

airmoTWA

New Expert System for GC-FID/MS

Chromatotec[®]

Introduction

- Continuous air quality and emission gases monitoring



The challenges:

- Analyze precisely ambient air composition in different locations
- Continuous analysis with automatic validation of results
- More and more compounds
- In total compliance with government regulations

Air monitoring



Chromatotec® instruments have been designed to meet these new requirements (total compliance with EN 14 662-3).



Outline

I. General operation

II. Advantages

III. Applications



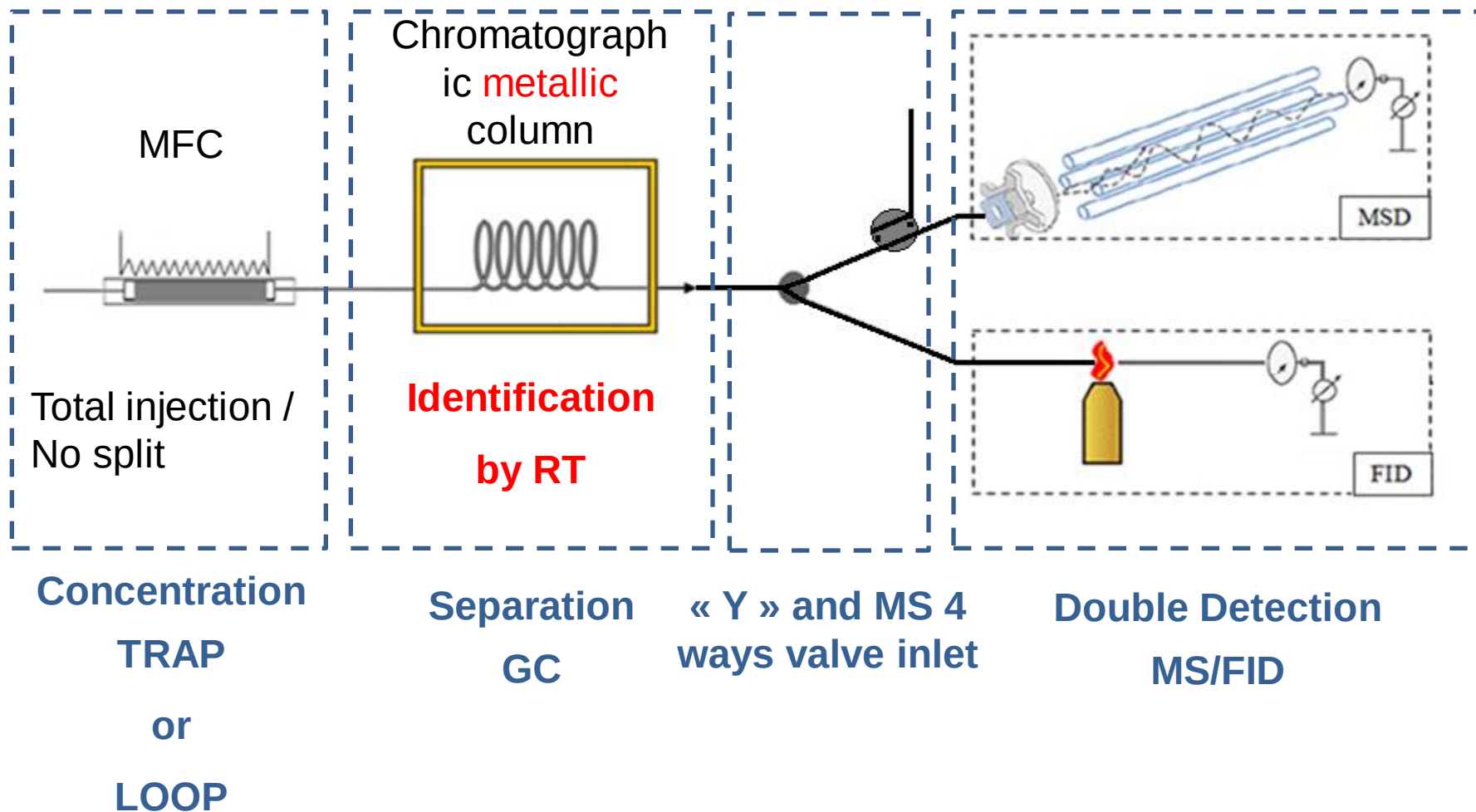
General operation

airmoTWA :

- Cabinet : 33 U + WHEELS + Safety rings
 - airmoCAL + multiplexer 16 streams 8U
 - Mass spectrometer (0-300 amu) 10U
 - airmoVOC C6-C12 5U
 - **mCERTS certified**
 - 1U rack with mouse and key board
 - Hydroxychrom (H2 generator) 4U
 - airmoPURE (zero air generator) and 2 sampling pumps



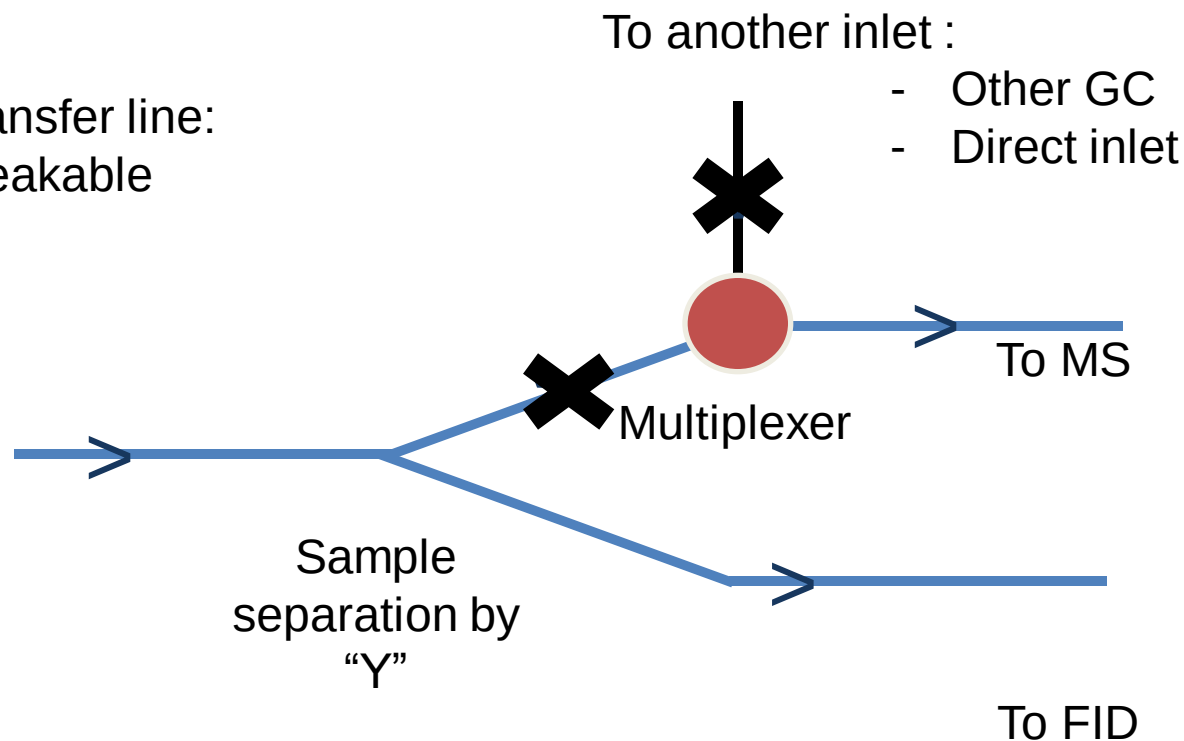
General operation



GC-MS/FID Coupling

Metallic heated transfer line:
Flexible and unbreakable
Up to 200°C

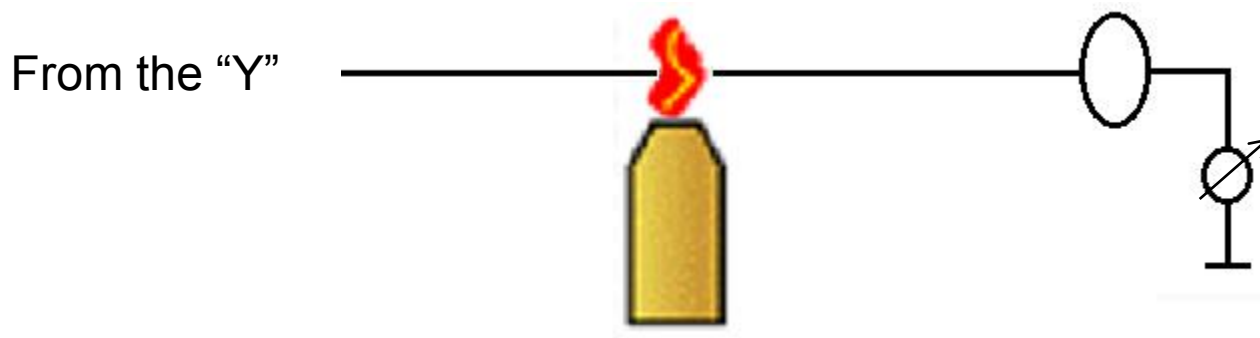
From metallic
chromatographic
column



General operation: airmoVOCexpert

FID

- Quantification by FID : Flame Ionization Detector

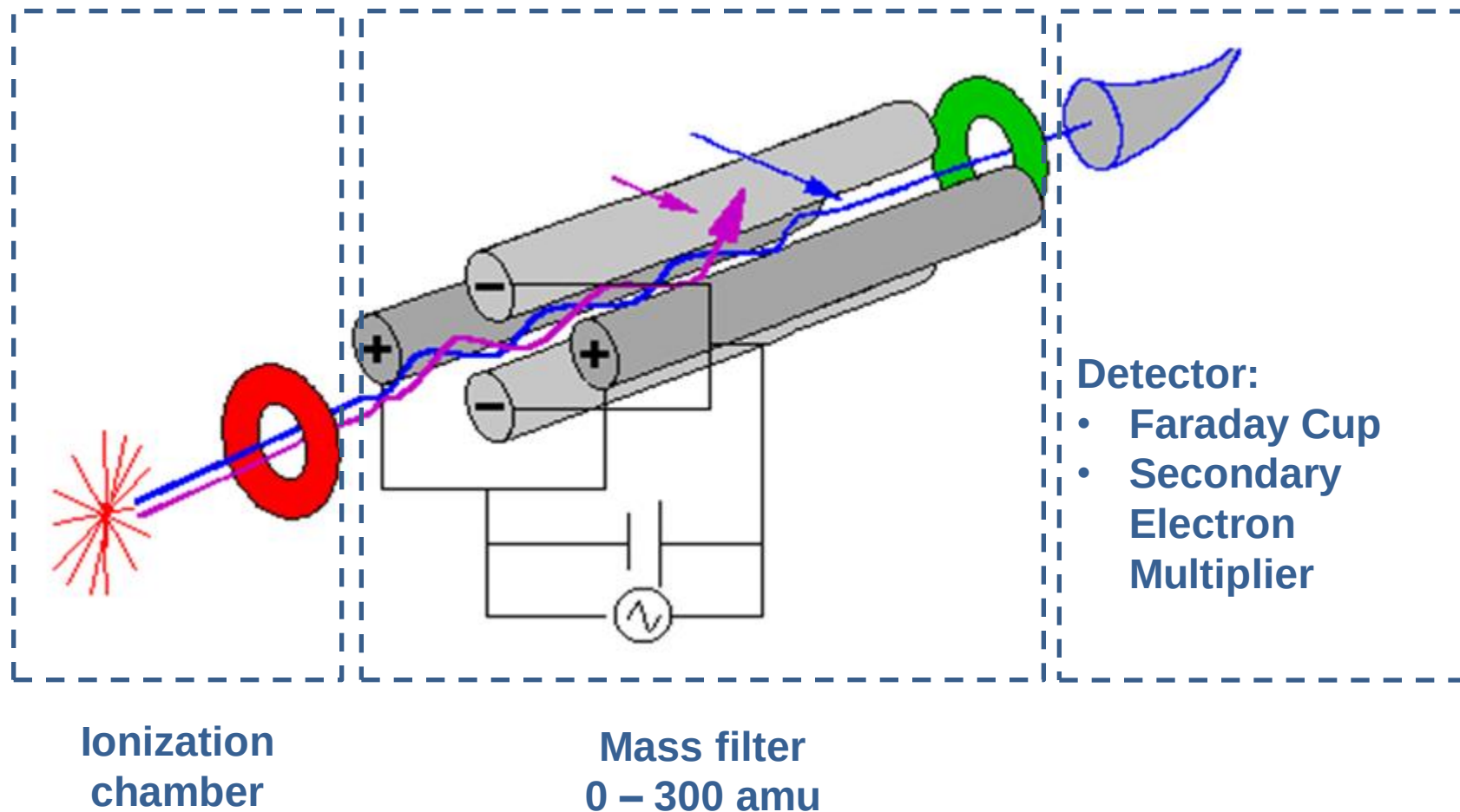


- Combustion of organic compounds
- The number of ions is proportional to the amount of organic compound
- **Automatic Quantification by Vistachrom**

