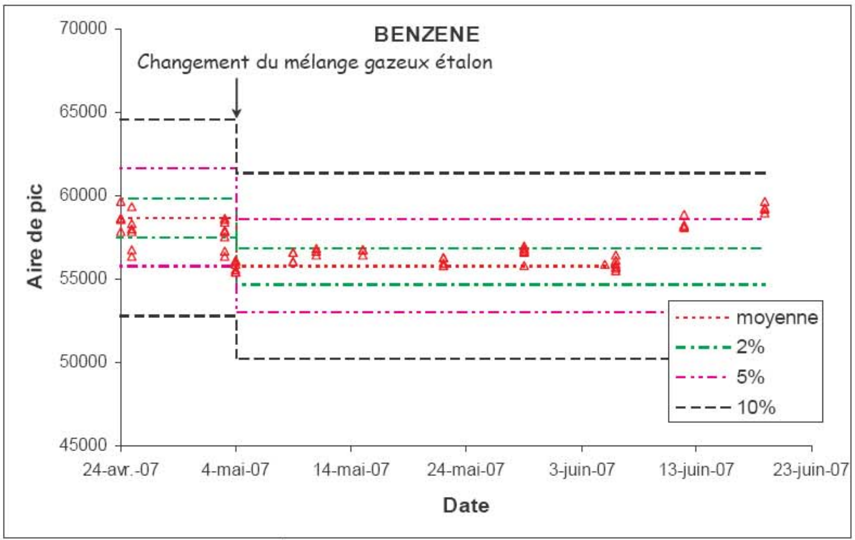
The long term drift of all the analyzers has been established in the period March 26th till June 19th with the exception of the analyzer by Chromatotec for which the drift was done from April 24th till June 19th.

For all the analyzers equipped with an FID detector, which are the analyzers Perkin Elmer, Chromatotec and VOC 71M Environnement SA/FID, we notice that the responses of the detectors are very stable in time.

On the other hand, concerning the two analyzers equipped with PID detectors which are the analyzers VOC 71M Environnement SA/PID and GC 955 Synspech, a long term drift is observed with the decrease of the size of the peaks recorded for the standard gas mixture. This drift of the response of the PID detector remains, all along the follow-up period, inferior to the performance criteria of 10% for the analyzer VOC 71M Environnement SA/PID; it is much more variable according to the period chosen for the analyzer by Synspech and can be sometimes beyond the performance criteria of 10%. Nonetheless, it can be observed that if a regular calibration is done (maximum interval of two weeks between calibrations), then this drift remains acceptable considering the requirements of the norm 14 662-3.

Analyseur
Perkin
Elmer





Analyseur
VOC 71M
Environnement SA
FID

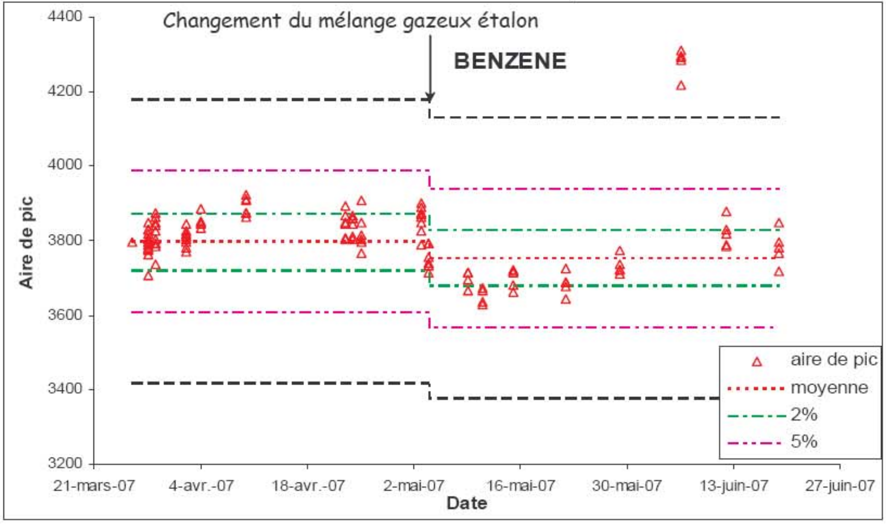
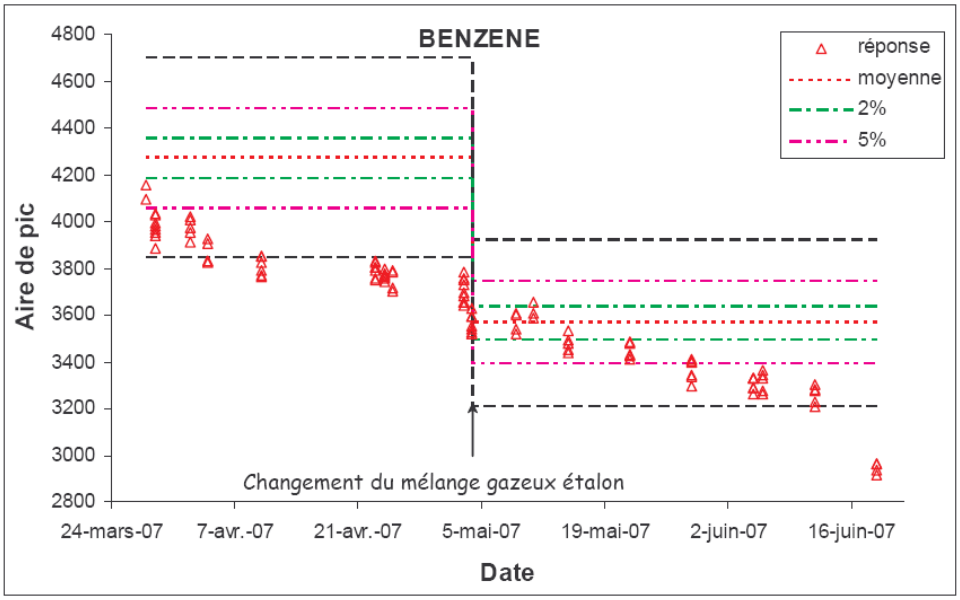


Figure 4.1: Follow up of the response of the analyzers in the long term with the area of the benzene peak = f(date of the analysis of the standard gas mixture)



