Development of on-line and field TD-GC-FID for automatic and continuous monitoring of VOCs in water

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INTRODUCTION

The monitoring of **Volatile et Semi-Volatile Organic Compounds** (VOCs and SVOCs) **dissolved in water** is crucial to prevent **adverse effects** on human health and environmental pollutions.[1] Some of these molecules can be **toxic at low concentrations**, necessitating the use **of sensitive systems** capable of analyzing concentrations ranging **from ppt to %**. Given that VOCs and SVOCs are frequently byproducts of industrial processes, accurately quantifying specific molecules becomes challenging due to the **numerous potential interferences**. This complexity makes it difficult to achieve precise quantification of all compounds using cost-effective sensors. There are numerous analytical methods for the characterization of VOCs in liquids.[2] Typically, laboratory gas chromatographs, involving **off-line sampling**, are employed for the identification and quantification of molecules in complex mixtures. To enhance result accessibility and minimize the risk of losing sample information during transport, there is a pressing need for **user-friendly, continuous, on-site monitoring systems**. In this work, we present three different analytical systems for the continuous measurement of VOCs and SVOCs in water, including **sulfur, alkanes, chlorinated and oxygenated compounds**. These three systems are designed to measure from low **ng/L up to 50,000 mg/L of VOCs in water**. For low VOC concentrations in water, an automated **Purge and Trap system** is used for quantification of molecules listed in the EPA method 502.2. The system allows identification and quantification down to ng/L up to µg/L. This system can be optimized to perform the analysis of OVOCs in water such as acetone or isopropanol. For VOCs at higher concentrations (mg/L), a **specific dilution system** has been designed and implemented to the Purge and Trap system. For this application, we have validated the system using BTEX liquid standard solutions. Finally, for the analysis of liquids with very high VOCs concentrations, a **continuous headspace system** has been designed and evaluated.

THE PURGE AND TRAP SYSTEM

The analysis of **trace level VOCs** in water is performed using an automated thermal desorption gas chromatograph equipped with a flame ionization detector (auto-TD-GC-FID) and a Purge and Trap sampling system:

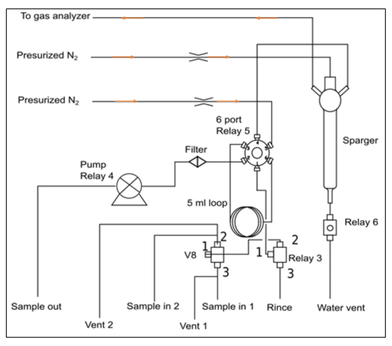

Figure 1: Purge and trap system

The Purge and Trap system (Figure 1) consists of an automatic sparger to extract VOCs from liquid samples in 11 min.
- The loop is filled with 5 ml of liquid sample
- The content of the loop is injected inside the sparger
- An inert gas (N_2) 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 injected into the gas chromatograph for pre-concentration and analysis.

The liquid samples were prepared using 502.2 standard solution diluted in water to reach 4 µg/L. The obtained chromatogram can be seen in Figure 2.
- **Good separation** of the VOCs included in the 502.2 standard solution
- All the compounds are **successfully extracted** from the liquid sample to the gas phase