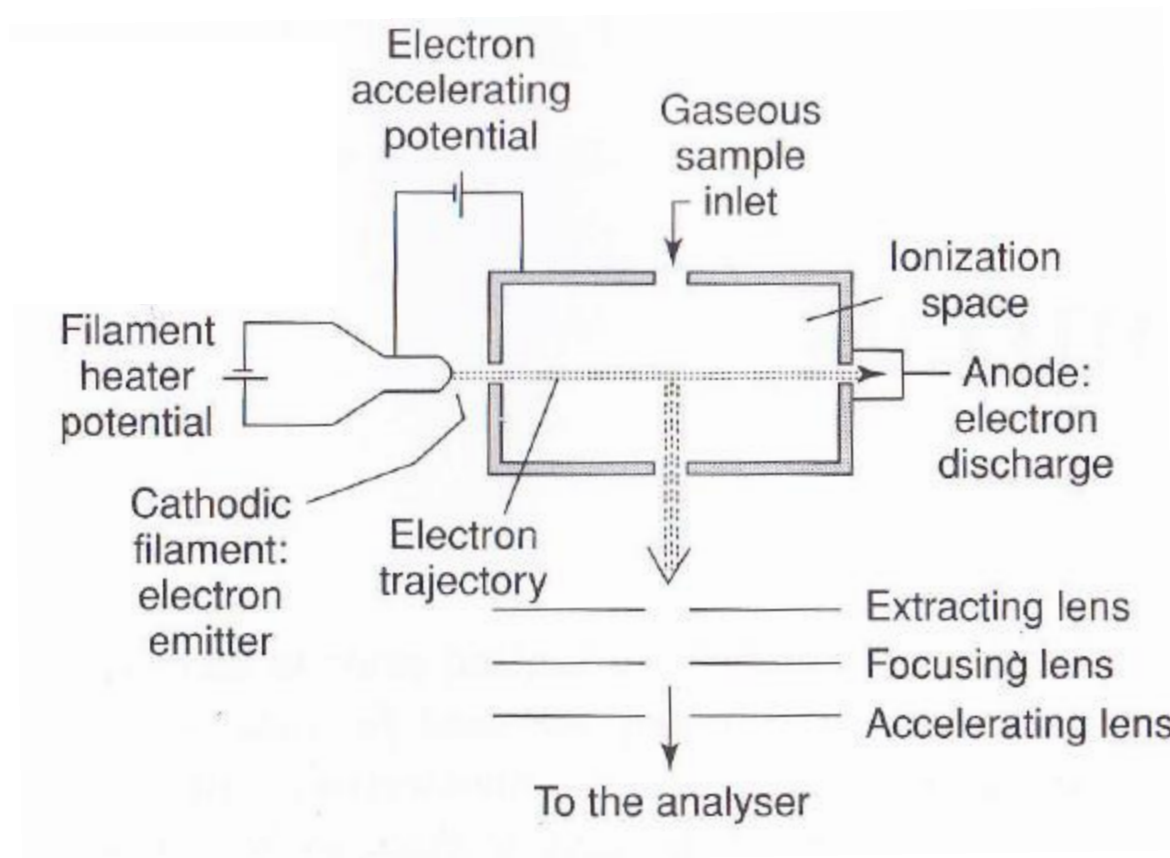
General operation: MS

MSD

- Identification by MSD : Mass Spectrometer Detector



General operation: MS

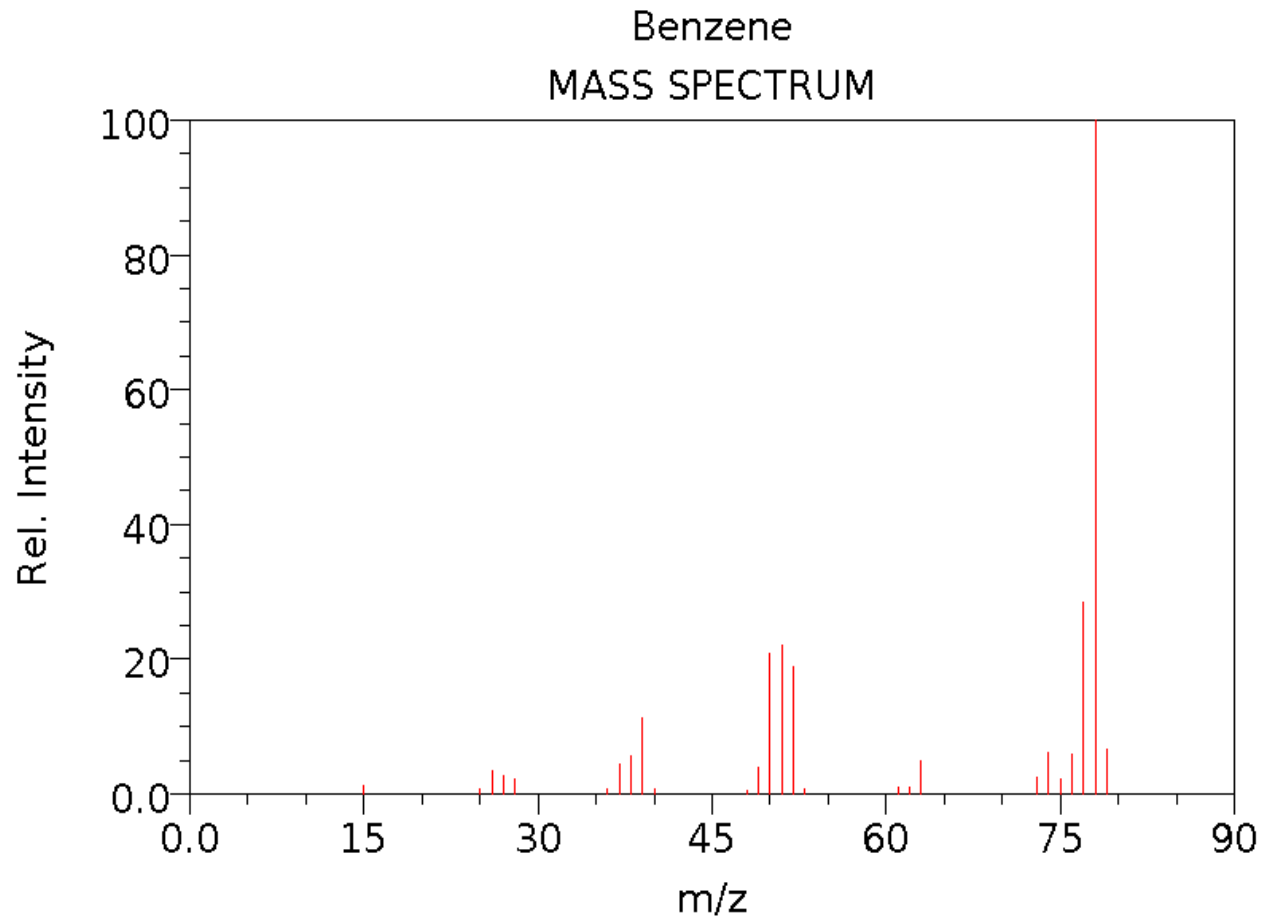


Electron associated to a wavelength:

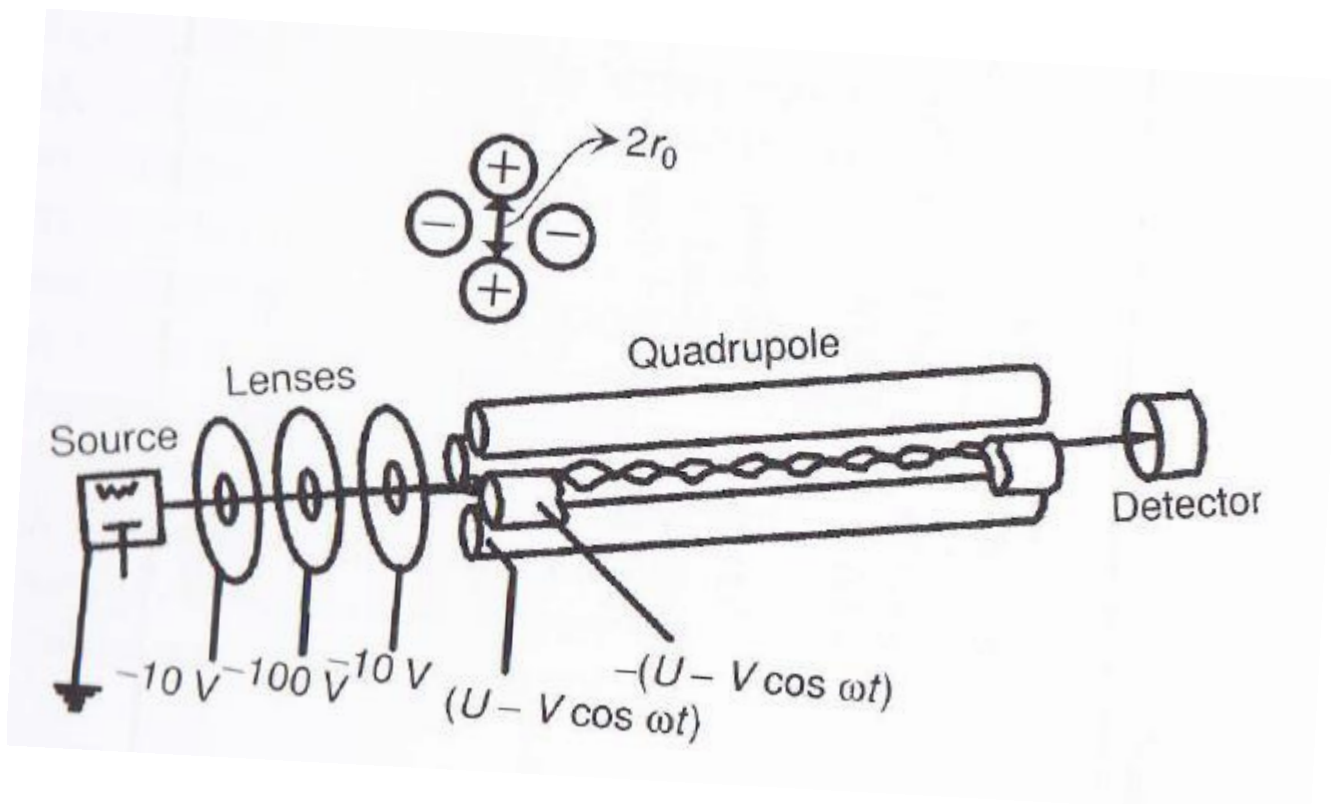
$$\lambda = \frac{h}{mv}$$

If one of the frequencies has an energy $h\nu$ corresponding to a transition in the molecule, various electronic excitations can occur.

General operation: MS



General operation: MS



Trajectory stability of ions in the quadrupole

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Advantages

- Expert analysis
 - Combination of two technologies : Very high sensitivity
 - Gas Chromatography with μ -FID
 - Concentrate the compounds in a trap : Low ppt
 - Separate compounds in pure hydrogen **First identification by RT**
 - Automatic quantification certified by different organisms
 - » mCERTS 2013 ...