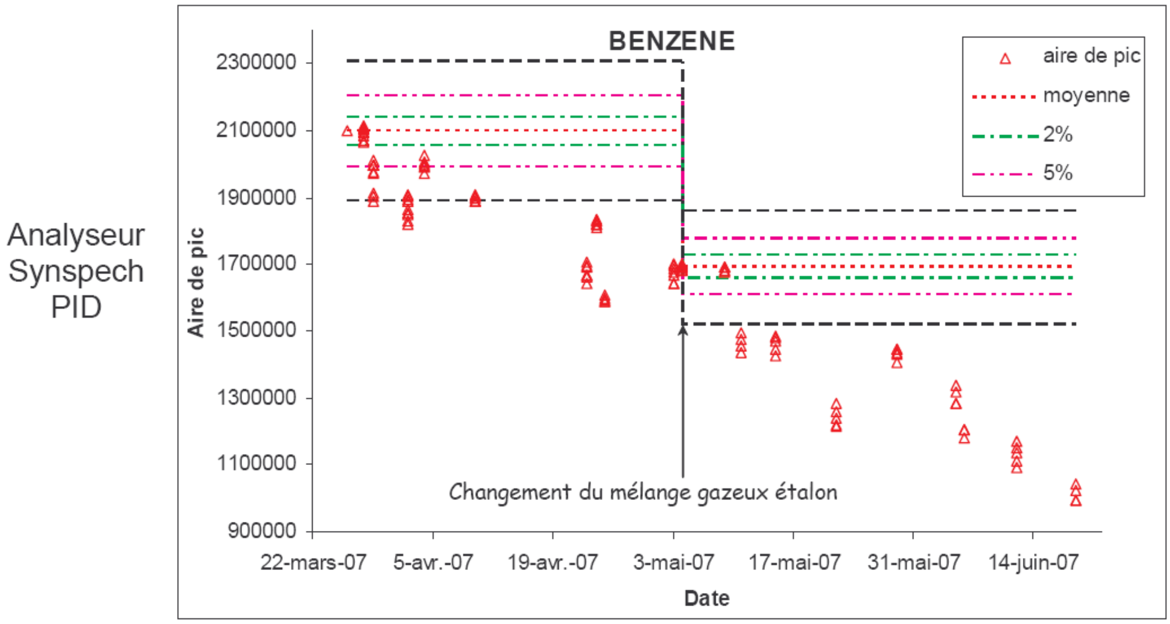


Figure 4.1bis: Follow up of the response of the analyzers in the long term with the area of the benzene peak = f (date of the analysis of the standard gas mixture)

4.2 – Time evolutions of the concentrations

Figure 4.2 presents an extract of the curves of time evolution of the concentrations of benzene measured with 5 analyzers in parallel on the site “Porte d’Auteuil” from Sunday, May 20th till Monday, May 28th 2007. You notice a homogeneous time dynamics of the analyzers with overall two daily peaks corresponding to 2 period of traffic at rush hours.

A zoom is presented in figure 4.3. It shows clearly significant differences in the level of benzene measured.

In fact, we can notice that the analyzer GC 955 by Synspech under-estimates significantly the values of benzene comparatively to the other analyzers. On the opposite, the analyzer VOC 71M/FID Environnement SA over-estimates significantly at the same concentrations. The 3 other analyzers have a relatively good coherence in the concentrations measured.

4.3 – Correlations between analyzers

In order to study the correlations between the different analyzers, in particular for benzene, the analyzer by Perkin Elmer has been used as reference and the concentrations of the other analyzers have been measured against the concentrations of the analyzer by Perkin Elmer. To do the curves, it has been necessary to do an average of 2 values corresponding to quarter hour runs delivered by the automatic analyzers of BTEX corresponding to the 2 samples the closest in time to that done by the Perkin Elmer analyzer. The samples of the different analyzers are close in time within a few minutes.

Figure 4.4 presents the correlations obtained for all the analyzers for the period May 11th till June 2nd 2007, with 460 dual values. We observe that the concentrations of benzene which have enabled to do the curves (average of concentrations on ½ hour) do not exceed 6 $\mu g/m^3$ for the analyzer Perkin Elmer.

Consistently with what was presented previously, it appears that the correlations are relatively good with coefficients R^2 varying between 0,87 and 0,90. Nonetheless, the slopes of the curves obtained show the following:

- Good coherence of the concentrations of benzene for the analyzers Perkin Elmer and Chromatotec
- Clear under-evaluation of the concentrations measured by the analyzer by Synspech
- A very significant under-evaluation of the concentrations of benzene by the analyzer VOC 71M/FID Environnement SA (A slope superior to 2 is obtained)
- An over-evaluation by 25% of the concentrations in benzene measured by the analyzer VOC 71M/PID Environnement SA against the analyzer Perkin Elmer