Benzene	
RSD (%)	LOQ (ng/L)
0.027	≈ 3.5

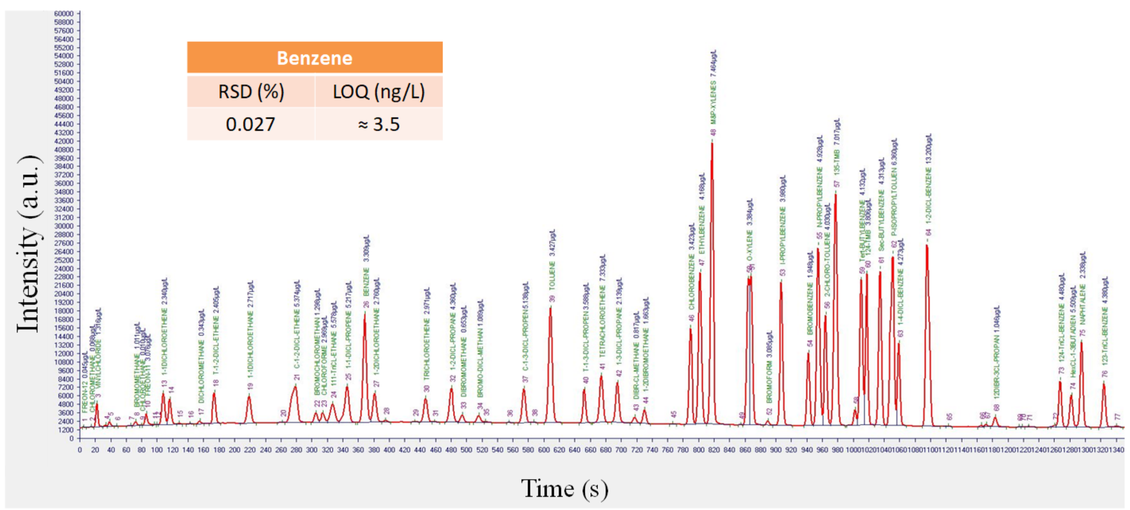

Figure 2: Chromatogram obtained with auto-TD-GC-FID coupled with purge and trap sampling system for the analysis of 502.2 standard solution.

PURGE AND TRAP WITH DILUTION MODULE

Very high VOC concentrations (mg/L) can be measured for water used for industrial processes (refinery, wastewater treatment plants). Therefore, a specific **dilution module** can be added to the Purge and Trap system for the analysis for VOCs in the ppm range.

Before injection into the sparger, 50µL of the sample is withdrawn into a 1mL automated syringe. Then, 950µL of deionized water is added to the syringe and injected into the sparger. 4mL of water are used to fill the 5mL of the sparger. This dilution step decreases the sample concentration by a **factor of 100** and reproduces the condition previously described in the 502.2 method. This allow for

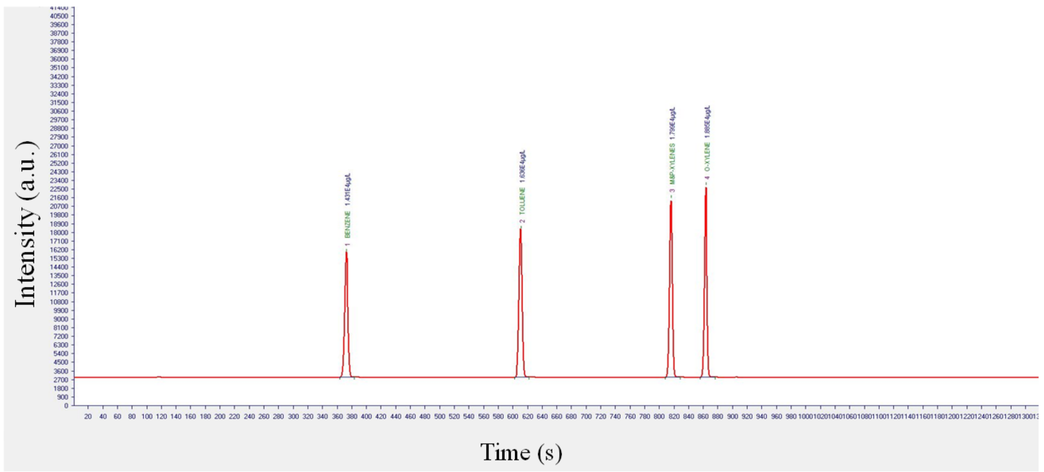

Figure 3: Chromatogram obtained for the analysis of BTEX with a concentration of 1500 µg/L

Figure 3 shows a chromatogram obtained for the analysis of benzene, toluene, m-xylene and o-xylene at 1500 µg/L.
- **Very good separation and quantification** of the dissolved BTEX.
- **R^2 > 0.99** for all BTEX (Figure 4).

