Why do you Need to Measure BTEX in Ambient Air?

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Accurate and reliable BTEX testing (Benzene, Toluene, Ethylbenzene and Xylenes) is critical in determining the levels of exposure and contamination in the environment. High levels of BTEX exposure can affect human health and the environment, which has resulted in a European Directive and with EPA guidelines to set allowable limits. The World Health Organisation (WHO) considers the exposure to Benzene (even at a very low concentration of part per billion) a major public health concern because human exposure to this VOC has been associated with a range of acute and long-term adverse health effects and diseases (severe effect to the central nervous system, severe damage to the liver, lungs and so on), including cancer and leukaemia. Occupational Safety and Health Administration (OSHA) recommendation for benzene exposure is very restricted and also the European air quality directive gives the limit value of 1.5 ppb for the annual mean. It also recommends to not exceed 1 ppm as time weighted average (TWA) or 5ppm for short term exposure limit over a period of 15 minutes. The carcinogenic (leukemogenic) potential of benzene is well established as indicated by its consensus classification as a human carcinogen by the National Toxicology Program (NTP 2001), US Environmental Protection Agency (EPA) (IRIS 2001), and International Agency for Research on Cancer (IARC 1987). Ethylbenzene is possibly carcinogenic to humans based on a recent assessment by IARC (2000). Toluene and xylenes have been categorised as not classifiable as to human carcinogenicity by both EPA (IRIS 2001) and IARC (1999a, 1999b), reflecting the lack of evidence for the carcinogenicity of these two chemicals. [1]

BTEX analysis gives a great indication of VOC emissions from an extended range of sources. The primary man-made sources of BTEX are via emissions from motor vehicles and aircraft exhaust, losses during petrol manufacturing, spills and cigarette smoke. BTEX are created and used during the processing of refined petroleum products and coal; during the production of chemical intermediates and consumer products such as paints and lacquers, thinners, rubber products, adhesives, inks, cosmetics and pharmaceutical products. BTEX compounds are among the most abundantly produced chemicals, with worldwide annual production of 8-10 million tons of benzene, 5-10 million tons of toluene, 5-10 million tons of ethylbenzene and 10-15 million tons of xylenes.

Benzene for instance, is commonly found throughout the petrochemical industry, vehicle exhaust and burning of solid and liquid fuels. It gives a great indication of the dominance of petrol vehicles in the vehicle fleet, and it is useful as an indicator for home heating emissions from solid fuels. As Benzene occurs naturally in crude petroleum at levels up to 4 g/l, human activities using petroleum (extraction and transport of crude oil, refineries, transport and use of gasoline) lead to exposure. Therefore personnel on on-board ships that transport crude oil or gasoline or on offshore platforms for well drilling and exploration, extraction, storing and processing petroleum are potentially exposed to those harmful VOCs.

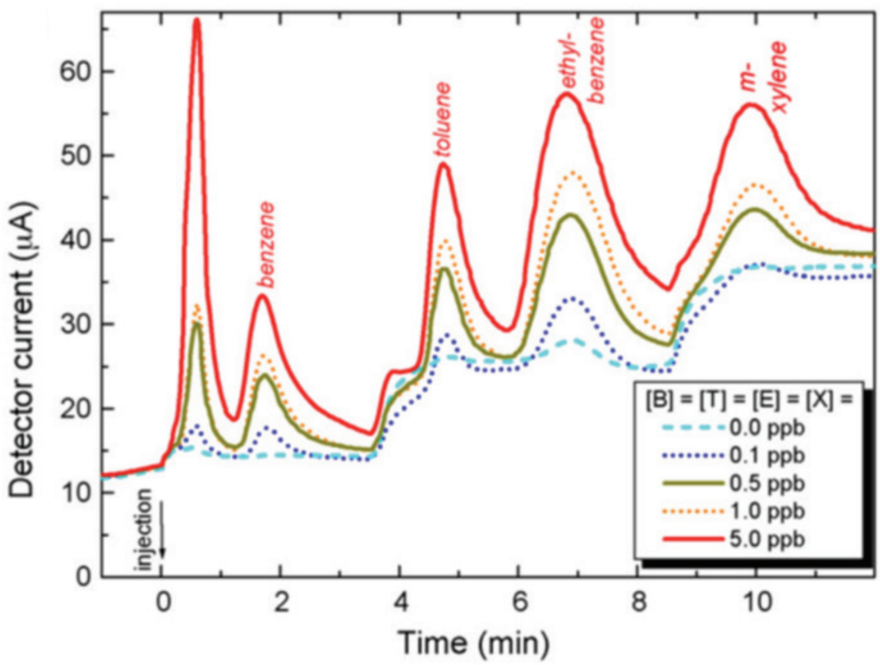


Figure 1: Calibration chromatograms at different span gas concentrations (0-5ppb).