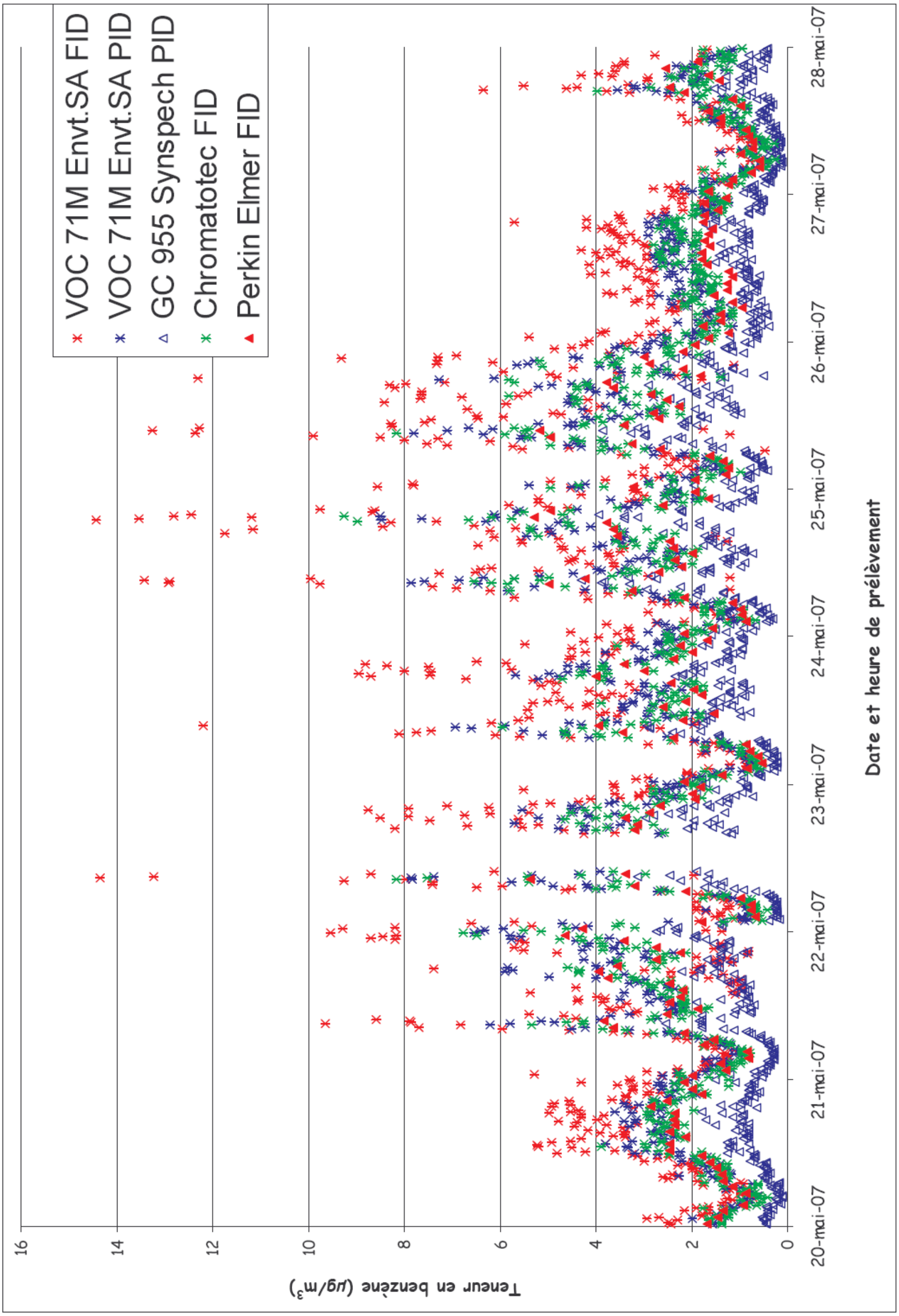


Figure 4.2: Time evolution of the concentrations of benzene measured in the period May 20th till 28th 2007 with 5 automatic VOC analyzers.

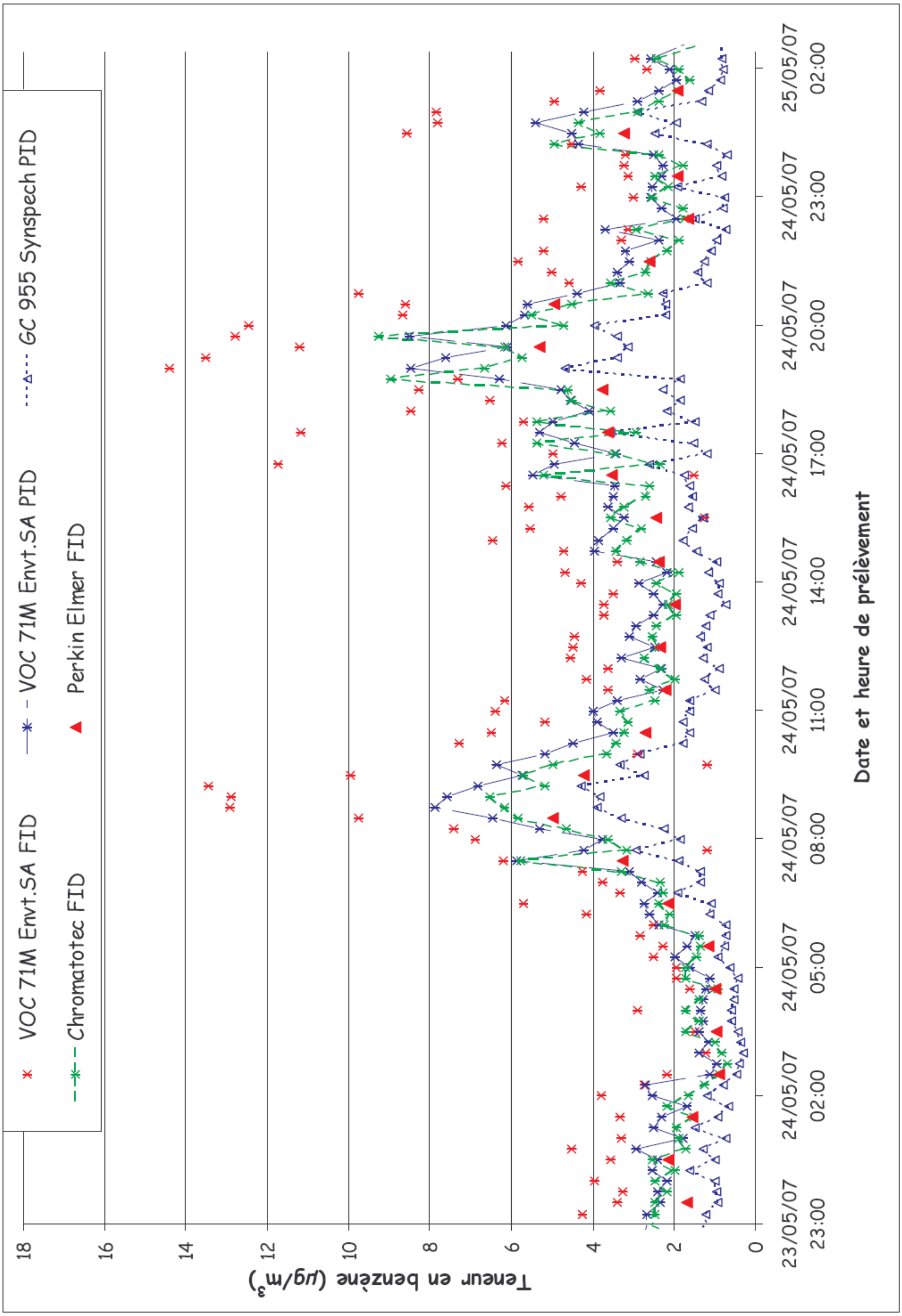


Figure 4.3: Time evolution of the concentrations of benzene measured (Zoom on one day: Thursday, May 24th 2007) with 5 VOC automatic analyzers

