CONTINUOUS ANALYSIS AND MONITORING OF VOCS IN WATER AND WASTEWATER SAMPLES FOR INDUSTRIAL PROCESSES

Introduction

Today more than ever, environmental health is of great concern to everyone, from politicians and scientists to the general public. All organizations must recognize the importance of protecting our ecosystems. Prosecution for polluting the environment cannot only lead to expensive fines, but can also result in a company's image and subsequent devaluation.

Water utility companies, industries with their own wastewater treatment plants, and petrochemical industries are recognizing the importance of pollution control. These organizations are investing in high-detection technologies and monitoring equipment, not only for clean water intake, but also for wastewater treatment that ensures water quality is acceptable before it is returned to nature.

Figure 2: Purge and Trap system

Figure 1: airmoVOC WMS

Analysis of trace level VOCs in water using airmoVOC WMS
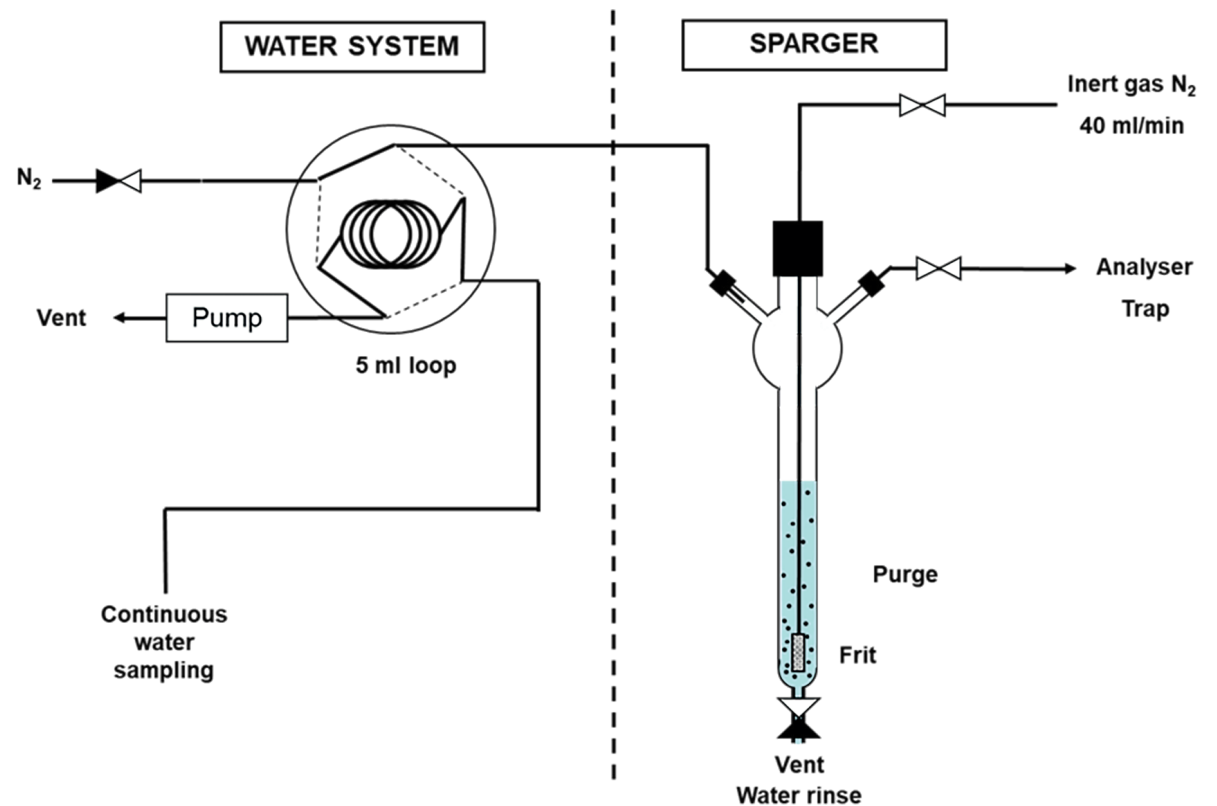
VOCs contribute up to 10% of the total dissolved organic carbons in relatively unpolluted water and represent a much greater proportion in water used for industrial processes (Huybrechts et al., 2003). There are numerous analytical methods for the characterization of VOCs in water and liquids that have been reviewed by Chary and Fernandez-Alba, 2012. The analysis of dissolved VOCs in wastewater, drinking water and liquids from industrial processes is not a simple issue due to the complexity of the matrix in which there are present and also by the range of concentrations to be measured. To ensure water quality and to help regulating industrial processes, cost-effective continuous automatic monitoring systems are needed.