So more generally, the BTEX chemicals are released into the environment either through emissions or leakages. In particular benzene has been recognised as the major source of fugitive emissions and it is very well known to cause cancer even at very low exposure limits.

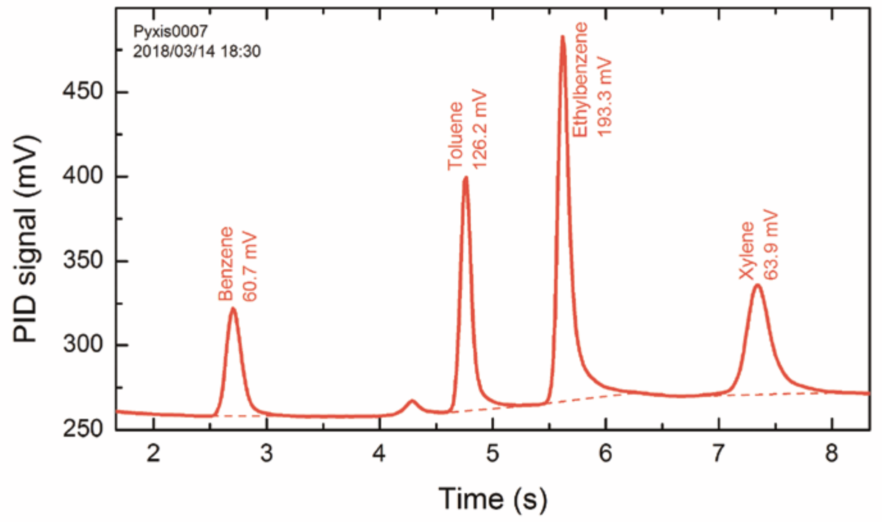


Figure 2: PID Signal for BTEX analyses.

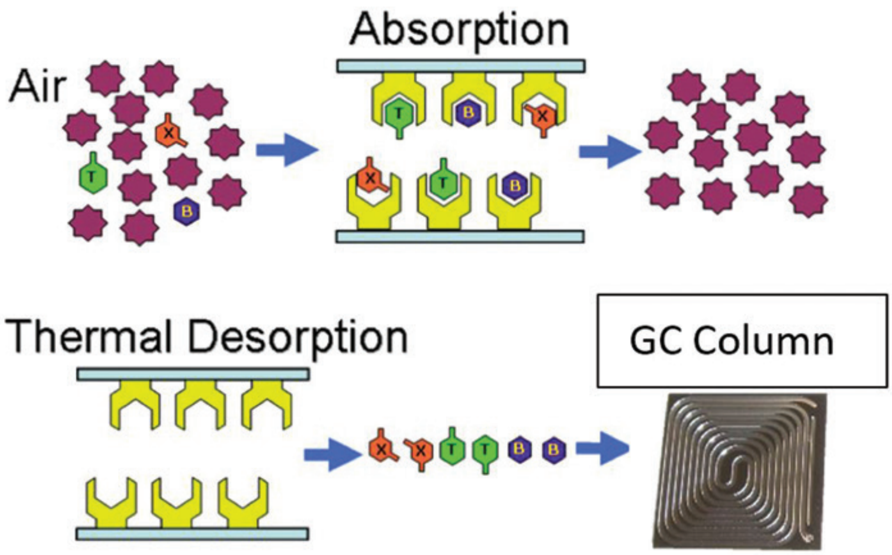


Figure 3: Pre-concentrator operation.

US EPA released Methods 325A and 325B especially designed for the refinery sector rules. These methods describe the use of passive absorbent tubes. In Europe the monitoring of benzene is also mandatory according to European Air Quality Directive - EN14662-3:2015.

The EN14662-3:2015 defines the standard method for the measurement of benzene concentrations. Part 3 of this legislation, in particular describes the use of automated pumped sampling with in situ gas chromatography. This standard specifies the performance characteristics and sets the relevant minimum criteria required to select an appropriate automated gas chromatograph (GC) by means of type approval tests. It also includes the evaluation of the suitability of an analyser for use in a specific fixed site so as to meet the data quality requirements as specified in Annex I of Directive 2008/50/EC [1] and requirements during sampling, calibration and quality assurance for use. The method is applicable to the determination of the mass concentration of benzene present in ambient air in the range up to 50 µg/m3 benzene. This concentration range represents the certification range for the type approval test.