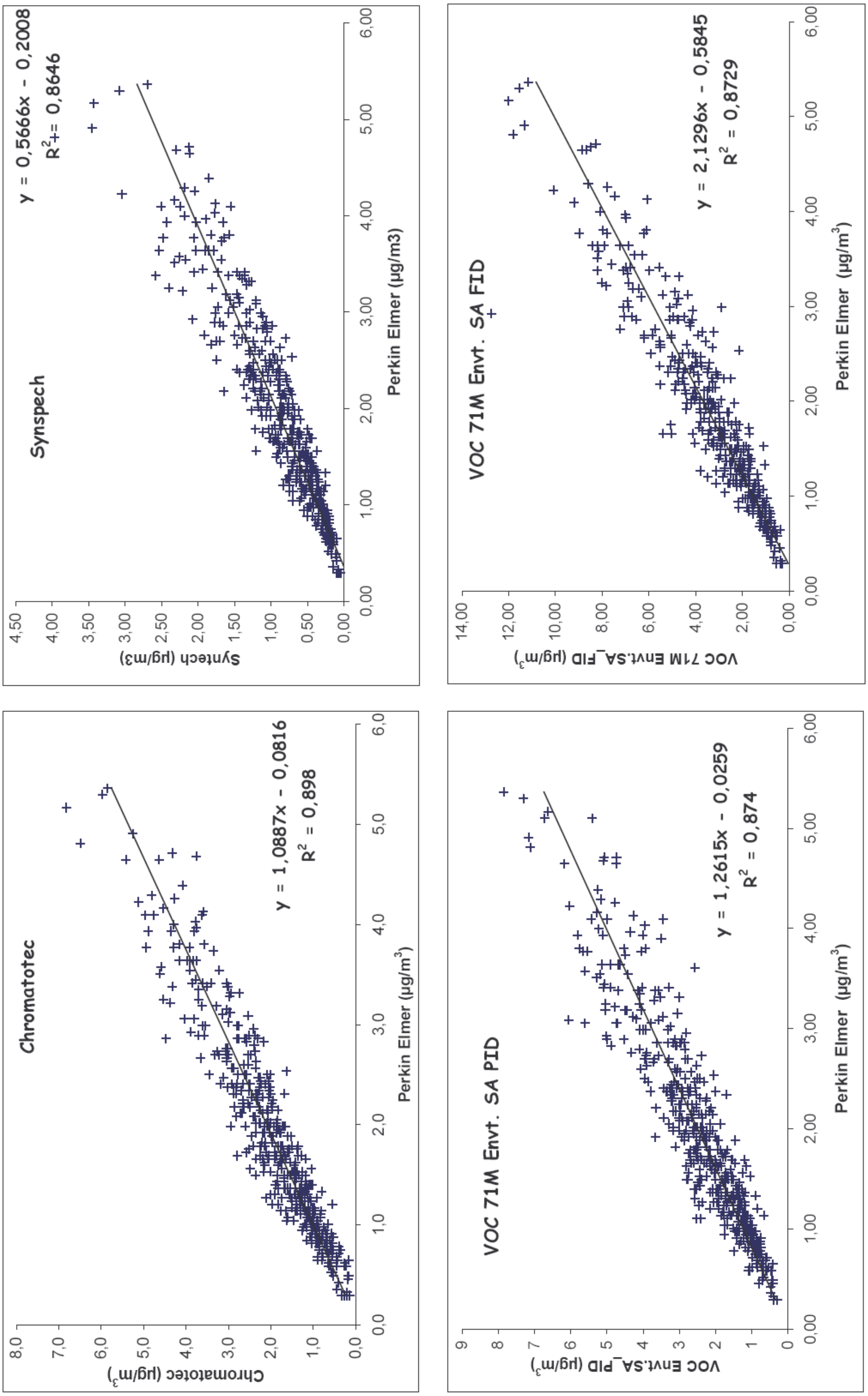
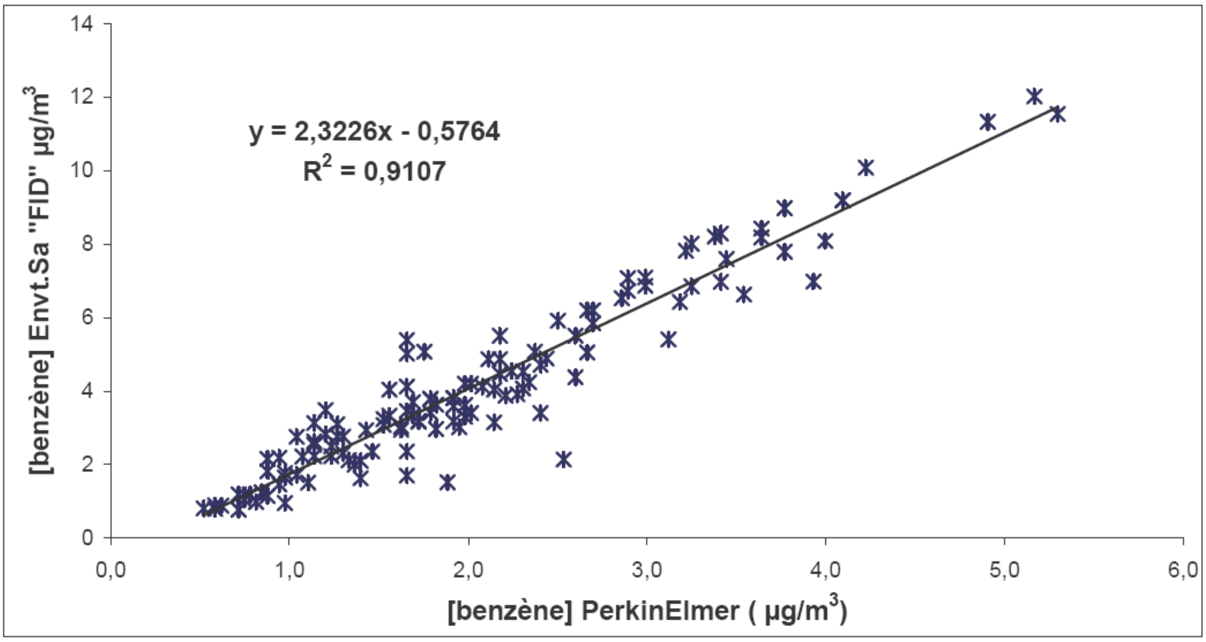


Figure 4.4: Correlations between the concentrations of benzene measured with 5 VOC automatic analyzers and the analyzer by Perkin Elmer