Advantages

- Expert analysis
 - Combination of two technologies : Very high sensitivity
 - Mass Spectrometer
 - GC coupling
 - » Highly sensitive universal detector
 - » Selective detector
 - » Identification of unknown compounds
 - » Allow deconvolution of chromatographic peaks
 - » Mass analysis **Second identification by Mass Spectrum (from ppt level)**
 - » Quantification (ppt level)
 - Leak detection from ppm to % level

Why two detectors after separation

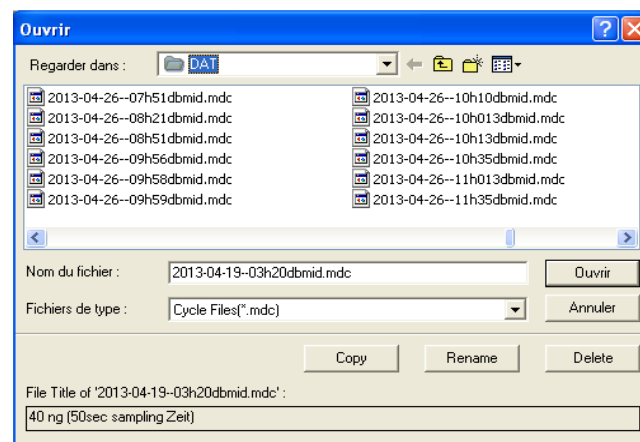
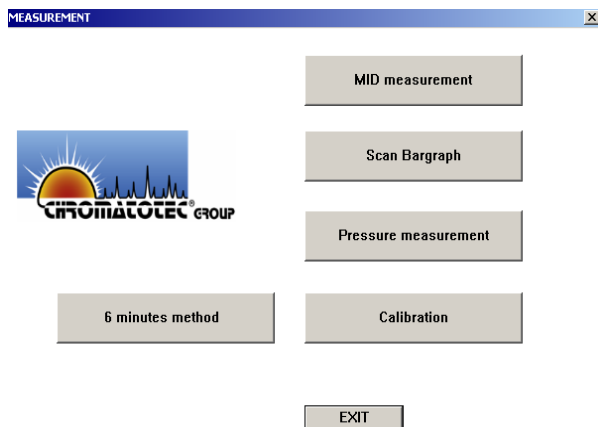
- Quantification with mass spectrometer:
- Response factors must be determined experimentally
 - Variation of source conditions require the calibration to be done
 - **on all compounds**
- Quantification with Flame Ionization Detectors:
 - Theoretical response (ECN)¹ factors verified experimentally
 - No variation of **Benzene** relative response factors. Calibration can be done on
 - **one compound**
 - airmoVOC is mCERTS certified

One complete system can analyze up to **90 compounds**

¹ Scanlon, J.T., and Willis, D.E., *J. Chromatogr. Sci.* 23, 333-340 (1985)

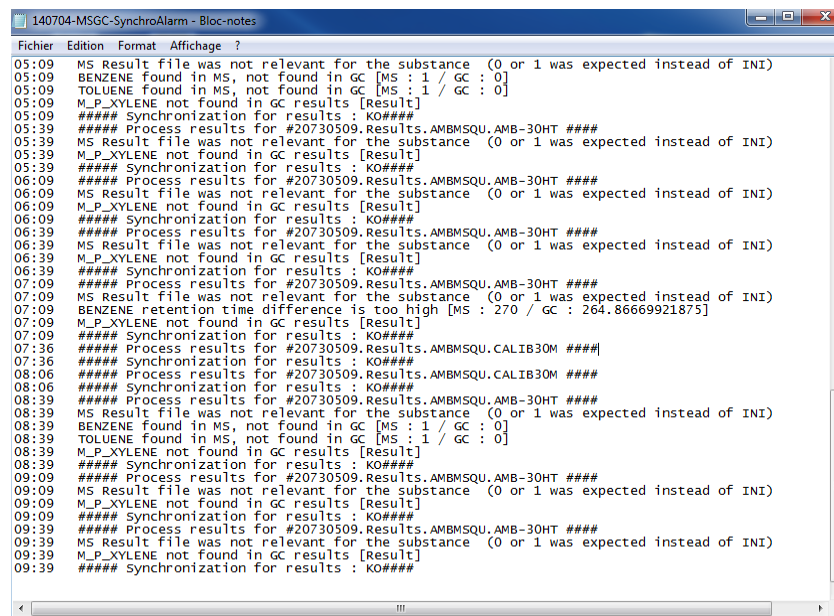
Advantages

- Software
 - Analysis controlled by **Vistachrom**
 - Easy to use and tunable depending on the application
- Continuous analyzer
 - Design for online analysis
 - Traceability of data
 - Stability (industrial computer and software)
 - Alarms



Advantages

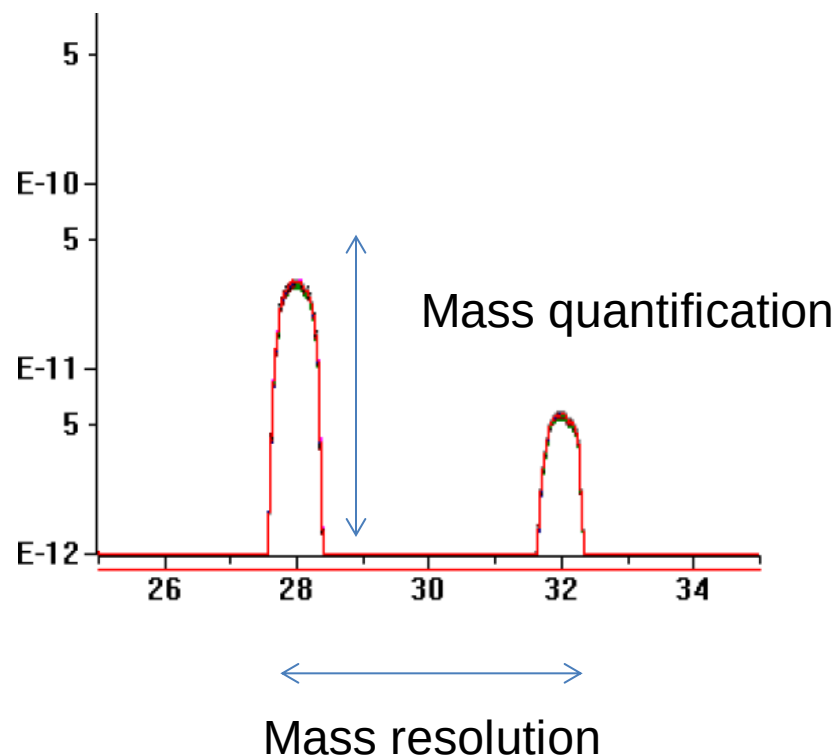
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A screenshot of a Windows-style application window titled "140704-MSGC-SynchroAlarm - Bloc-notes". The window contains a text editor with a log of system messages. The messages are timestamped and include status reports for Benzene, Toluene, and m,p-Xylene, as well as synchronization and process results for various substances and parameters. The log shows a series of checks and results, including some errors or warnings like "MS Result file was not relevant for the substance" and "Synchronization for results : KO####".

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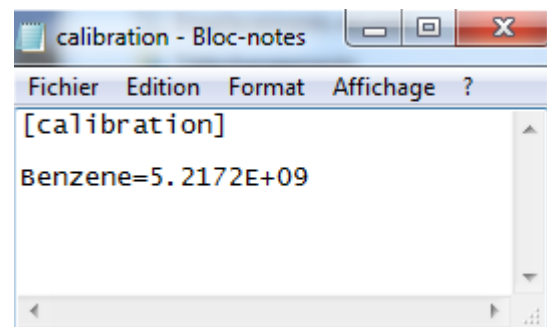
Calibration

- Calibration carried out automatically using permeation tubes
 - For quantification
 - FID
 - Automatic validation (mCERTS)
 - MS
 - Auto-correction
 - For mass resolution
 - MS
 - Validation by user (optimized once a year)



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For other substances, relative response factors will be used

Standards

- PAMS
 - 56 compounds (Plus α - and β -pinene)
 - TO14
 - 44 compounds (BTEX included)
 - Halogenated compounds
 - TO15
 - 63 compounds (BTEX included)
 - Halogenated, amines, and oxygenated compounds
 - BTEX
 - Included in all standard bottles
- $\Rightarrow$ **> 100 different compounds**
- $\Rightarrow$ Many other compounds in option
- FID
 - Relative response factors
 - Calibration
 - Peak separation
 - Mass Spectrometer
 - Calibration
 - Library for fragmentation patterns

Outline

I. General operation

II. Advantages

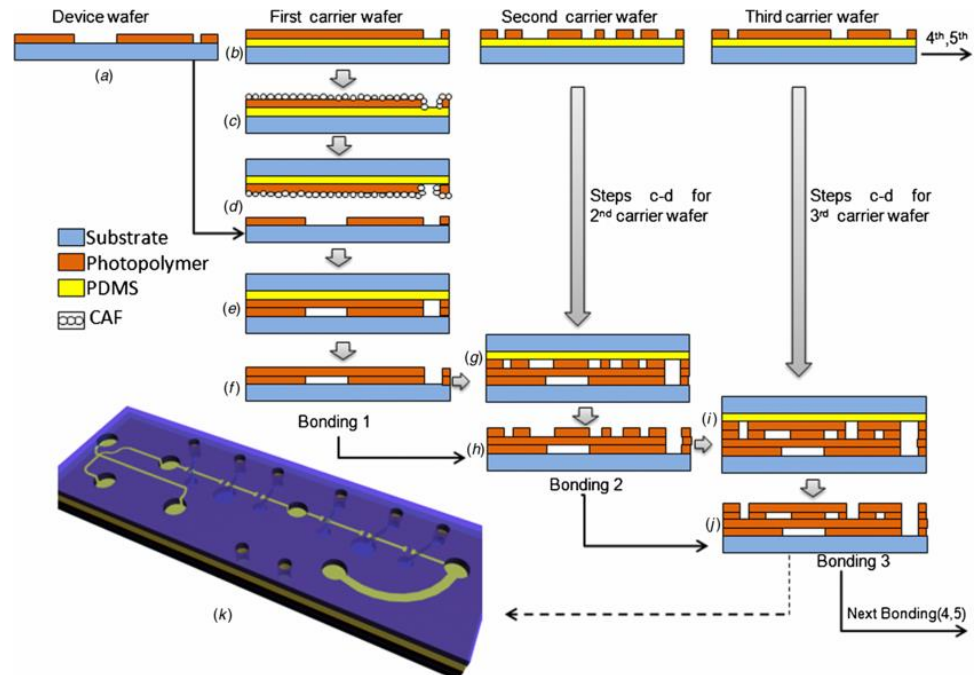
III. Emissions monitoring

- Clean air room (indoor industrial air)
- Air monitoring (outdoor air – field environment)
- Quantification of co-elutions



Clean air room

- Lithography process
- Need to perform accurate and fast measurements of chemicals
 - People safety
 - HMDS
 - Substance table
 - Leak control



Control the influence of particles and molecular concentrations on process efficiency

Clean air room

From diffused emission to identification of sources

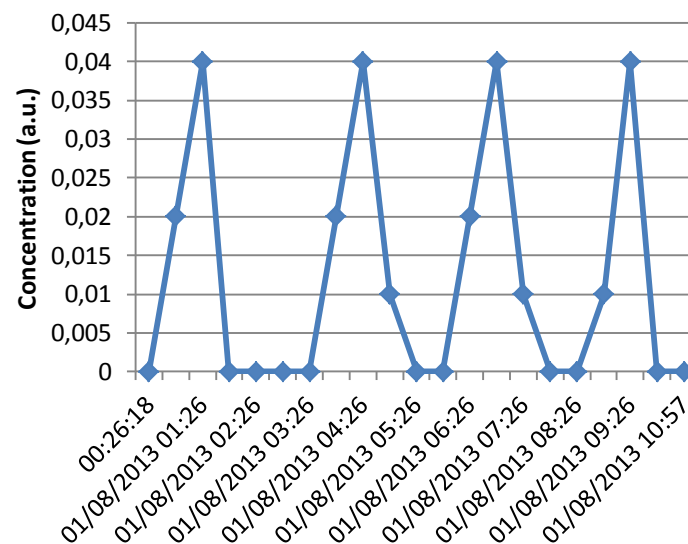
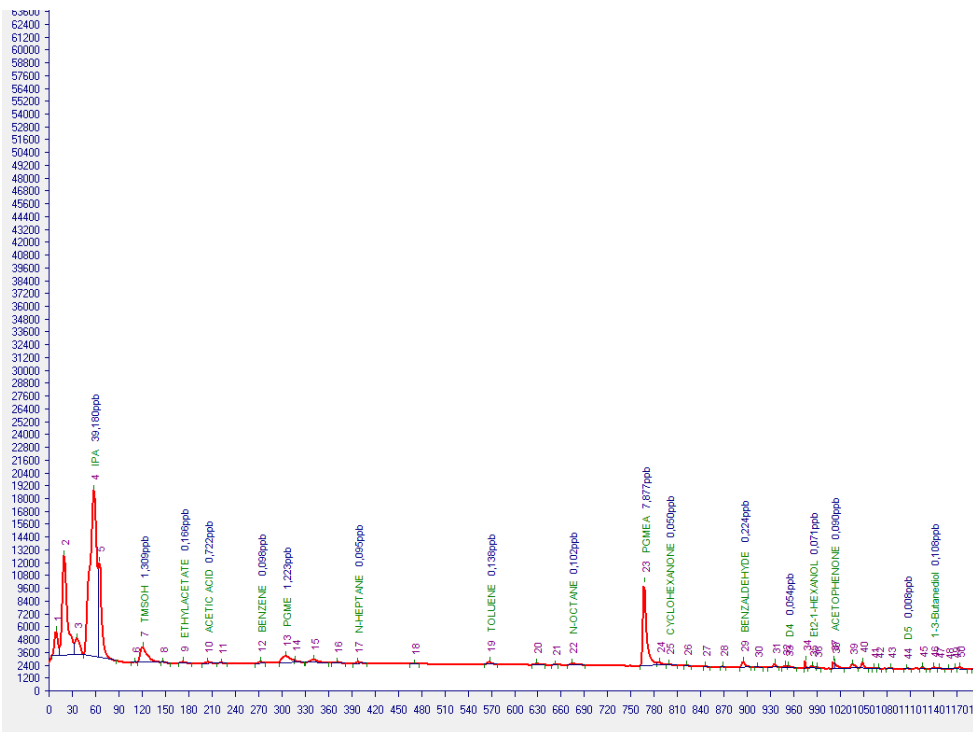
- 30 minutes analysis
 - High sensitivity
 - High resolution
- 6 minutes analysis
 - Leak detection
 - Compound detection
- Direct measurement
 - Leak detection
 - Alarm system