With a long history in gas chromatography, Chromatotec® provides several analytical solutions, including liquid sample handling for the measurement and quantification of VOCs and BTEX (Benzene, Toluene, Ethylbenzene and Xylene) in liquid samples. The airmoVOC WMS (Figure 1) is an Mcerts-certified gas chromatograph that has already proven its suitability for VOCs and BTEX analysis in liquid samples. Depending on the concentration range of the sample, the solution can be tailored to accommodate from µg/L to g/L concentrations. In this paper, we describe three different technics for the measurement of dissolved VOCs in drinking water, wastewater and industrial solvents.

The analysis of VOCs at a trace level in water is performed using an automated thermodesorption gas chromatograph equipped with a flame ionization detector (auto-TD-GC/FID) and a specific sampling system following the US EPA 502.2 method, for the extraction of VOCs from water liquid sample (Purge and Trap).

The Purge and Trap system consists of an automatic sparger to extract VOCs from liquid samples in 11 minutes (Figure 2). The loop is filled with 5 ml of the liquid sample by a pump and then
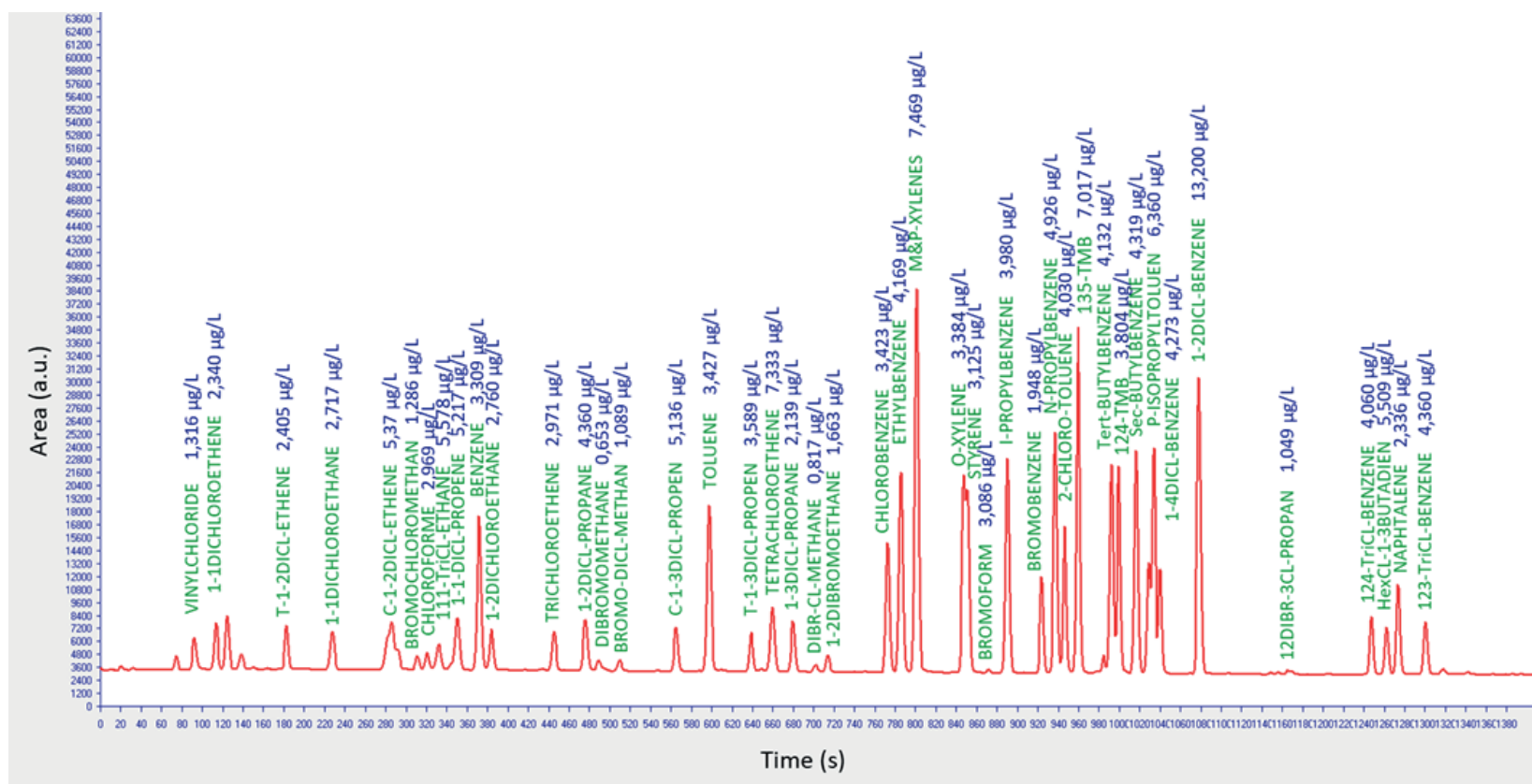
Figure 3: Chromatogram obtained with auto-TD-GC/FID coupled with Purge and Trap sampling system for the analysis of 502.2 standard solution.

injected inside this glass purging device. An inert gas (nitrogen) is used to purge the water sparger with bubbles of less than 3 mm of diameter at the origin of the frit. The gas is then injected into the gas chromatograph for pre-concentration and analysis.

