CYLINDER-FREE PROCESS GC WITH AUTOMATIC HEADSPACE SAMPLING SYSTEM FOR VOC ANALYSIS IN LIQUID MATRICES

Gas chromatographs are used in process analytical chemistry for a variety of different purposes. One of its tasks is to periodically analyse chemical or biological processes in order to identify and quantify toxic compounds or to monitor the quality of process streams. In this scenario, the systems can be operated in laboratories by trained personnel. The samples are collected from the process and brought to the lab. Another use is to improve process efficiency and control using automatic on-line continuous monitoring. In this case, the analytical instrument should provide sufficient selectivity and work autonomously and reliably. In addition, the instrument has to be robust and can work for long periods of time without maintenance.

Among the different gas chromatograph sampling systems, the headspace systems are commonly used for the analysis of monomers and polymers2, for volatile components in drinks3, for blood alcohol4, for water and environmental analysis5 and for cosmetics6. In the pharmaceutical industry, headspace gas chromatography is widely used to determine solvent traces in active pharmaceutical drug substances1. This technique is a preferred method because it enables the analysis of low-molecular-weight compounds which can migrate to the vapour phase, while other compounds remain in the liquid phase. This is especially beneficial when high-molecular-weight species react or condense in the analytical column. The headspace systems are an efficient way to separate these species from the sample being analysed in the gas chromatograph.

In Static Headspace Extraction (SHE), a liquid is usually introduced into a sealed container by an operator after which the analyte vapours can be transferred to the gas chromatograph using a gas tight syringe. In this piece, we present a SHE gas chromatograph which can sample, automatically and continuously, direct from the process itself without human intervention. The system can identify, quantify and then send results to a control process engineer. Moreover, the system does not need cylinders because it is equipped with embedded pure gas generators (hydrogen and air) as well as an autonomous calibration system. The integrated multiplexing system allows the analysis of unknown gaseous samples, reference cylinders, embedded calibration (permeation tubes) and samples from the SHE system. Analyses can be performed automatically by the system without operator supervision for sampling, analysis, data treatment or system cleaning.

Chromatotec® solutions

Chromatotec Group® specialises in the manufacturing and development of autonomous gas analysers based on automatic Gas Chromatography (autoGCs) technology for online monitoring. The turnkey solutions provided enable automatic tracking of VOCs at very low concentration levels (from ppt – using preconcentration tubes) as well as high concentration levels (ppm to % level – using loop injection system) in the event of large-scale industrial pollution. Chromatotec® has many decades of experience in developing new turn-key solutions for gas analysis at industrial sites to satisfy the specific needs of customers needing a fully automatic system.

The headspace chromaFID analyser is a loop injection gas chromatograph equipped with a Flame Ionisation Detector (FID) and two apolar columns. The first column, also called the 'pre-column', will permit only very light compounds to migrate into the analytical column. During each cycle, the pre-column is backflushed (carrier gas travels in the opposite direction of the injection) and heated at high temperatures to ensure that all the compounds are eluted. The analytical column is installed into a temperature-regulated oven at a very stable temperature to obtain repeatable retention times (the temperature can be controlled from 32°C to 200°C). The embedded multiplexing system allows the analysis of gaseous samples (ambient air, process gas and calibration) as well as gaseous samples generated by the headspace sampling system.

The SHE sampling system is installed in an external enclosure and can analyse two liquid streams (Figure 1). Only 15 ml/min are required to obtain enough of a sample for analysis. Deionised water is also connected to the sampling system to automatically perform the cleaning procedures within the apparatus. In normal operation, the liquid goes through a 5 ml sampling loop. Then the liquid is injected into a glass container which is pressurised at 1 bar(r) and kept at a constant temperature (pressure and temperature can be operator-defined depending on the application). During this step, the volatile analytes originally present in the solvent, will be distributed between the liquid and the gas phase. Most extraction and chromatography theory is based on the assumption that the system is at equilibrium. Failure to bring the system to equilibrium is one of the most common causes of problems with reproducibility in extractions1. To solve this problem, the glass container showed in the Figure 2, has been equipped with very accurate pressure and temperature regulation systems to improve the repeatability of the sampling system. Additionally, all parameters are controlled, displayed and recorded directly in the software (Vistachrom).

The fully integrated air generators (airmopure, Chromatotec, France) with dew point below -40°C and hydrogen generators (99.9999% purity) with dew point below -15°C (Hydroxychrom, Chromatotec, France) are used for FID flames and the carrier gas and the valve actuators of the chromaFID Headspace. VOC gas concentrations of below 0.1 µg/m³ were generated by both generators and were verified experimentally using auto-thermal-desorption gas chromatographs equipped with a flame ionisation detector.