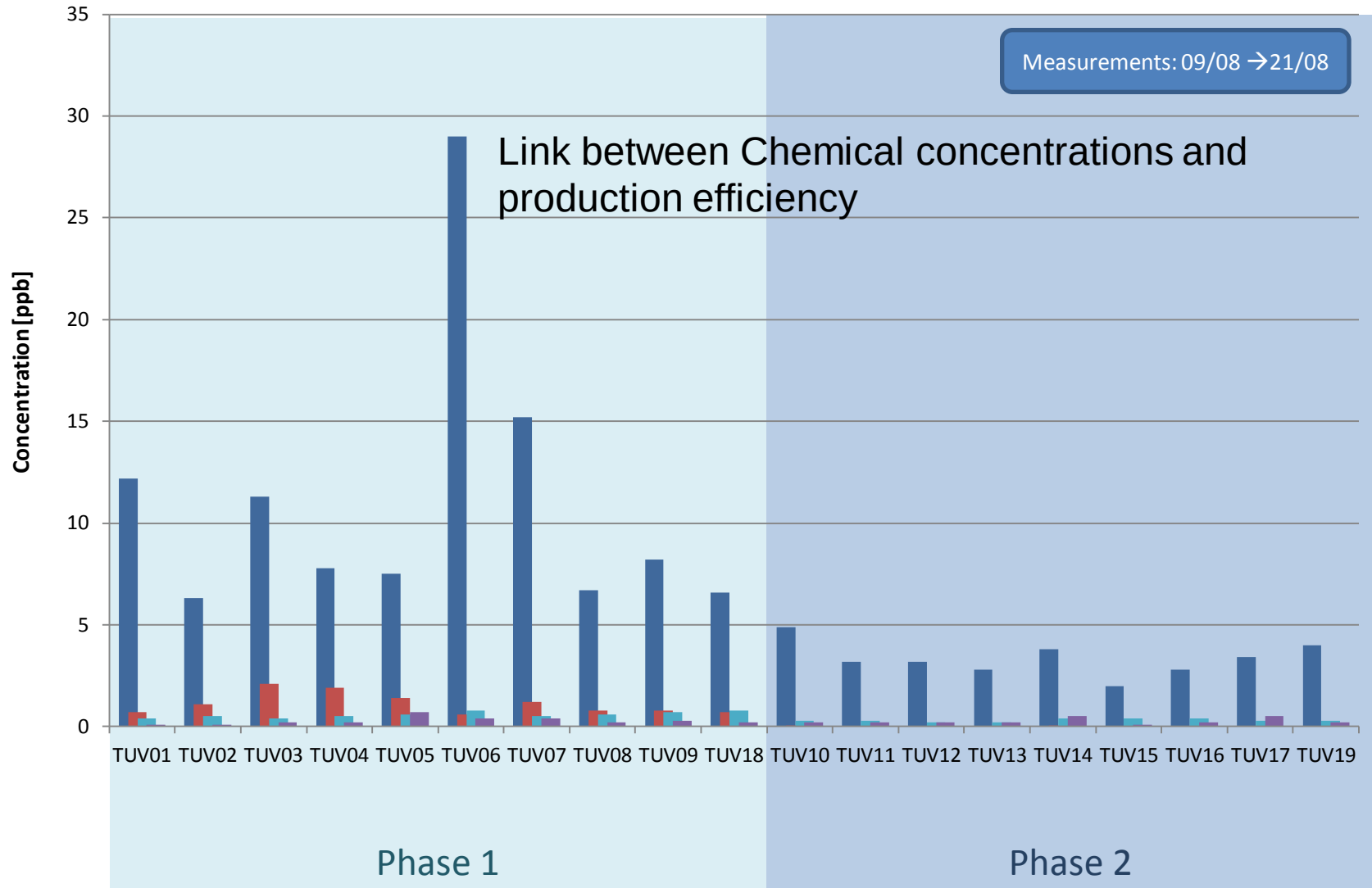
Clean air room

- 30 minutes analysis of 16 streams
 - High sensitivity (low ppt)
 - High resolution

One night of analysis
after installation

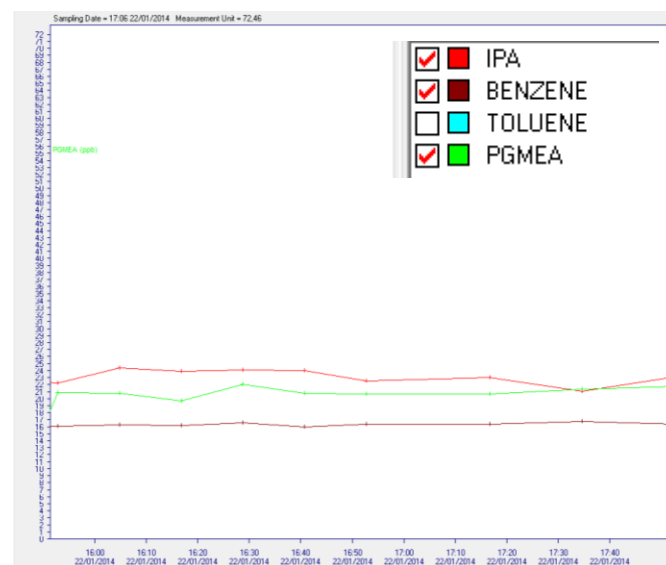
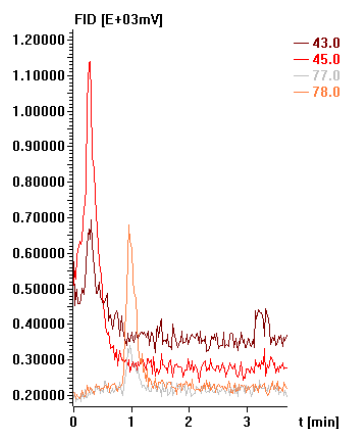
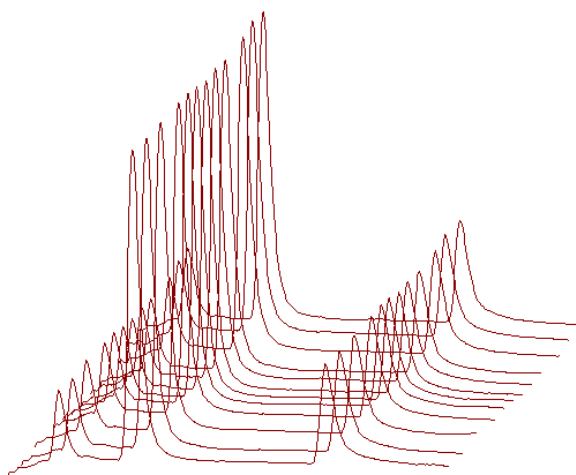


Clean air room



Clean air room

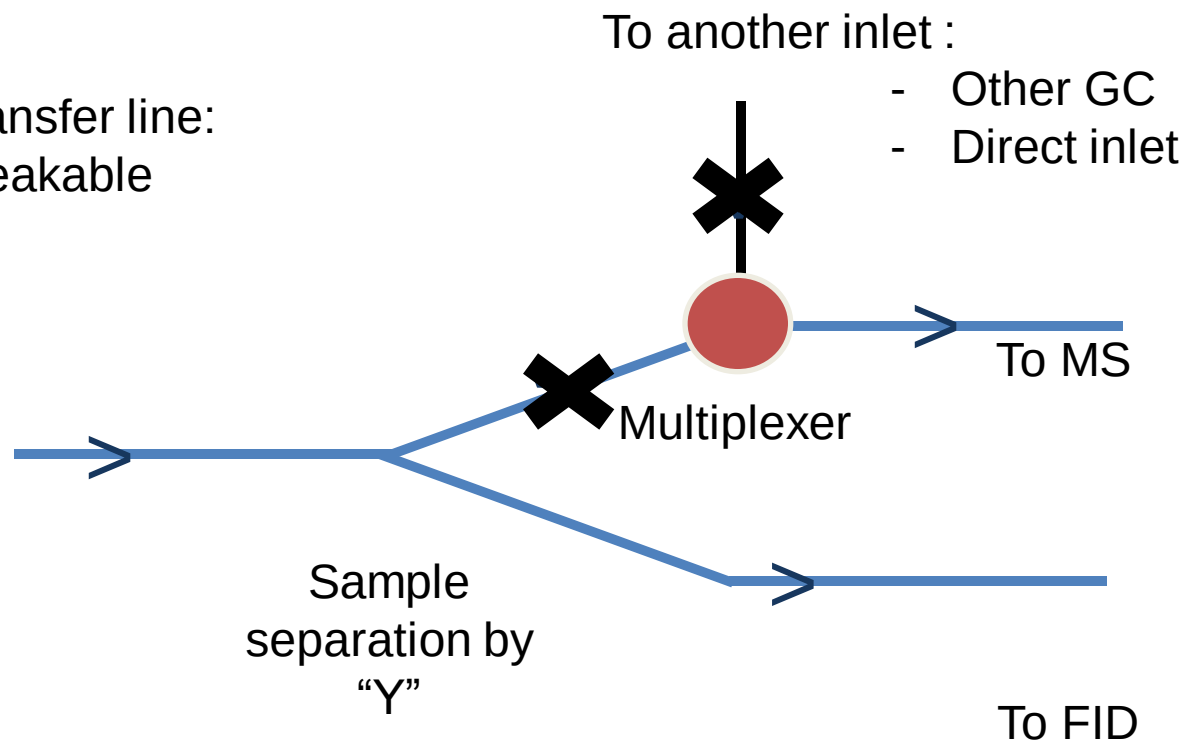
- 6 minutes cycle time
 - Can also be used for quantification



