CONTINUOUS MONITORING OF VOCS IN WATER AND WASTEWATER FOR ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS

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 can not only lead to expensive fines, but can also result in a company's image and subsequent devaluation.

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

In cases where hydrocarbon pollutants are involved, instruments capable of measuring VOCs at an early stage can prevent and reduce the impact on the environment as well as mitigating the costs related to the cleanup process. There are several VOC detection methods already available in the market that are simple to use and that require very little maintenance and calibration. Most of VOC detection technologies are designed for ambient air monitoring, but some high-profile companies have developed similar solutions for liquid analysis.

With a long history in gas chromatography, Chromatotec® has now launched an analytical system, the airmoVOC WMS, that incorporates liquid sample handling and has already proven its worth. This unique and efficient Mcerts-certified gas chromatography solution measures and quantifies VOCs and BTEX (Benzene, Toluene, Ethylbenzene and Xylene) compounds dissolved in liquid matrices.

This unique instrument is comprised of several components, the most important of which is its purge and trap (P&T) system. This analytical tool, developed internally follows the US EPA 502.2 method and consists of an automatic sparger that extracts VOCs from liquid samples in 11 minutes. The loop is filled with 5mL of the liquids sampled using a pump and then injects them into a glass purging device. Pure nitrogen is produced by an integrated gas generator and is used to purge the water sparger with bubbles of less than 3mm of diameter at the origin of the frit (Figure 1).

In general, the P&T technique is applied to analyze low-molecular-weight (C_2-C_{12}) compounds which can migrate to the vapor 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. P&T is the most frequently used method for the extraction and concentration of VOCs in water thanks to its high sensitivity and reduced matrix effect.

The gaseous sample extracted from the liquid matrix is then injected automatically and in continuous mode into the system with a flow rate of 40mL.min^{-1}, regulated by a critical orifice of 76µm. The sample passes first through a dryer to remove the humidity and then hydrocarbons are pre-concentrated on a trap filled with a mixture of Carboxen and Carbopack. The pre-concentrated air sample is thermally desorbed at 380°C for 4 minutes and directly injected into a metallic capillary column located inside the oven of the GC. The column is temperature-regulated at a very stable temperature to obtain repeatable retention times. Within the first minute of the analytical procedure, the oven temperature rises from 32°C to 34°C. Afterwards, a constant heating rate increase of 7°C.min^{-1} is applied until reaching 100°C, followed by a 10°C.min^{-1} until reaching 200°C. The temperature is then kept at 200°C for 600s before cooling. Hydrocarbons are detected by FID at 170°C.