At the moment, there are several technologies and sensors available for the detection of BTEX: each of them has advantages and disadvantages. PID (Photoionisation detection) is very sensitive to Benzene but not selective, therefore Benzene, Toluene and Xylenes cannot be distinguished – in fact the PID lamp usually responds to molecules with carbon double bonds and aromatics. Metal oxide sensors (MOX), are similarly not specific to individual organic compounds, and suffer from the lack of specificity, due to a range of potential interferences from other gases. In addition temperature and humidity can affect the results. Electrochemical detectors are another type of detectors that are not specific, like MOX and PID but can also suffer from a range of interferences. Gas chromatography, because of the intrinsic capability to separate each single component, is the best solution to selectively quantify BTEX. In fact, this approach allows for detection and quantification of BTEX compounds in a sub-ppb concentration.

To ensure the optimal performance, a GC requires the instrument to be operated by a trained and qualified technician. Most commercial GC instrumentation requires a reasonable amount of fixed footprint in a laboratory environment. It also requires a carrier gas, which will be derived from a generator or a gas cylinder, as a consequence traditional GC's are not the best solution for large network monitoring area.

Equipment developments since the early 1990's have provided on-site analytical instruments fine-tuned to the user's specific requirements (e.g. Pollution Analytical Equipment (PAE)). The PyxisGC BTEX by PAE for BTEX monitoring provides a miniaturised GC on chip that can work as a stand-alone gas chromatograph for real time environmental monitoring of aromatic hydrocarbons and other volatile compounds (VOCs). There is also a High-sensitivity PID - Photo Ionisation Detector (10.6 eV). The small size makes it more applicable than larger fixed instrumentation for use in remote location (i.e. industrial area) or urban installations. The system integrates miniaturisation with ease of use combining Micro-Electro-Mechanical-System (MEMS) microfluidics for selective pre-concentration and GC separation using a micro column on a chip.

The miniaturised GC, specifically the micro column on a chip, allows for substantially reduced gas consumption, and it also allows for continuous automonous operation over long periods of time. When the miniaturised GC-PID is switched on, the module operates in sampling mode, i.e. the sampling pump provides a constant flow of sample through the pre-concentrator, while at the same time the GC pump cleans the separation column using ambient air as carrier gas.

After approximately 10 minutes, the preconcentration column is connected to the GC pump and heated to 100°C: the

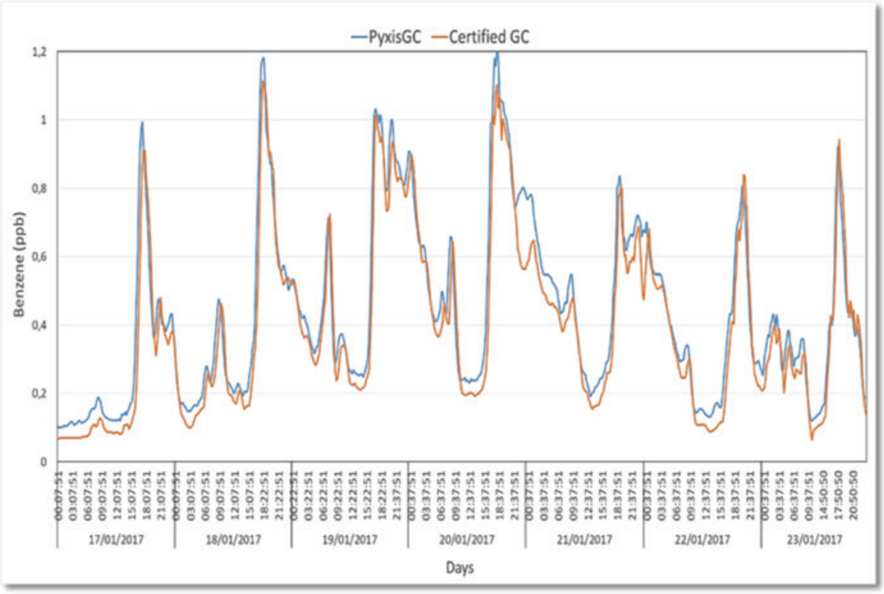
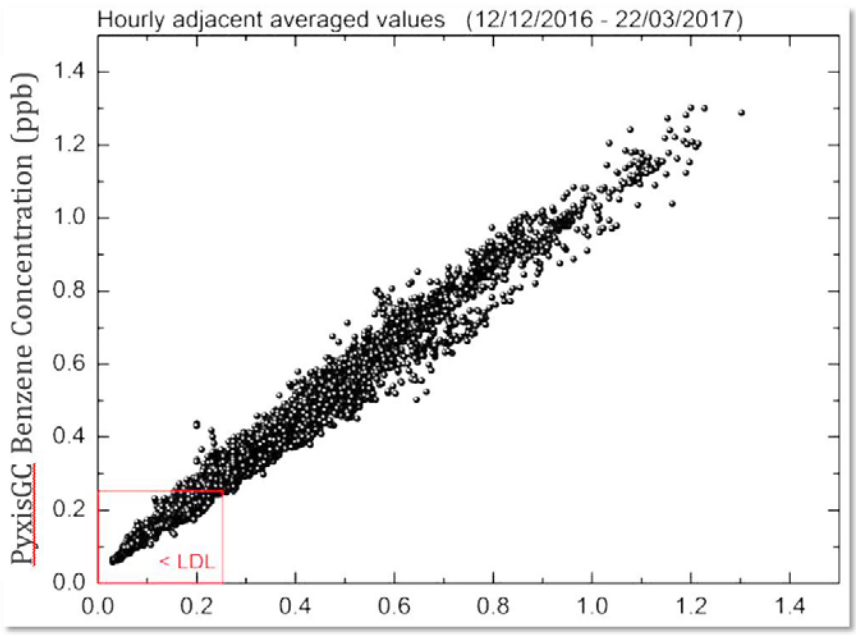