For each analysis, 385 ml of gaseous sample is drawn into the auto-TD-GC-FID at a flow rate of 35 ml/min (sample is integrated over 11 min). The VOCs were pre-concentrated at room temperature in a trap filled with Carbopack. The pre-concentrated sample was thermally desorbed at 380°C for 4 minutes and directly injected in a 30 m MXT 624 column (0.53 mm ID, 3.0 um dF) located inside the heated oven of the GC. VOCs were then detected by the FID and the detection limit has been determined to be less than 5 ng/L.

The liquid samples were prepared using 502.2 standard solutions with a concentration of 2000 µg/ml diluted in water to reach 4 µg/L. The chromatogram obtained can be seen in Figure 3. The column gradient has been optimized to achieve a very good separation of the VOCs included in the 502.2 standard solutions. The Purge and Trap system allows the evaluation of the efficiency of the GC and the liquid sampling system by performing twice the analysis of the same sample and also by comparing the theoretical injected mass and with the experimental measurements. The result of this experiment shows that 100 % of the dissolved VOCs in the liquid were transferred from the Purge and Trap system to the auto-TD-GC-FID and were analyzed and quantified.

Analysis of ppm to % VOC concentrations in water using airmoVOC WMS

The 502.2 method has been developed for the analysis of trace-level VOCs in water (ppt and ppb level). However, water used for industrial processes (refinery, wastewater treatment plants) may contain very high VOC concentrations (mg/L). Therefore, a specific sampling system has been added to the Purge and Trap system for the analysis for VOCs in ppm range.

Before injection into the sparger, 50 µl of the sample is withdrawn into a 1 ml automated syringe. Then 950 µl of pure deionized water is withdrawn and injected into the sparger. After that, 4 ml of water will be added to reach 5 ml of liquid in the sparger. The dilution before analysis decreases the concentration by a factor of 100 and reproduces the conditions described in the 502.2 method. The sample is then analyzed following the procedure described in the previous section.

The analytical system allows very good separation and quantification of the dissolved BTEX. The same sample was twice analyzed to check that the purge was 100% efficient. The linearity has been studied and a correlation coefficient superior to 0.99 was obtained for all BTEX.

Analysis of VOCs using a headspace sampling system

Industrial processes often used more complex matrices than just water. In such a case, the Purge and Trap system cannot be used: if the matrix components are extracted from the liquid, they could saturate the trap. Chromatotec has designed a specific liquid sampling system comprised of a pre-concentration module (AirmoCAL) containing a dynamic headspace module.

An automatic gas chromatograph (chromaFID) equipped with a flame ionization detector (FID) has been used for the monitoring of linear alkanes containing from 6 to 11 carbon atoms in a water/ triethylene glycol mixture. The Purge and Trap system cannot be used with triethylene glycol because the trap would be saturated.

The liquid sample flows inside the stainless-steel headspace vial. Then, the carrier gas goes into the vial and collects the analytes. The gaseous sample is sent into a 100 µl sampling loop and then injected in the GC system. This system was designed in a specific backflush mode, called CP backflush, to prevent potential matrix impurities to go into the analytical column. The CP backflush includes a 2 m MXT30 CE pre-column (0.28 mm ID, 1.0 µm dF) and 28 m MXT30 CE column (0.28 mm ID, 1.0 µm dF) located inside the heated oven of the GC. Alkanes from n-hexane to n-undecane were detected and quantified by a FID from ppm to % levels.

Conclusion

In this paper, three different analytical methods for continuous and automatic measurement of VOCs in liquids were presented. First, the airmoVOC WMS is designed for the quantification of trace-level VOCs in water. For higher VOCs concentrations, a specific dilution module was added. For samples composed mainly of organic molecules (alcohol, oil), the dynamic headspace module is better suited. For aqueous samples, the Purge and Trap system is preferred (with or without the dilution module) for two reasons: first, the analytical performances (linearity and stability) are better for purge systems than headspace systems. Then, the headspace can be very sensitive to matrix effects because the solubility of the VOCs will be affected.

All three systems can be fully autonomous thanks to our gas generators: nitrogen, hydrogen and zero air. An internal calibration system can be added to validate the results. The integrated multiplexing system allows the analysis of unknown gaseous samples, reference cylinders, embedded calibration (permeation tubes) and samples from the Purge and Trap system. The instrument is enclosed in a robust housing and can work for long periods of time without maintenance. The main goal is to improve process efficiency and control using automatic on-line continuous monitoring with little, if any, human interaction. These characteristics make these systems perfectly suitable for measurements in industrial contexts.

References

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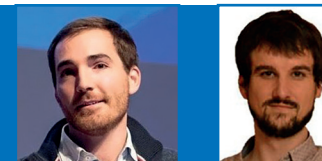
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