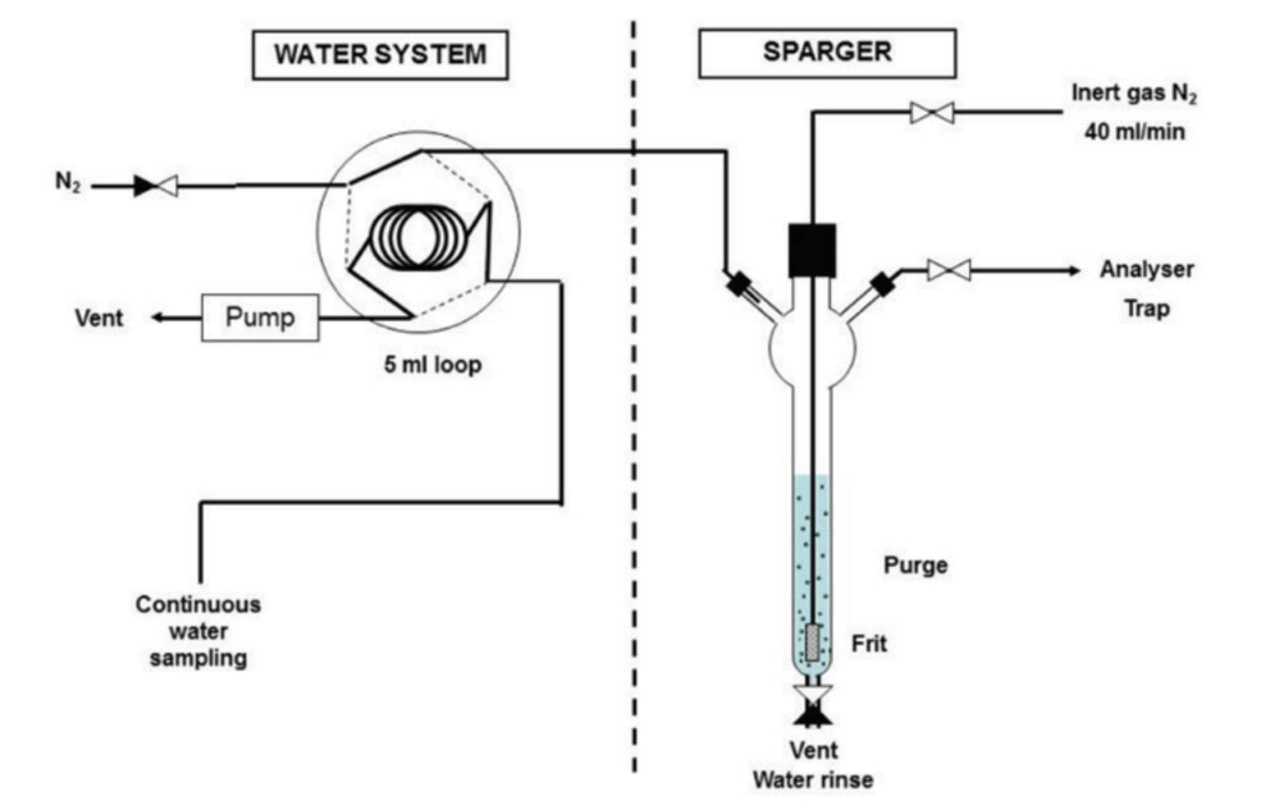

Figure 1: Purge and trap system

The typical cycle time is 60 minutes. This includes the following steps: automatic rinse (once with deionized water and then once with the sample), sampling, liquid injection in the sparger, nitrogen purge, injection into the system, thermo-desorption, evacuation of the sparger, separation in the analytical column, detection, quantification and cleaning of the system during acquisition.

This all-in-one solution is composed of an airmoVOC analyzer, hydrogen generators, nitrogen generator and zero air catalyzer. In addition, an internal calibration system can be inserted in order to validate the results and certify them in real time. 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

Industrial air monitoring waste water plant

process efficiency and control using automatic on-line continuous monitoring with little, if any, human interaction.

A real-life application of this unique solution is described hereafter; The Jiangsu province is an important industrial region in China. Industrial emissions lead to the release of VOCs into the atmosphere. VOCs are dangerous pollutants and can find their way into groundwater used for drinking purpose because of their high-water solubility and polarity. These compounds are known to have adverse effects on human and environmental health and also contribute significantly to the formation of ozone.

In order to ensure drinking water safety, the Jiangsu Provincial Department of Ecology and Environment released in 2018 a "Three-Year Development Plan". This action plan aims to significantly improve VOC groundwater contamination control and treatment. The analyses of VOCs in water require preconcentration of the analytes. The most common sample-enrichment methods for determining VOCs in water are P&T, headspace (HS) and solid-phase microextraction (SPME).

The system used in this study is an auto-GC-FID system with P&T technology for the determination of the analytes included in the US EPA 502.2 method. The main goal was to improve process efficiency and control using automatic on-line continuous monitoring.

Tests were performed using a TO14 cylinder (CPE-10010) and PAMS cylinder (CPC-03287) containing VOCs at 100 ppb for each compound (+/-2% of accuracy). Liquid samples were also used: a 502.2 liquid standard with a concentration of 200ng/mL diluted in water to reach 4µg/L and benzene and toluene diluted in water at 4µg/L. A benzene permeation tube with permeation rate of 11.5ng/min at 40°C was used for the internal calibration of instruments and response factor calculations, in accordance with the requirement of the ISO:17025 for benzene calibration. The relative response factors to benzene were determined experimentally, then values were compared with the theoretical relative response factors obtained using the equivalent number theory.

The analytical system's measurement of liquid samples was then tested using a P&T sampling system and a standard diluted in water with concentration of around 4µg/L. Prior to the analysis, the system was calibrated with a TO14 gas standard. The VOCs concentrations in liquid were determined given that 100% of VOCs contained in the water sample could be extracted and preconcentrated into the sampling trap.

A total recovery of mass injected (4µg/L) was obtained for most VOCs such as benzene (4.2µg/L), toluene (4.5µg/L), or trichloroethene (3.8µg/L). The results indicate that calibrations can be performed using gas standards, which makes the system preparation much simpler. Also, for very volatile compound, the liquid standard preparation is difficult, as these compounds may become vaporized before the analysis. Therefore, gas calibration may be considered more reliable for such compounds.

A water sample containing benzene and toluene at 4µg/L was diluted to various concentrations to test the linearity of the response. Also, a gaseous dilution system equipped with a Mass Flow Controller (airmoCAL D-MFC, Chromatotec, France) was used to achieve four points of different concentrations in a range between 0 and 100ng/L. The detector gave an excellent correlation between their response (RSD < 2%) and the concentration (R2=1).

The results obtained for the online quantification of 59 VOCs in 60min without memory effects using an auto-TDGC-FID analytical system in both gaseous and liquid samples when using a P&T sampling system are excellent and validated by many existing industrial customers. A quadrupole mass spectrometer can be coupled to the system to identify unknown compounds, either after the chromatographic column or from direct measurement, thus increasing the number of molecules analyzed to at least 123. The system used is fully automatic, linear, precise down to ppt levels and very stable. All generators needed for the continuous operation of the gas chromatograph are integrated into the cylinder-free analytical system. The system requires little maintenance because all cleaning procedures are performed automatically. Only the deionized water level in the hydrogen generator has to be checked monthly. The measurement system performance evaluation is completed with internal calibration using NIST-traceable permeation tube technology to provide automatic data validation.

The system automatically quantifies VOCs in water, including

AirmoVOC WMS

BTEX, to stay in compliance with wastewater discharge regulations from environmental protection agencies by taking corrective actions if maximum limits are exceeded. This solution will allow improving the ground water quality monitoring network through effective and comprehensive drinking water source monitoring using early warning systems and providing emergency backup water sources in Shuoxiang Lake, Guannan County, Lianyungang City.

The autonomous airmoVOC WMS can be also used in water markets for food processing, pharmaceutical industries, cosmetics and perfumeries. It can also be used for monitoring drinking water (beverages or source water), surfaces and wastewater as well as other types of liquid foods (milk, soda, wine, spirits, etc.) and organic liquids.

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