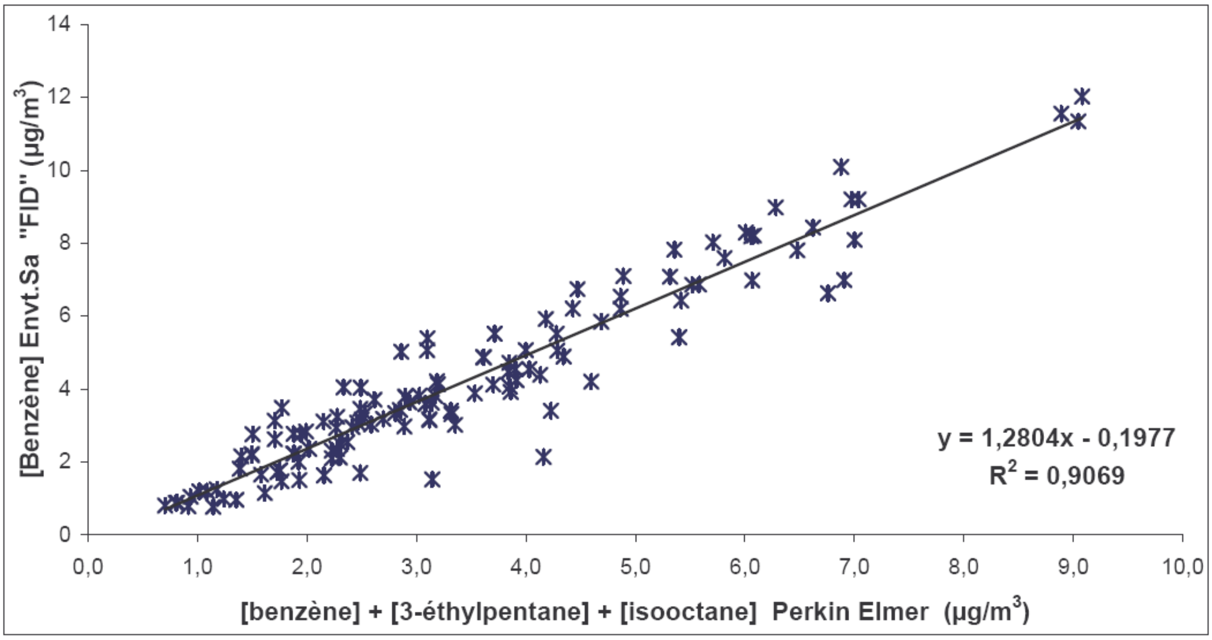


Figure 4.5: Correlations between the concentrations of benzene measured by the automatic analyzer VOC 71M/FID Environnement SA and the sum of the concentrations in benzene, 3-Ethylpentane and isooctane measured by the analyzer Perkin Elmer for the period May 22nd to 27th, 2007

4.4 – Complementary analysis

Concerning the results obtained by the analyzer VOC 71M/FID Environnement SA, considering the interferences shown during the technical reception of the analyzers in the laboratory (See 3.4.2.3 and 3.4.3), it is interesting to study how would evolve the correlation between the 2 analyzers if the sum of the 3 compounds coming together with benzene is quantified against the data provided by the analyzer by Perkin Elmer. With the data collected on 5 days (from 22nd till 27th of may 2007) which is 125 couple of points, the sum: [benzene] + [3-Ethylpentane] + [Isooctane] quantified with the data of Perkin Elmer has been calculated and plotted. Figure 4.5 presents the results obtained. We can also see that the concentration of benzene is significantly over-evaluated by the analyzer Environnement SA against the analyzer by Perkin Elmer (Slope = 2,32) and that the coelution of benzene with 3-Ethylpentane and Isooctane can explain for the most part this over-evaluation (slope = 1,28 if the data Perkin Elmer on benzene are added to the concentrations of 3-Ethylpentane and Isooctane).

Concerning the analyzer by **Synspech**, exchanges with the company that distributes Synspech in France for this analyzer (Néréides) concerning the results obtained in the linearity study (see § 3.1.6) has lead to the consequence that a different calibration of the analyzer has to be done versus what is normally done.
It was thought correct to do an "auto-linearization" of the response of the automatic analyzer. The objective of this "auto-linearization" is to do a multi-points calibration of the analyzer with a single gas standard mixture. As a matter of fact, as it is specified in see § 2.4, the air sample is done via a calibrated sampling syringe which enables to do a sampling of air by suction by a volume of 18,5 ml of gas. The volume of the syringe is relatively weak, 5 successive aspirations with the syringe are done to ensure that all the volume of sample requested is taken. As a consequence, it is very possible to do a calibration of the analyzer by doing one aspiration (Which is a volume of 18,5 ml), then 2 aspirations (or a volume of 2*18,5 ml), then 3 aspirations and so on until 9 aspirations as it is planned in the auto-linearization program of the analyzer. In the end, this procedure enables to stimulate the analysis of several gas mixture standard by using only one single gas mixture standard. More precisely:

- The program of "auto-linearization" requires 9 "aspirations" starting from the highest concentration possible. Once the first measurement with the last "aspiration" is done, it goes to a point at ¾ of the "aspiration", then through a point at half "aspiration" and finally through a point at quarter "aspiration". This is a total of 12 points including 9 with a full number of "aspirations" and 3 with a fraction of "aspirations".
- Each point is measured during a unique "run" of 30 minutes which implies a duration of "auto-linearization" of 6 hours. There are not several "runs" per point, that is to say there is no repetition of the measurement.
- If we start with a 5 ppb bottle, the concentration of the9 "aspirations" corresponds to 13,5 ppb, 8 stroke to 12 ppb and so on until 1 "aspiration" corresponding to 1,5 ppb, ¾ "aspirations" to 1,125 ppb, ½ "aspirations" to 0,75 ppb and ¼ to 0,375 ppb.

The "auto-linearization" must be always done before the calibration. In the same way, any "auto-linearization" must be followed-up by a calibration which makes the procedure 10 hrs long.

This procedure with the analyzer by Synspech was done on June 12th and the 5 automatic analyzers were put in parallel from June 12th to 19th 2007.

Figure 4.6 shows the correlations obtained for all analyzers on the period of June 12th to 19th, 2007, with about 150 couples of values.

Consistently with what was presented previously, it appears that the correlations are relatively good with coefficients varying from 0,86 to 0,87. Nonetheless concerning the slopes of the curves obtained the same conclusions can be drawn between the analyzer by Environnement SA and Chromatotec:

- A good coherence between the concentrations of benzene measured with the analyzers Perkin Elmer and Chromatotec
- A very significant over-evaluation of the concentrations of benzene measured by the analyzer VOC71M/FID Environnement SA (A factor superior to 2 is obtained)
- An over-evaluation of the value of benzene by 28% measured by VOC 71M/PID Environnement SA against the analyzer by Perkin Elmer.