Clean air room

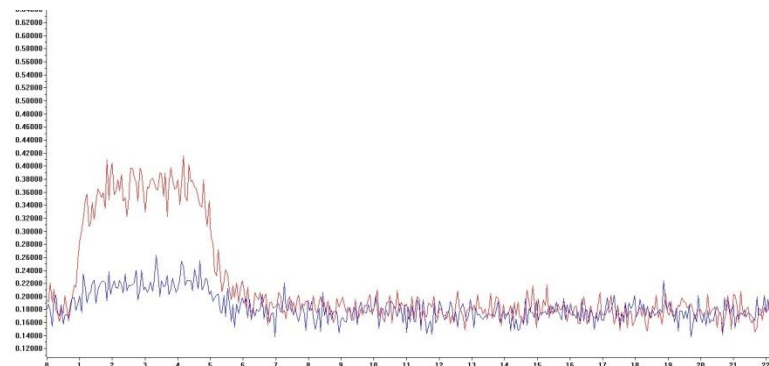
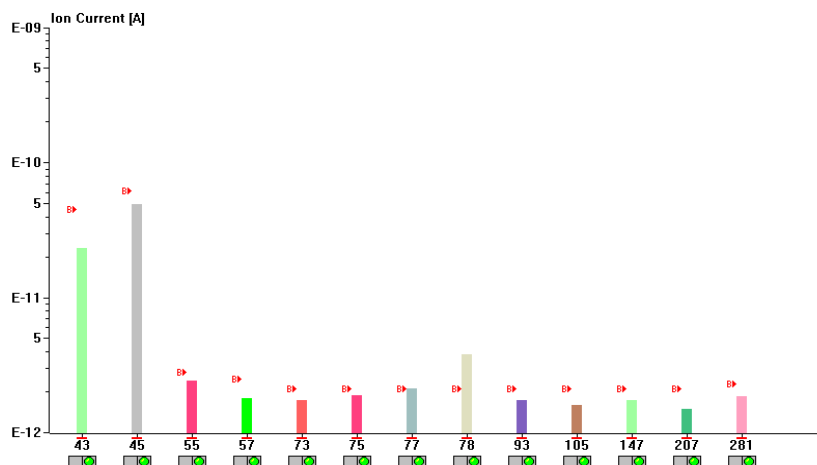
Metallic heated transfer line:
Flexible and unbreakable
Up to 200°C

From metallic
chromatographic
column



Clean air room

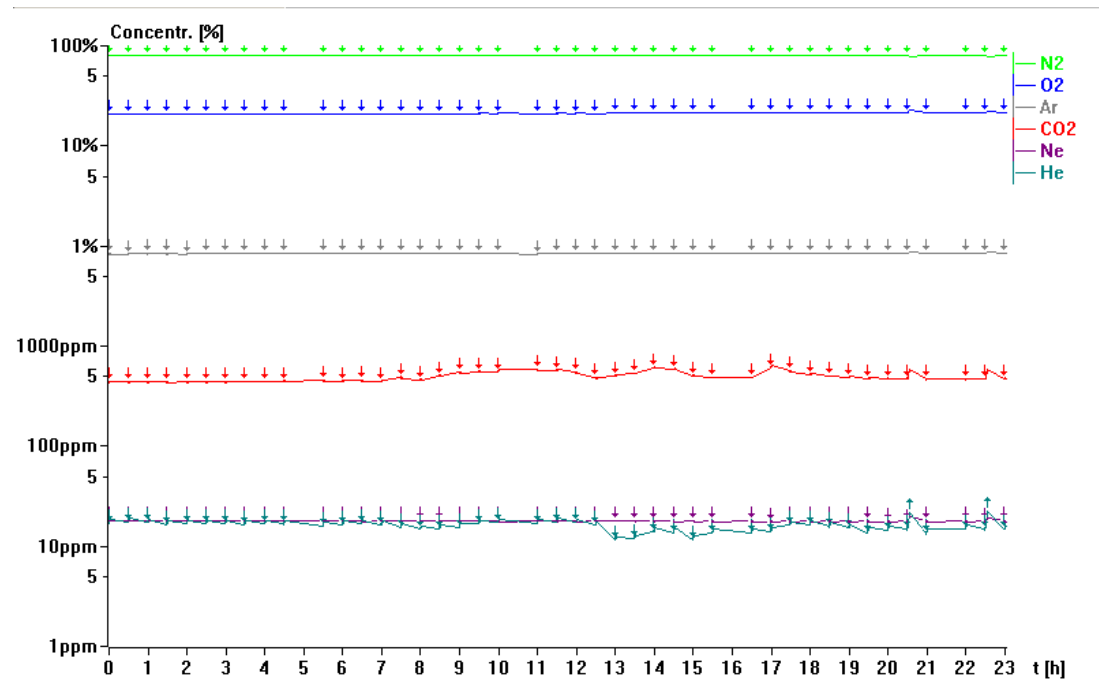
- Direct measurement
 - Leak detection with a flexible sampling probe
 - Alarm system



From 0.5 ppm to %

Clean air room

- Direct measurement
 - Leak detection with a flexible sampling probe
 - Alarm system



airmoTWA

- Flexible system
 - 30 minutes method
 - 6 minutes method
 - Direct analysis (few seconds)
- Started within few minutes
 - Mapping of the room within one day
 - Online measurement
- Easy to use for non-specialized
 - Automatic validation of results
 - Automatic trend display
 - Assistance at Chromatotec®
- Money saving
 - **Process improvements**
 - No need to send samples to laboratories

Outline

I. General operation

II. Advantages

III. Emissions monitoring

- Clean air room (indoor industrial air)
- Air monitoring (outdoor air - field environment)
- Quantification of co-elutions



Field environment simulation

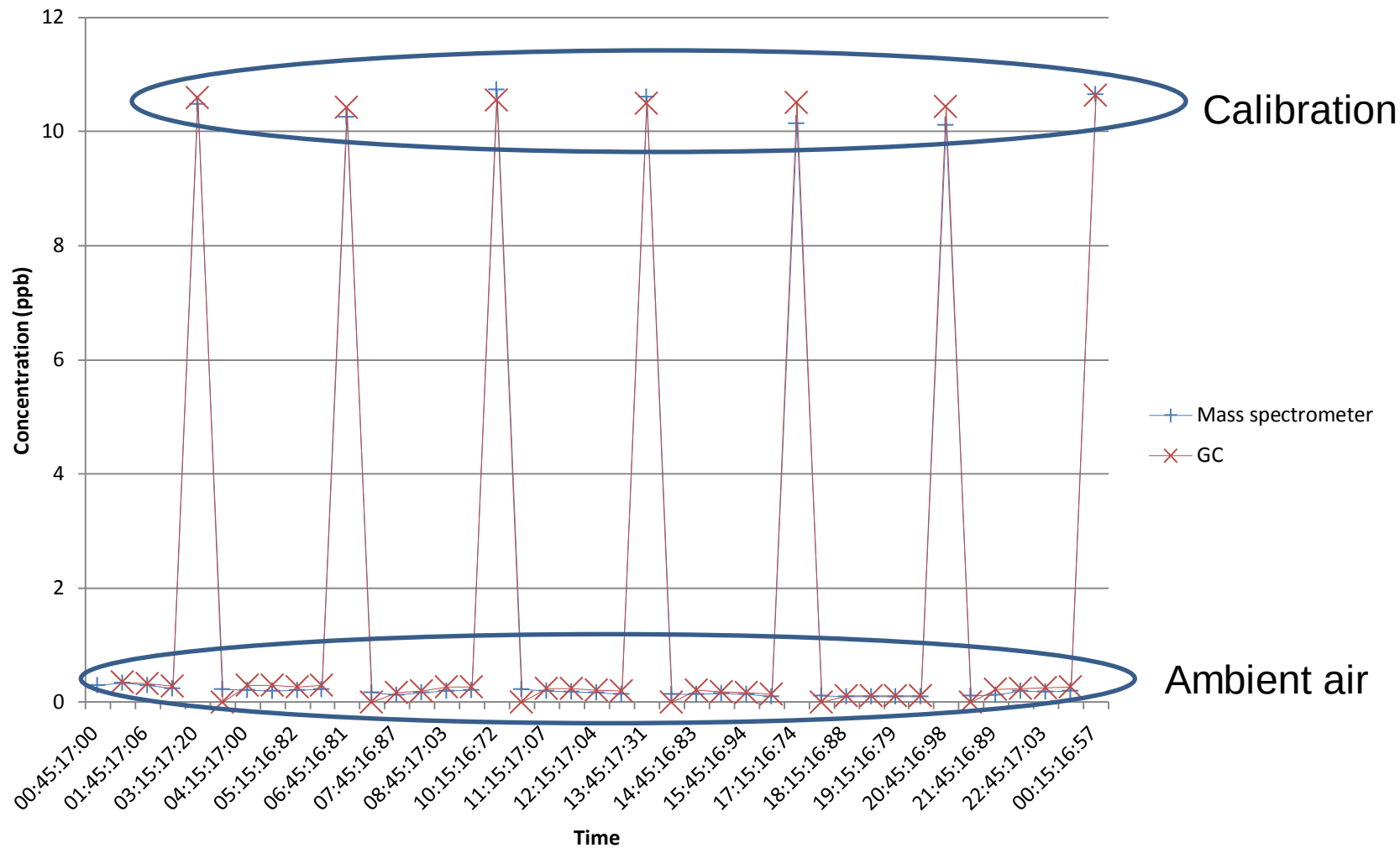
Problems which can happen with instruments in field environment

- Important variations of external conditions
 - Temperature
 - Vibration
- Important variation of sample concentration and matrix
 - Humidity
 - High increase of concentration
 - Apparition of unknown compounds and or co-elution
- Modification of retention times
- Signal saturation
- Over-estimation of signal due to co-elution

Field environment

- Measurement for 24h
- Sequence
 - CalibMS (one time)
 - Used for MS calibration
 - CalibA2 (one time)
 - Used for check MS and GC calibration
 - VOCMSQU (5 times)
 - For ambient air quantification
- Each method: 30 min
- The mass spectrometer and FID record the Benzene:
 - Concentrations
 - Retention times

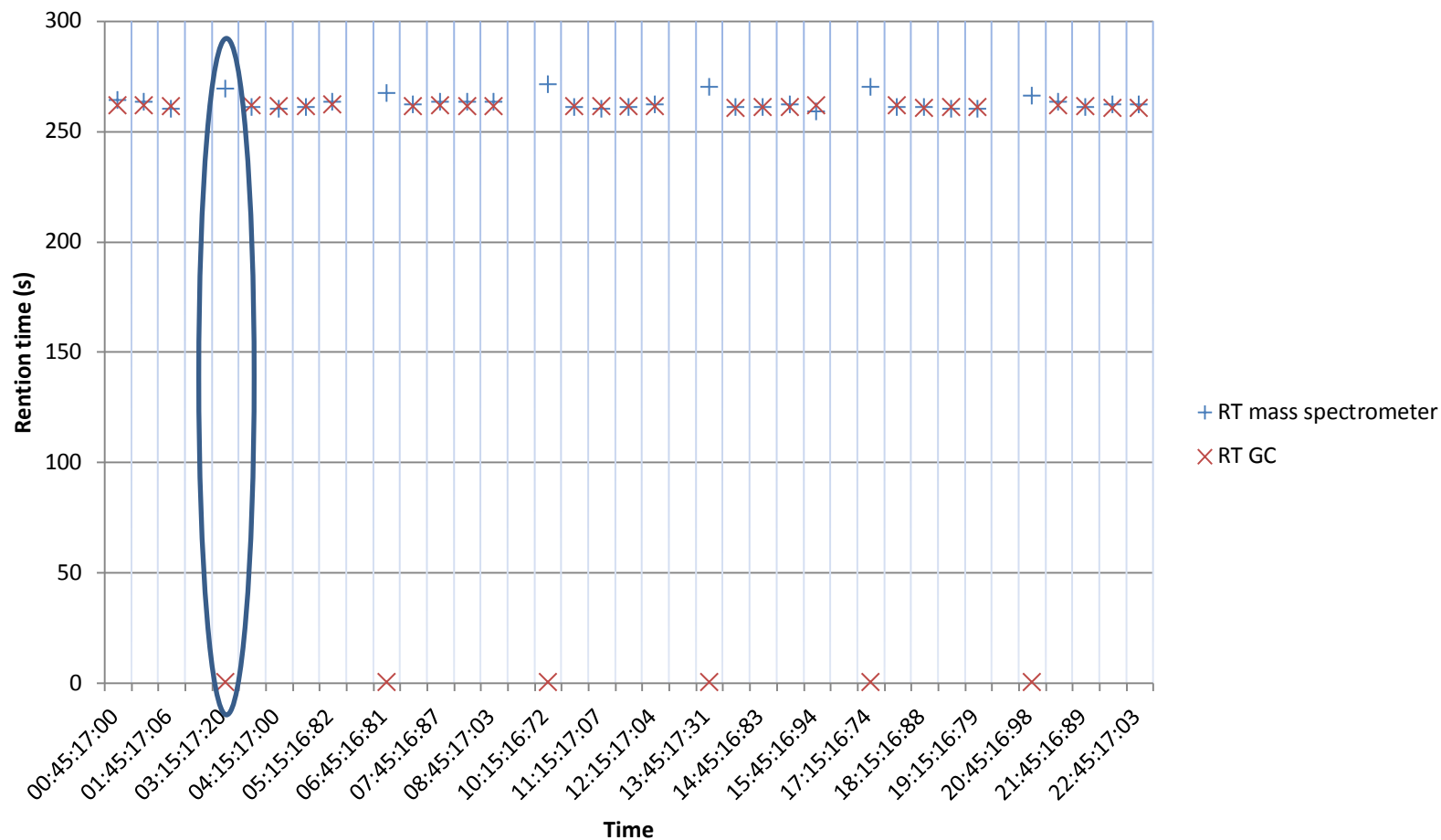
Measured Benzene concentration for 24h



Field environment simulation

- Retention times can be altered by rapid modification of external conditions
 - ⇒ Important temperature change
 - ⇒ Very humid sample ...
- **To simulate this event**, the first VOCMSQU has been modified to induce a modification of RT:
 - Gradient temperature modification
 - RT change by few seconds