Figure 1: The headspace chromaFID analyser

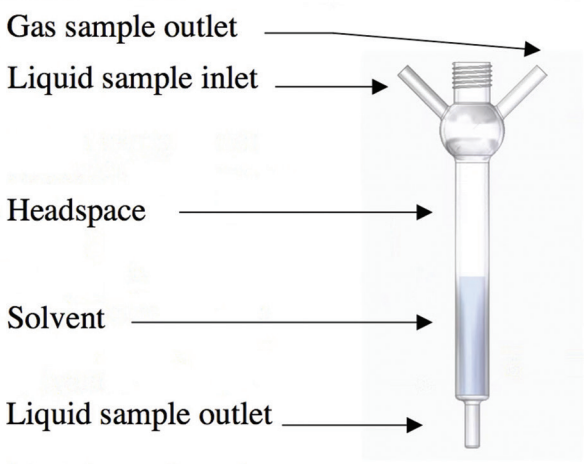

Figure 2: Schematic representation of the glass container for SHE analysis.

Gas analysis and liquid measurements

Initially, the analytical system was tested for the measurement of gaseous samples without a SHE sampling system. Samples containing benzene at concentrations ranging from 0.65 to 3.09 mg/m³ were injected into the system (0.20 to 0.95 ppm). The linearity curve obtained is displayed in Figure 3. The linearity is excellent with R2≥0.9997.

For each concentration, five measurements were performed. For all points, we obtained RSD < 3%.

The analytical system was then tested during the measurement of liquid samples with a SHE sampling system. A sample containing benzene at concentrations ranging from 5 to 100 mg/L was injected into the system (5 to 100 ppm(W/W)). The linearity curve obtained can be seen in Figure 3. Again, the linearity is excellent with R2≥0.9997.

For gaseous analyses, the typical cycle time is 20 minutes which can be reduced to 5 minutes, depending on the sample to be measured. The liquid analysis usually requires 30 minutes. This includes: sampling, liquid injection, system equilibrium (which can vary depending on the sample), headspace injection, separation in the analytical column, detection and quantification and finally, cleaning of both the pre-column and the SHE sampling system.

In this example, we used only benzene for the characterisation, but the number of molecules to be analysed can be increased to as many as 123. Also, a quadrupole mass spectrometer can be added to the system to identify unknown compounds, either after the chromatographic column or from direct measurement.

Conclusion

The headspace chromaFID analyser is a fully-automated analytical system which enables the on-line analysis of gaseous and liquid samples. The system requires little maintenance because all cleaning procedures are performed automatically by the system. Only the Hydroxychrom's water level, for H2 production, has to be checked monthly. Data, alarms and parameters of the analytical system can be transferred using all the recognised types of communication protocols used in the industry. Depending on the sample, the cycle time varies from 5 to 30 minutes. All generators needed for the operation of the gas chromatograph are integrated into the analytical system. The operator needs only to provide an electricity supply and deionised water to run the system continuously, 24 hours a day, 7 days a week.