For the analyzer by Synspech, there is a clear improvement of the results with a slope of 0,73 (instead of the 0,57 obtained previously), but an under-evaluation of the concentrations by 25% remains if one considers the analyzer Perkin Elmer as a reference.

4.5 – Results obtained for other compounds

In order to study the correlations between different analyzers, in particular for toluene and para+meta-xylenes, just like for benzene, the analyzer by Perkin Elmer has been used as reference and the values of the other analyzers are traceable to the one obtained by the analyzer Perkin Emer. To establish those curves, just like for benzene, it has been necessary to average the two values quarter hour delivered by the automatic analyzer BTEX corresponding to two sampling as close as possible to the one done on the Perkin Elmer. The sampling of those two different analyzers is close by about a few minutes.

Figure 4.7 and 4.8 show correlations obtained for all the analyzers on the period May 11th to June 2nd 2007, with 460 couple of values. It is worth noticing that the concentrations of toluene and para + meta-xylene which have enabled those curves (average of the concentrations on ½ hour) reach respectively 25 and 10 µg/m^3 for the analyzer Perkin Elmer.

For toluene, it appears that, with the cloud of points drawn, the correlations are relatively good with coefficients R2 varying between 0,82 and 0,86. The slopes of the correlation curves vary between 1,08 and 1,20 which shows a good coherence between the values of toluene measured by the various analyzers.

For the para+meta-xylene, it appears that, with the cloud of points drawn, the correlations are significantly less good than for toluene and benzene with coefficients R^2 varying between 0,56 and 0,60. If we compare those results with those obtained for toluene, the large dispersion of points observed could be due to the relatively weak concentrations measured for para+ meta-xylene comparatively to toluene, but if we compare to that obtained for benzene, we can see that the concentrations for the para+meta-xylene are of the same magnitude or even slightly superior to the one for benzene. The slopes of the correlation curves vary between 1,08 and 1,27 which nonetheless shows that there is a good coherence between the values measured for para+meta-xylene measured by the various analyzers even though there is a large dispersion of points.

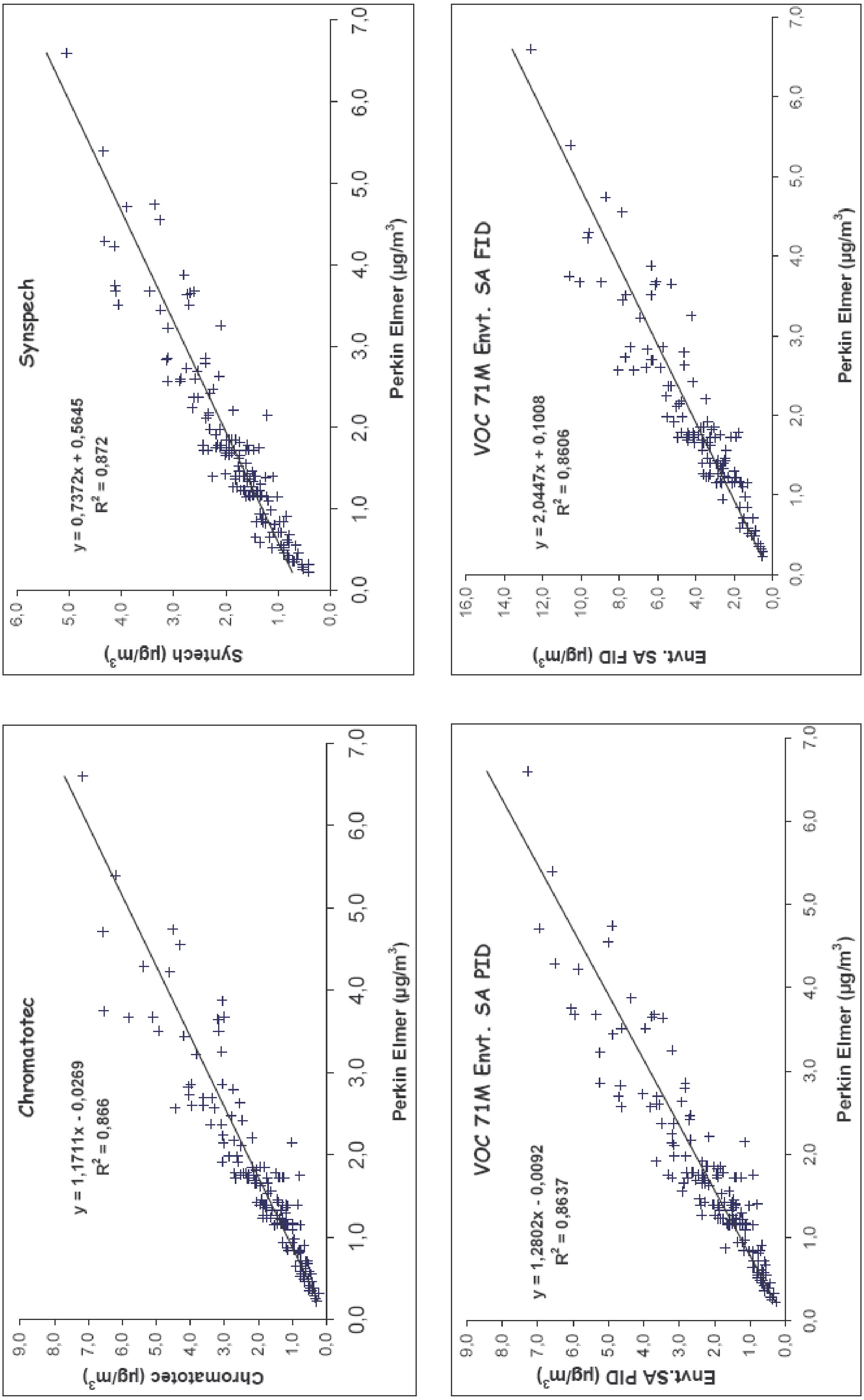


**Figure 4.6: Correlations between the values measured for benzene by the automatic analyzers of BTEX and the analyzer by Perkin Elmer.
The analyzer by Synspech has had an auto-linearization**