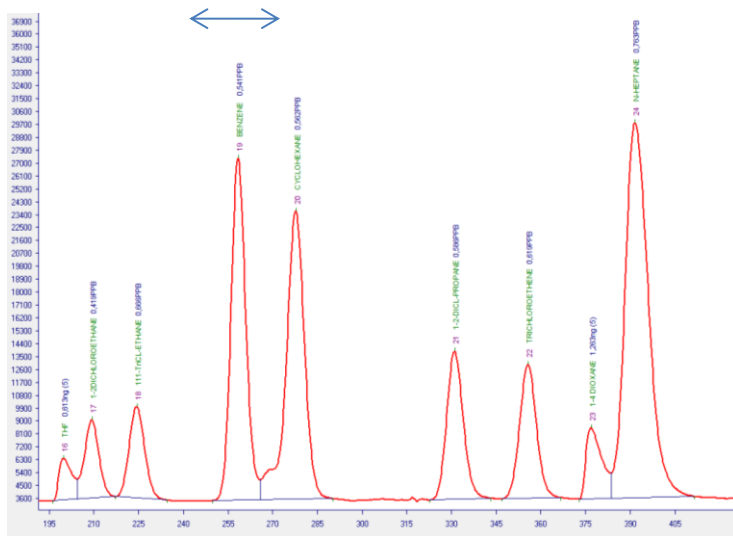
Benzene Retention times



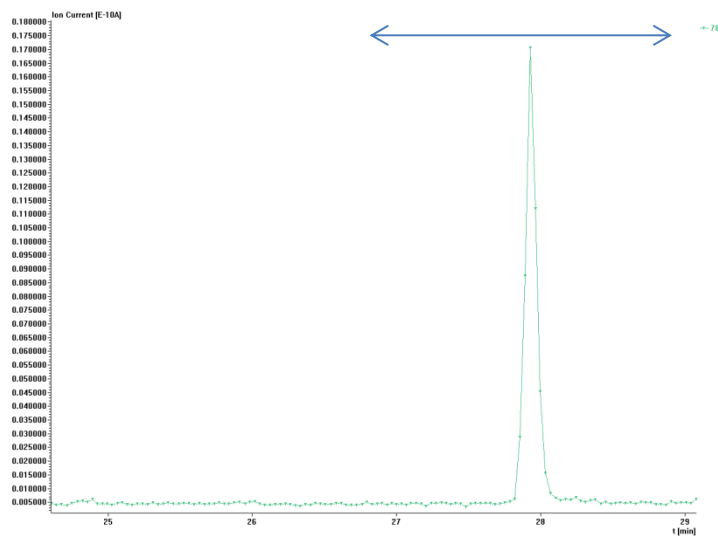
Benzene is not detected by the FID when the retention time has been changed

GC-MS/FID: RT

- Retention time measurement
 - MS: Seeking over one minute because ion 78 is specific to benzene
 - GC: 10 seconds because FID burns all molecules