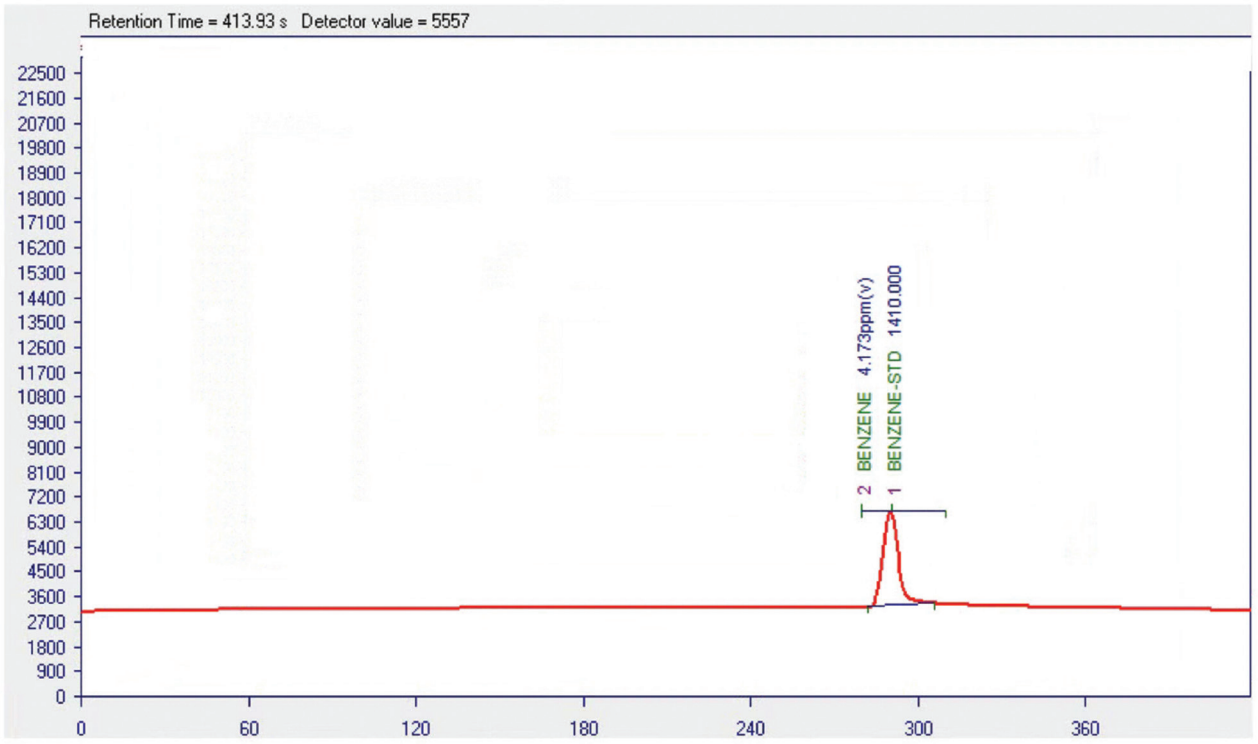

Figure 3: Area measured as a function of the injected concentration (mg/m³) for each gaseous sample.

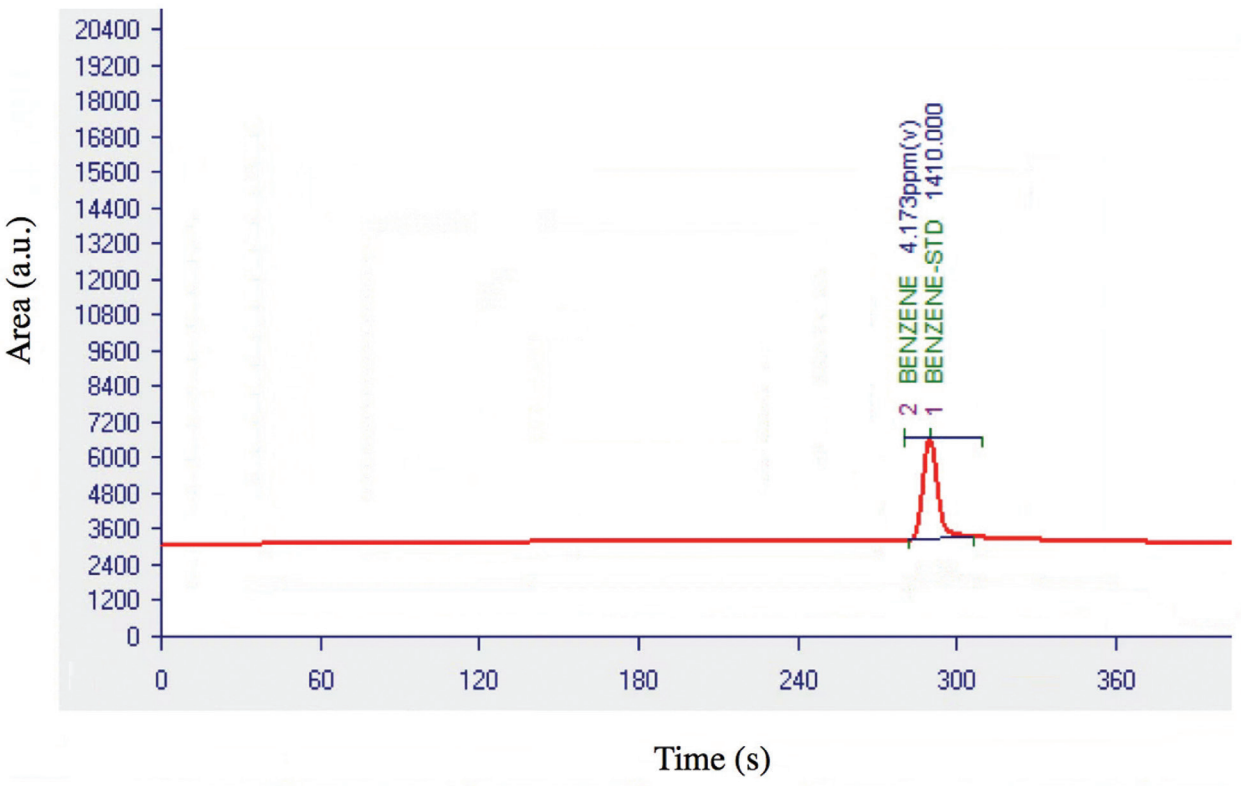

Figure 4: Area measured as a function of the injected concentration (mg/L) for each liquid sample.

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