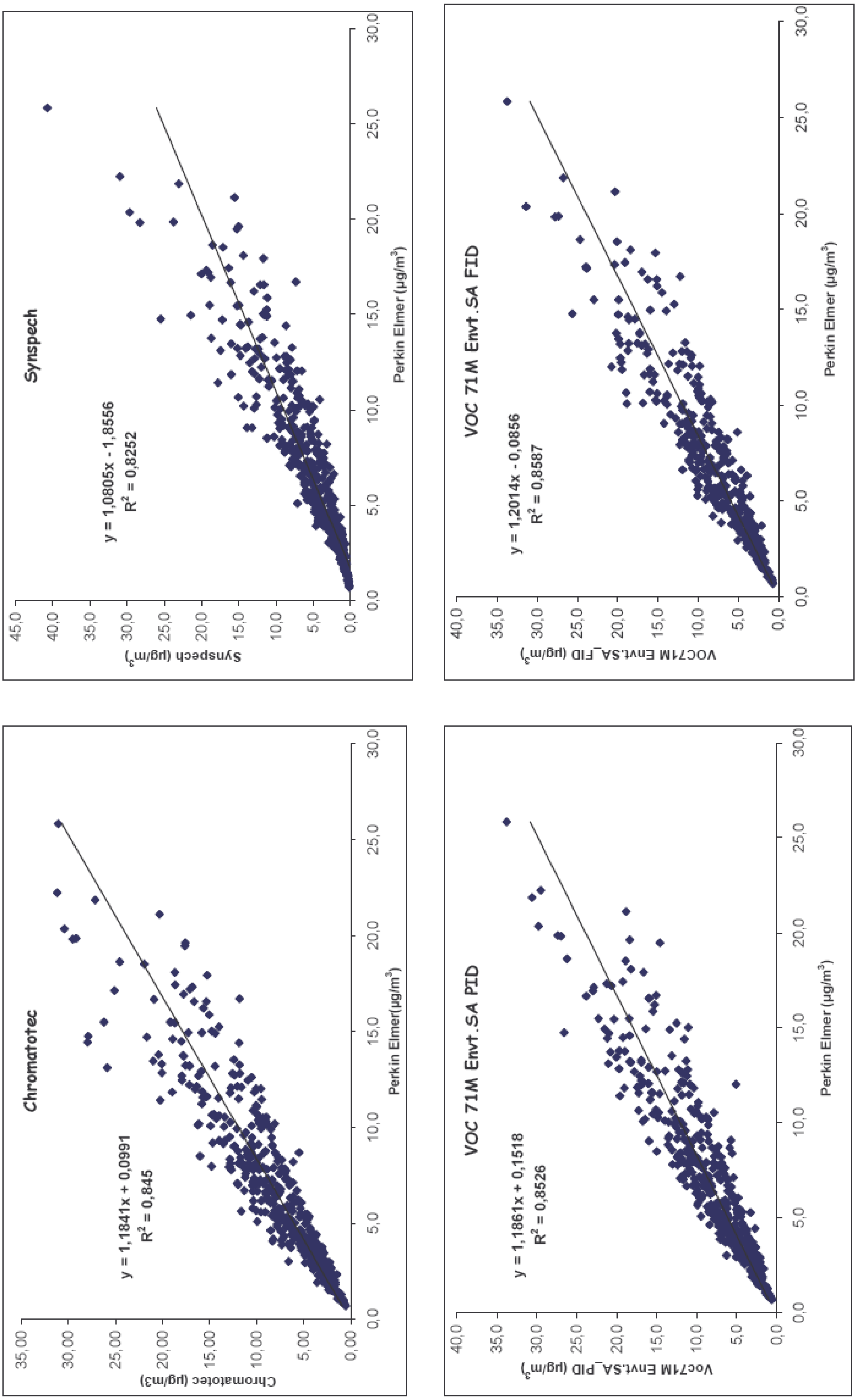


Figure 4.7: Correlations between the values measured of toluene by the automatic analyzers of BTEX and the analyzer by Perkin Elmer.