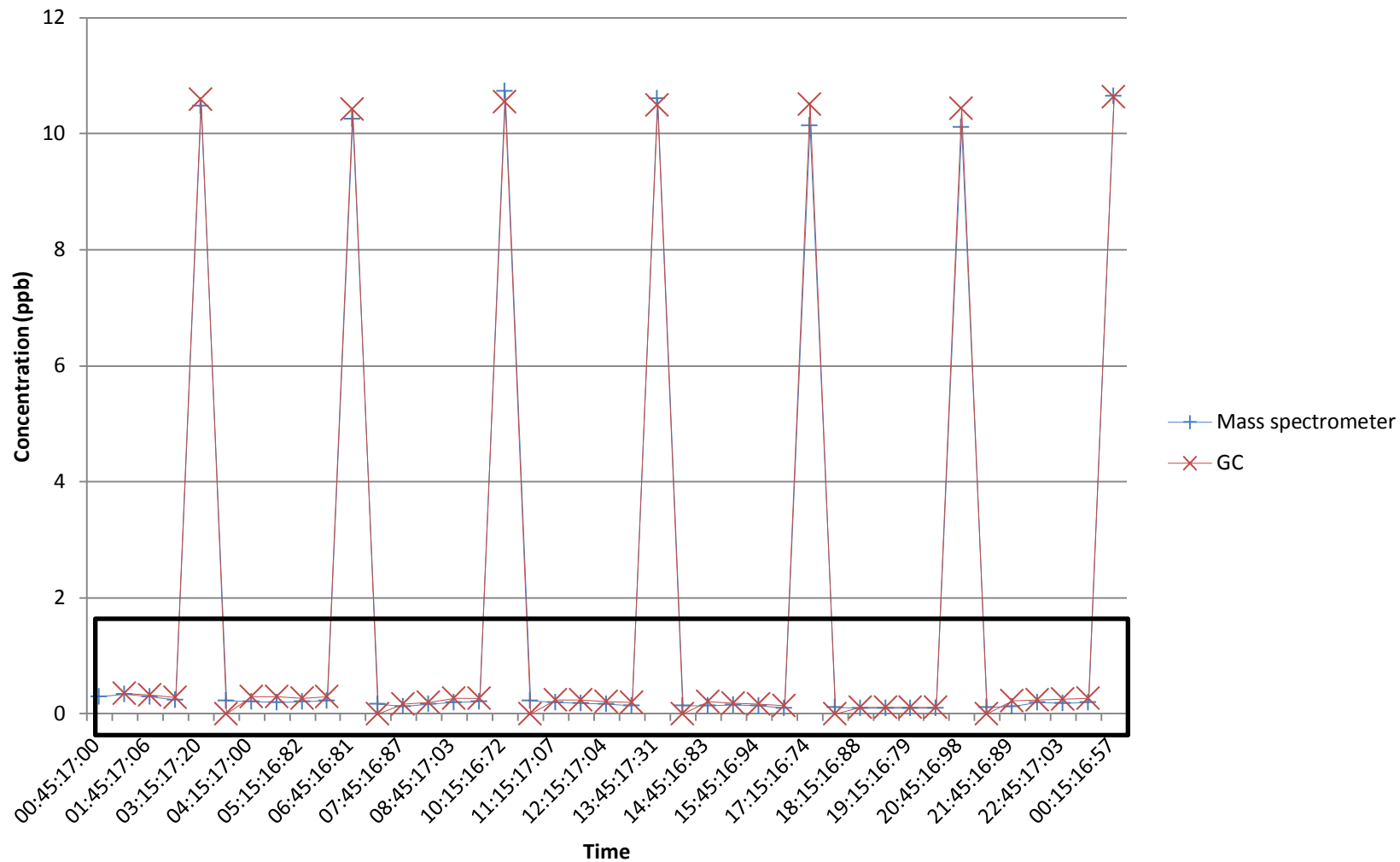


GC-FID

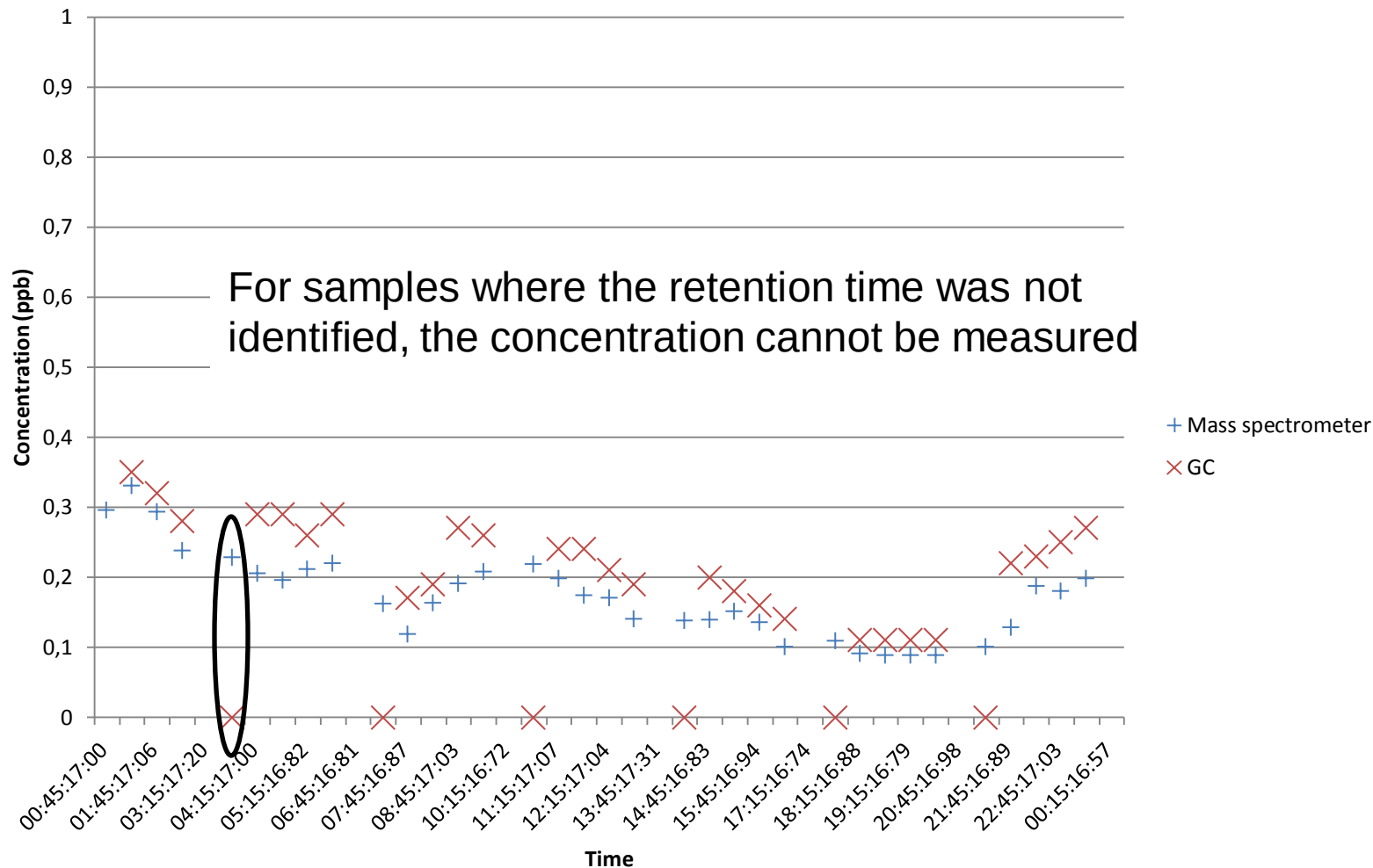


GC-MS

Measured Benzene concentration

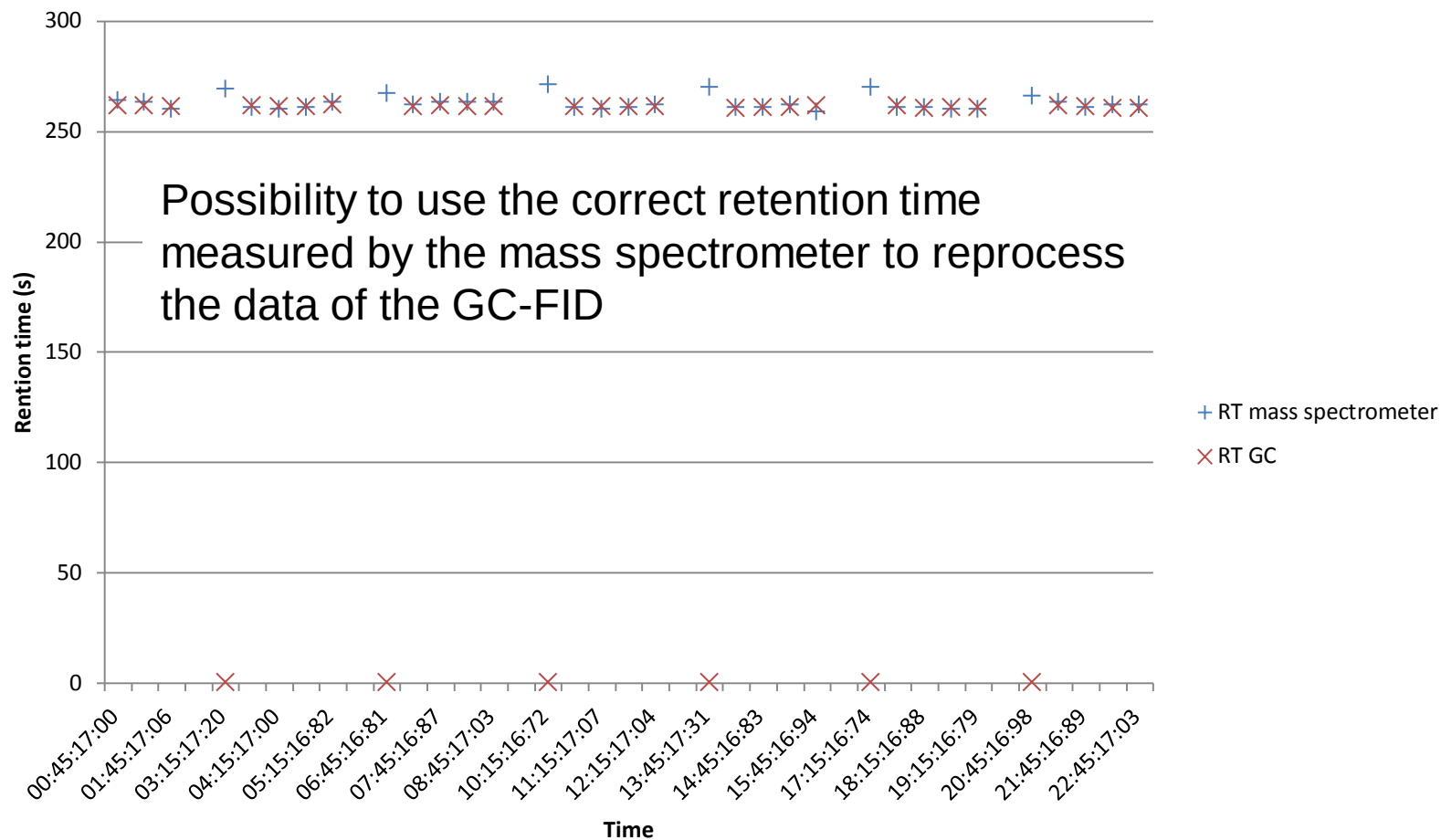


Measured Benzene concentration



One concentration not measured by the GC-FID

Benzene Retention times



Benzene is not identified by the FID when the retention time has been changed

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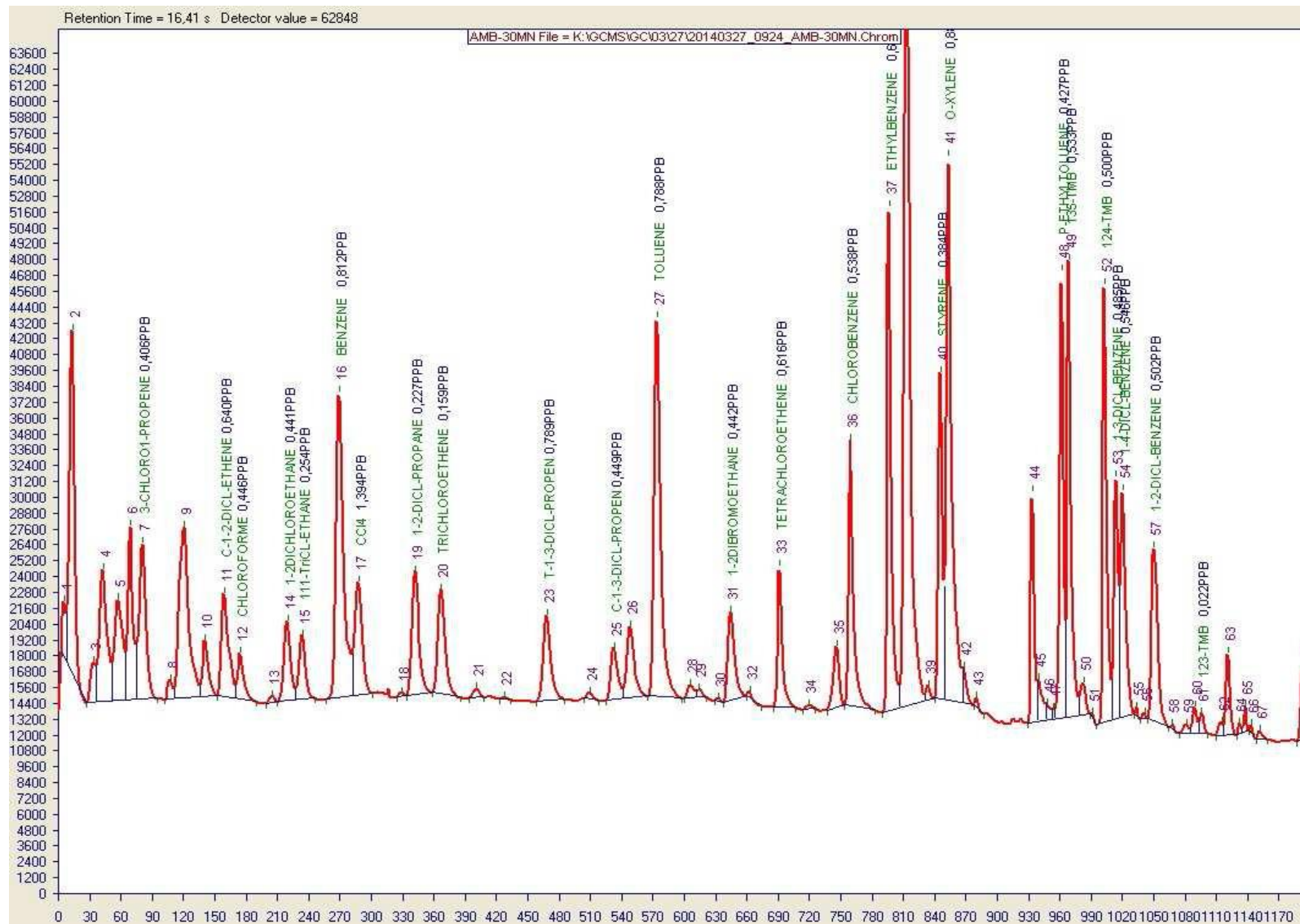
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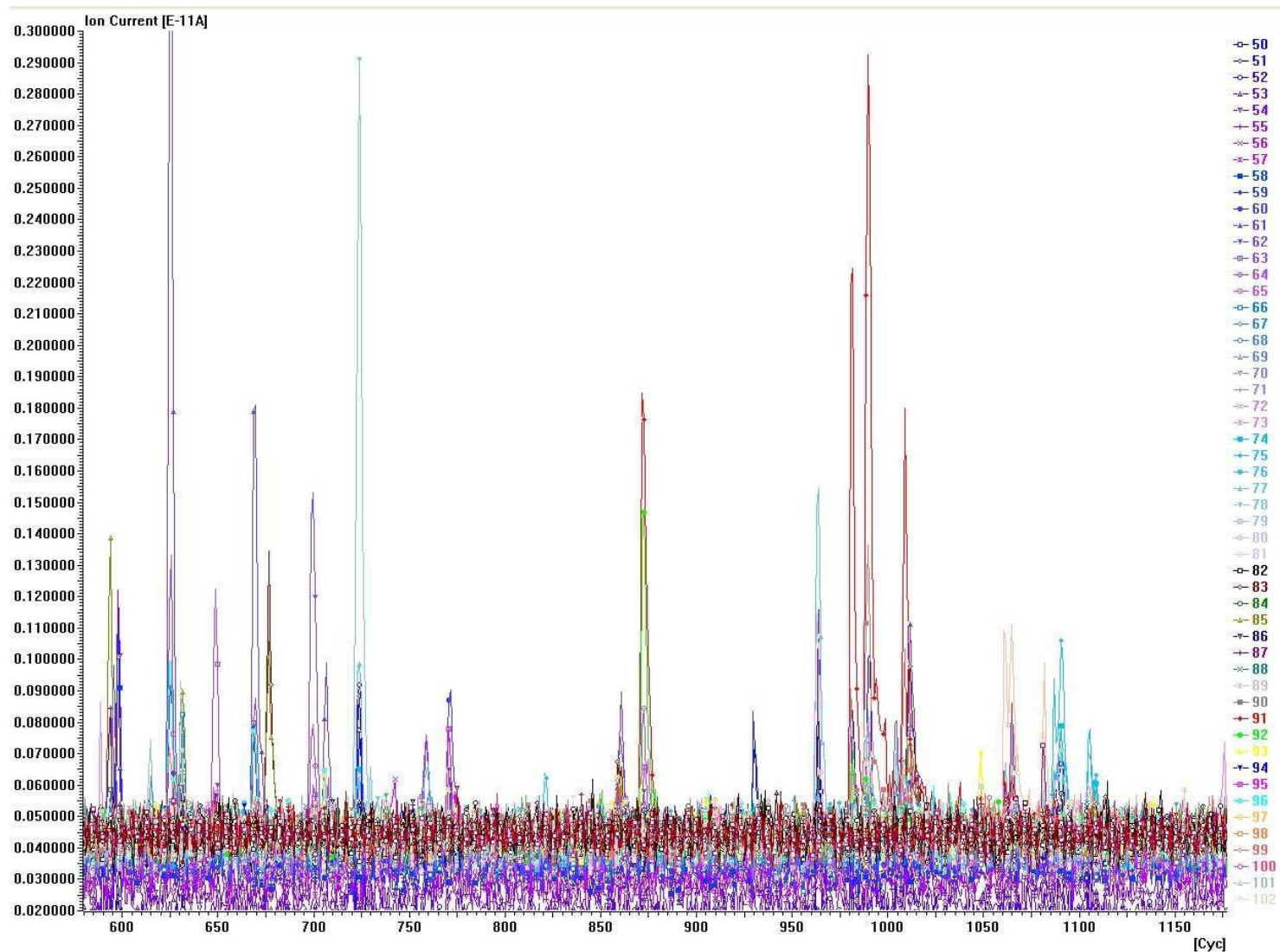
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- Quantification of co-elutions