Figure 4: Example of several days field measurement of Benzene versus certified GC system.



Figures 4 and 5 show chromatographic results of a field campaign over several days of continuous monitoring where we evaluated the performance against a reference instrument System. A good match is shown between the trend of the two measurements. This has also been verified in a long term field campaign lasting 3 months. In the correlation plot is important to highlight the fact that it is a comparison between two different systems, where the reference system requires an external cylinder with inert carrier gas, temperature controlled cabinet for the installation and periodic maintenance.

The other instrument (PyxisGC BTEX) does not require a carrier gas.

adsorbed BTEX gases are then released and consequently injected into the GC column for separation.

For 15 seconds, the 2 pumps work in series and ambient air is used to wash out the pre-concentrator. After the injection, the flow is switched again into sampling mode, while the PID sensor acquires the signals of the separated components as they elute from the column. This means that during the column elution, another sample is concentrated in the pre-concentrator. The whole cycle has a duration of 15 minutes. The area of each peak is proportional to the average concentration of the compound, as sampled during the collecting time of approximately 10 minutes. The remaining 4 minutes are used for the pre-concentrator cleaning, between successive measurement cycles.

The linearity of calibration function of the miniaturised GC has been tested in the range 0.30-50ppb for benzene using six concentrations (including the zero point). The performance characteristic complies with the performance criteria requested by EN14662-3:2015.

The pre-concentrator is made in micro-machined edged silica filled with a tailored supramolecular receptor, capable of complexing selectively with only BTEX (Figure 3). Heating the system, causes those BTEX components to be desorbed and then funnelled to the separation unit.

The separation column is a short spiral channel with a thin cross section that was etched into a silica wafer and filled with specific stationary phase. The small form factor of the miniaturised GC-PID assists with simplification in the analysis process.

A possible application would be the installation of the miniaturised GC-PID onboard ships and platforms: it can effectively monitor the air quality in the surrounding area. A network of several miniaturised GC-PID can be also installed along the perimeter of refineries in order to monitor the boundary compensating false results affected by the wind. Results data can be viewed through Guardian Cloud software. It is easily accessed via browser on your phone, tablet or PC. Pollution Guardian stores up and archives analysis data automatically, it allows the real time data and the historical data viewing (with creation of charts, tables, graphs and other statistical analyses). Pollution Guardian allows to set user-defined alarms on the data collected and to send notifications via SMS or email, if there is alarms of VOCs leakages or spillages to activate the procedures for remediation. In addition, push notifications on your smartphone are also available, thanks to the dedicated APP. Thanks to the Cloud it is possible to manage the instrument and the data: the remotely diagnostic has never been so simple.

References

1. INTERACTION PROFILE FOR: Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) U.S. Department of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry) (https://www.atsdr.cdc.gov/interactionprofiles/ip-btex/ip05.pdf -