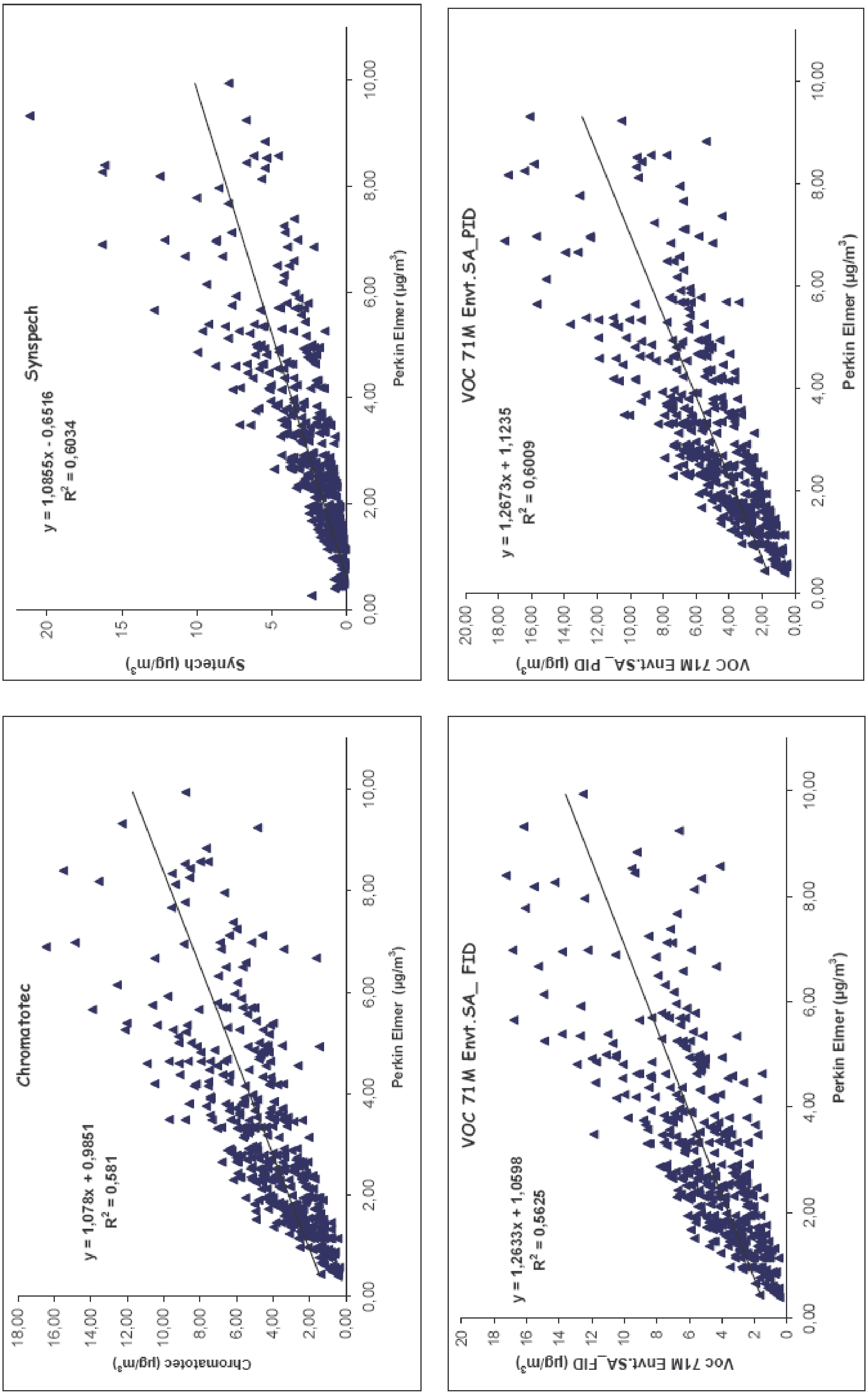


Figure 4.8: Correlations between the values measured with para+meta-xylene by the automatic analyzers of BTEX and the analyzer by Perkin Elmer.

5- CONCLUSION

The objective of this study is to evaluate the analytical performances of four automatic BTEX analysers in use since 2007 at various AASQA(*) (VOC 71M Environnement S.A./FID, VOC 71M Environnement SA/PID, GC 955 Synspech/PID, Chromatotec/FID).

First, this evaluation was about determined performance criteria of the analysers and the study of the results obtained to evaluate the conformance to the minimum requirements of the norm 14 662-3. The results obtained have shown that the results are significantly different according to the analysers and the parameters tested.

Regarding linearity, three of the four automatic BTEX analysers being tested (Chromatotec, VOC 71M Environnement SA FID, VOC 71M Environnement SA PID) meet the performance criteria of the norm (Relative residual of the linear correlation must be lower than 5% for the concentrations 5, 15, 25, 35, 45 µg/m^3) or be slightly above this criteria (5.2% for the analyser Chromatotec for the concentration 5 µg/m^3). For the analyser GC 955 Synspec, it was shown that the gap to linearity is significant with residuals reaching 10% for the concentration 5 µg/m^3. This gap to linearity enables to explain, that regarding the Synspech analyser, the results obtained during the comparison of the analysers on site and shows the need for an auto-linearization of the instrument during calibration on site or to use a standard mixture with a concentration of benzene close to the concentrations measured on site. Nonetheless it appears that the measurement of lower concentrations on the scale will be under-estimated and the concentrations above the scale will be over-estimated.

Regarding the memory effect, the analysers Chromatotec and Synspech measure, during the second analysis of zero air following the analysis of the highest concentration in benzene, concentrations for benzene below 5 µg/m^3 and thus meet the requirement of the norm. But, for the analysers VOC 71M Environnement S.A. FID and PID, the concentrations measured for benzene during the second analysis of benzene, are respectively 1.02 µg/m^3 and 0.88 µg/m^3 and thus do not meet the requirement of the norm.

Regarding repeatability, all the analysers have a repeatability to the limiting value lower than 5% and a repeatability at 0.5 µg/m^3 lower than the 0.1 µg/m^3 and thus meet the criteria of the norm.

Regarding the sensitivity to COV interferences, the analyser of Chromatotec is not sensitive to the COV tested which, in other words, mean that there is no overlap of benzene with any other species. For the analyser of Environnement S.A., the variation of the response is about 100% with the analyser equipped with an FID detector and it remains at about 10% with the analyser equipped with a PID detector. For the analyser supplied by Synspech, the response is strongly under-estimated when a mixture of organic substances is added, and the value is under-estimated by about 40%.

In terms of detection limit, for all the automatic analysers of BTEX tested, the detection limit is below 0,05 µg/m^3.

In a second phase, all the analyzers have been put in the same study site. The objective is to compare the behaviours and results of the instruments tested in the real conditions of usage by an AASQA.

Regarding long term drift, for all analysers equipped with an FID detector, such as the BTEX Chromatotec and VOC 71M Environnement S.A./FID, a very stable response of the PID is obtained. On the contrary, for the two analysers equipped with PID detectors, such as the analysers VOC 71M Environnement S.A. and GC 955 Synspech, a significant long term drift is observed with a decrease of the areas of the recorded peaks for the standard gas mixture. This drift of the response of the PID detector remains, during the course of the experiments, inferior to the performance criteria of 10% for the analyser VOC 71M

Environnement S.A./PID; it is much more variable depending on the period of time chosen for the Synspech analyser and can sometimes be beyond the 10% performance criteria.

Regarding the evolution of the concentrations over time, a homogeneous evolution is seen for all analysers with two daily concentration peaks at the two road traffic rush hours with significant differences depending on the level of benzene measured.

To study the correlations between the various analysers, particularly for benzene, the Perkin Elmer analyser was used as a reference and the concentrations of the other analysers have been compared against the measurements of the Perkin Elmer analyser. It appears that the correlation factors are relatively good with coefficients between 0.87 and 0.90. Nonetheless, the slopes of the curves obtained show the following:

- A good correlation for the concentrations of benzene between the analysers of Perkin Elmer and Chromatotec.
- A clear under-estimation of the concentrations measured by the Synspech analyser which can be explained by the gap observed to linearity by this analyser.
- A significant over-estimation of the concentrations of benzene measured by the analyser VOC 71M/FID Environnement SA (A factor of 2 is observed) which can be explained by the sensitivity of the instrument to COV interferences.
- An over-estimation of about 25% of the concentrations of benzene measured by the analyser VOC 71M/PID Environnement S.A. with respect to the analyser Perkin Elmer.

Additional analysis have helped explain the reasons for this over-estimation of the values for benzene measured on site near road traffic with the analyser VOC 71M/FID Environnement S.A. (Overlap of benzene with 3-Ethylpentane and Isooctane). Also, using the auto-linearization program by Synspech could improve significantly the results with a slope of regression of 0.73 (instead of 0.57 without auto-linearization), but an under-estimation of the concentrations by about 25% remains if we compare with the analyser by Perkin Elmer.