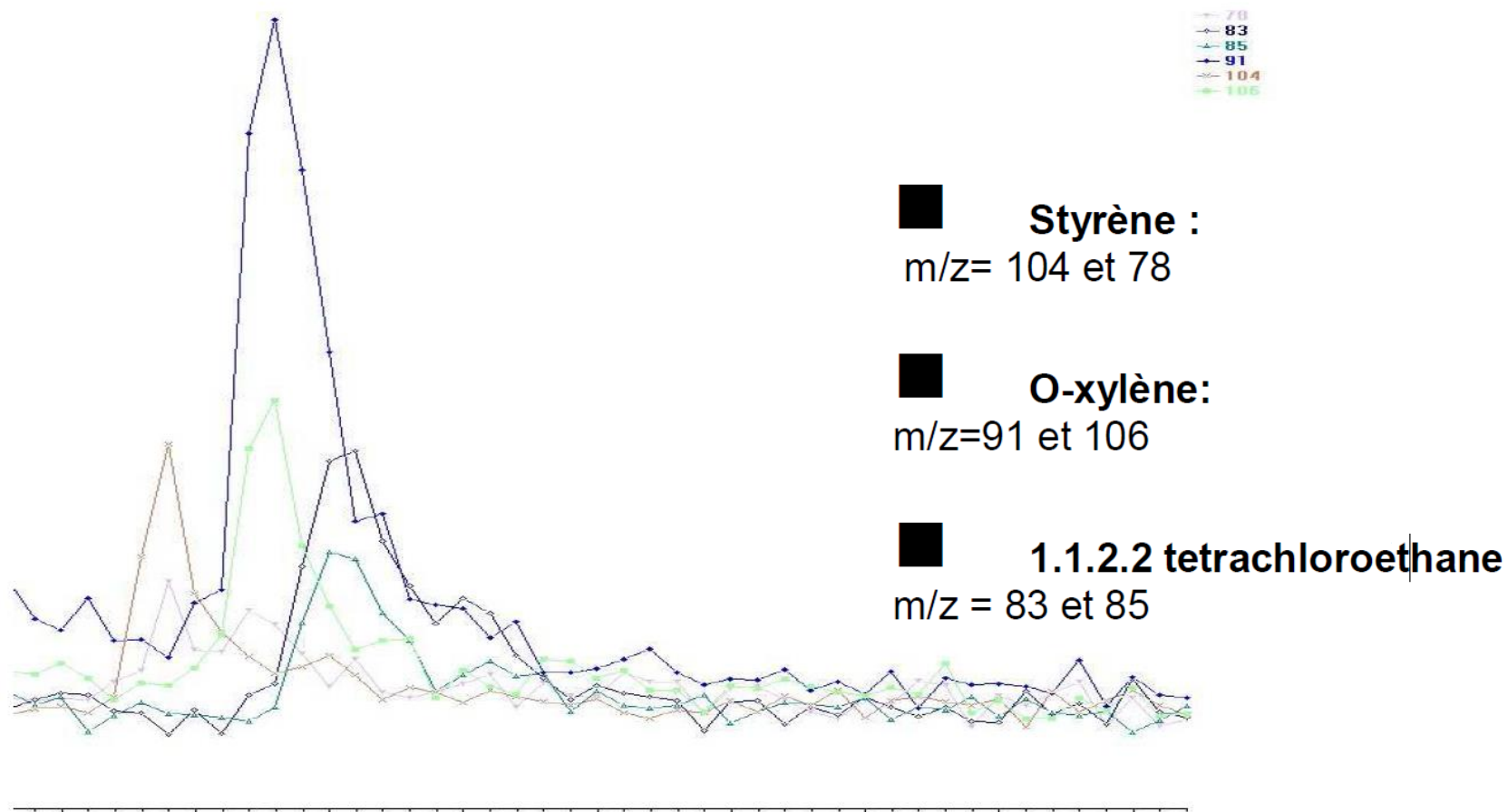
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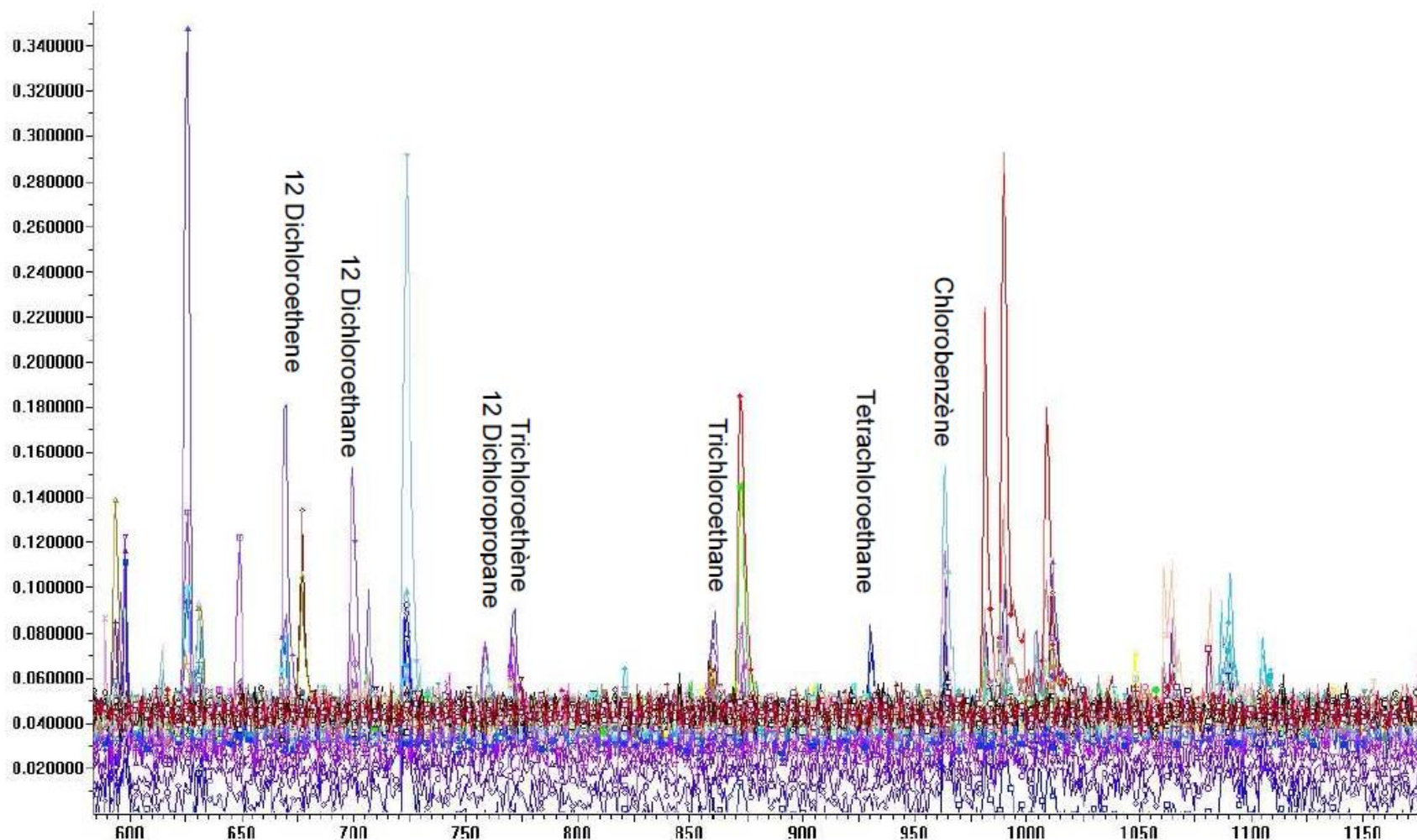
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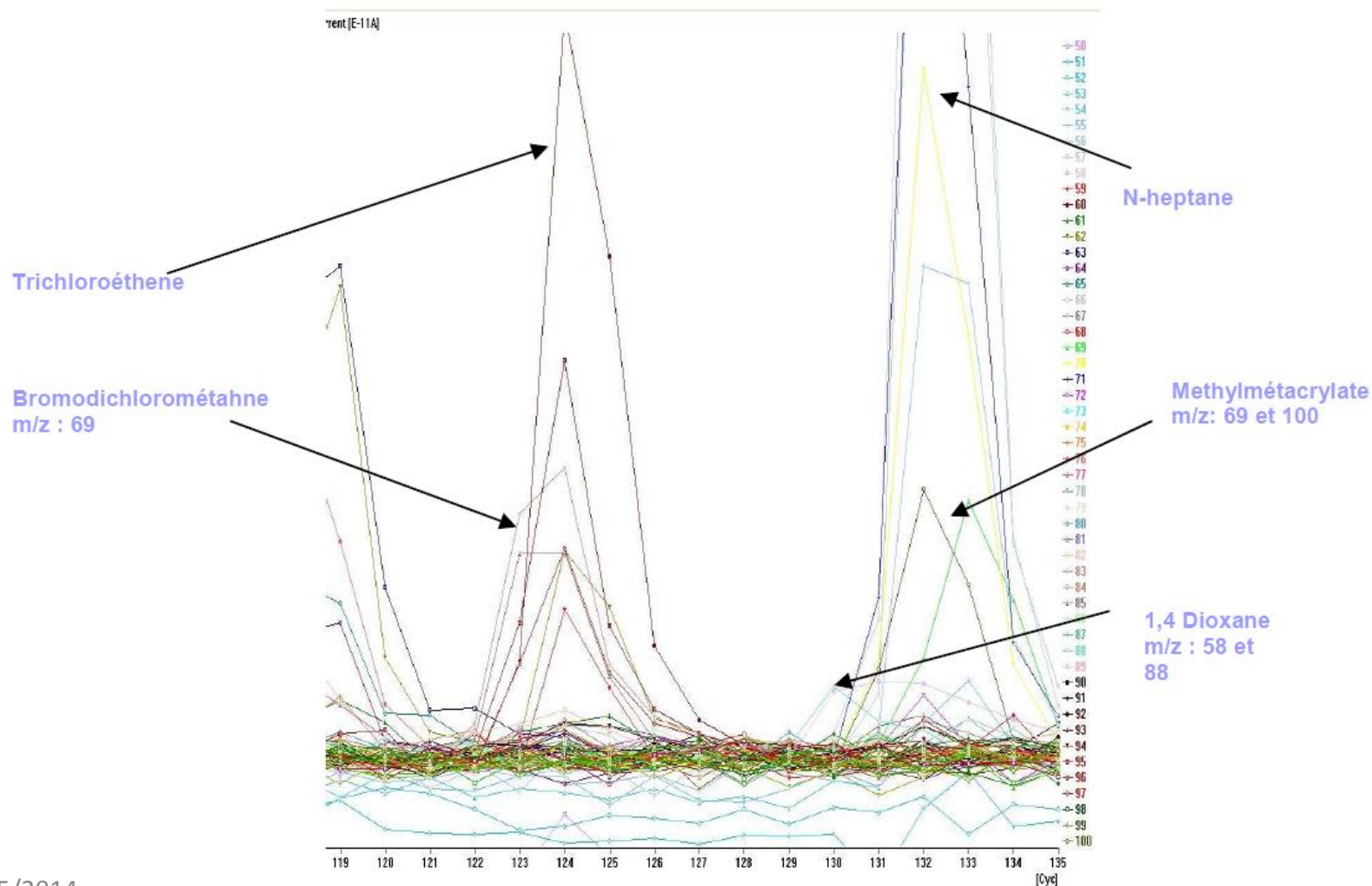


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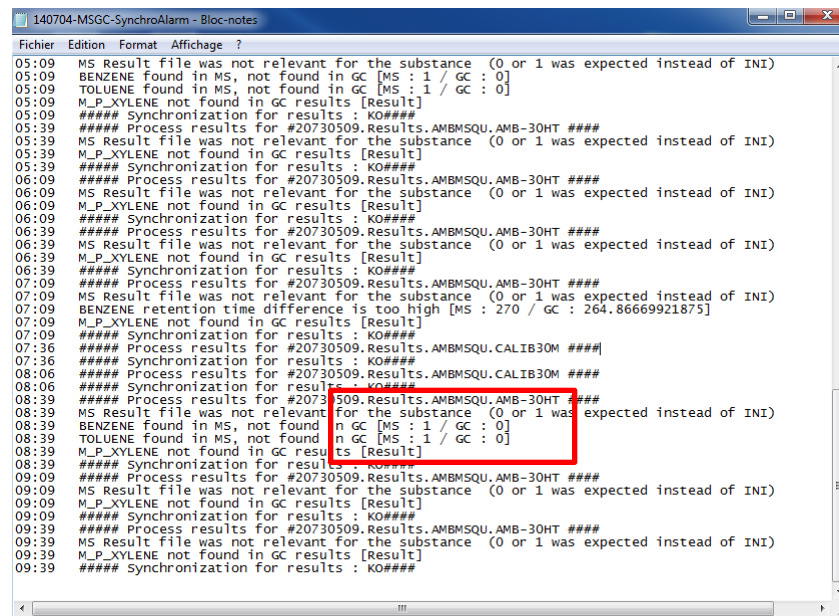
Quantification of co-elutions

TO15



Quantification of co-elutions

- Communication between mass software and vistachrom
 - Complementary information
 - Alarm systems for co-elution and modification of retention times



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09:09 MS Result file was not relevant for the substance (0 or 1 was expected instead of INI)
09:09 M_P_XYLENE not found in GC results [Result]
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09:39 M_P_XYLENE not found in GC results [Result]
09:39 ##### Synchronization for results : KO####
```

airmoTWA

- Quantification by
 - FID
 - Accurate for all compounds
 - MS
 - from ppt to %
 - No signal saturation
 - High degree of precision
- Automatic measurements
 - Automatic calibration
 - Calibration validation
- Retention times recorded by:
 - FID
 - MS
- MS records all RT even with very important RT modification
 - Easy data reprocess even with large number of molecules

Conclusion for airmoTWA

- Separation, identification and quantification of chemicals
 - Concentrations from ppt to %
 - In different matrix
- MS coupled with the TRAP GC FID
 - Start with GC analysis
 - Saves each chromatograph with time and date
- Flexible system
 - Easy to use for non-chemists
 - mCERTS certified for working 24h/24, 7d per week for > 3 month without operator maintenance



Applications

- Waste water treatment plant
- VOC from water
- Odor measurements and control





Thank you for your attention !