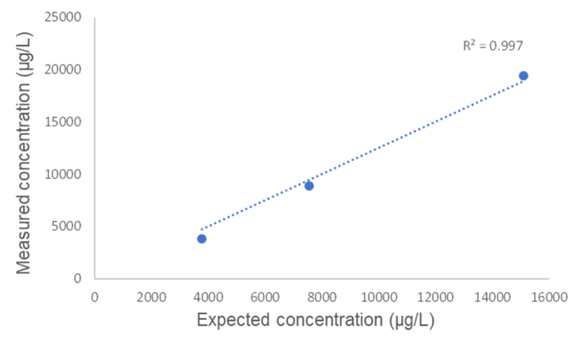

Figure 4: Linearity obtained for the measurement of o-xylene with concentrations ranging from 4000 to 16 000 µg/L

CONTINUOUS HEADSPACE SYSTEM

In case of **high organic compounds**, the Purge & Trap system cannot be used because the trap could be easily **saturated by the matrix**. A specific liquid sampling system was designed for the analysis of **linear alkanes** (from 6 to 11 carbon atoms) in a **water/triethylene glycol mixture**. Figure 5 is a schematic representation of this module:

This module contains :
- a dynamic headspace module for liquid sample analysis: liquid sample is introduced in a headspace vial and when the equilibrium is reached, carrier gas collects the analytes and send them to the GC
- a permeation oven for calibration of the GC

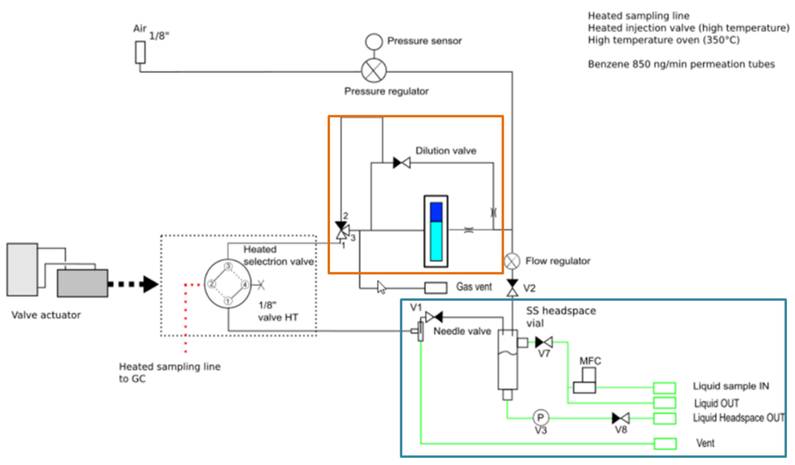

Figure 5: Sampling module used for continuous headspace analysis

The gaseous sample is sent into a 100µL sampling loop and then injected in the GC system. This system was designed in a **specific backflush mode** to prevent potential matrix impurities to go into the analytical column. When the sample is injected, the analytes enter a pre-column. When all the compounds of interest have entered the analytical column, the pre-column is backflushed and all the other potential impurities go directly to the vent.

Sample preparation is a crucial step in the development of this application. Alkanes are known to be insoluble in water. The following ratio was used: **water/TEG 35/65 (v/v)**.

Solutions of the alkane mixture were prepared at 500 ppm and 1000 ppm. Solutions of n-heptane were prepared at 500 ppm, 1000 ppm, 3500 ppm and 5000 ppm. **Samples were kept under agitation** during the analysis. These solutions were used to test the **linearity of the system**. Each point of the linearity was made in triplicate, each time with a new solution to be sure to have the correct concentration.
Figure 6 represents the linearity obtained for **n-heptane** and Figure 7 represents the linearity obtained on **all the alkanes**:

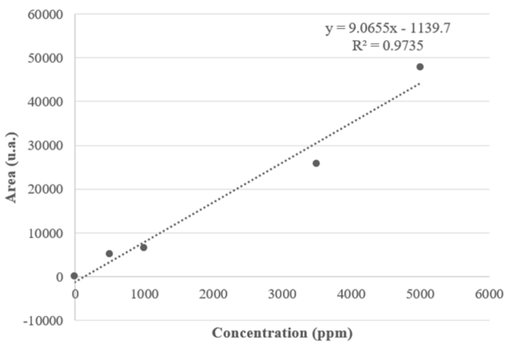

Figure 6: Linearity curve of n-heptane in a water/TEG mixture (35/65 v/v) in the range 0 – 5000 ppm

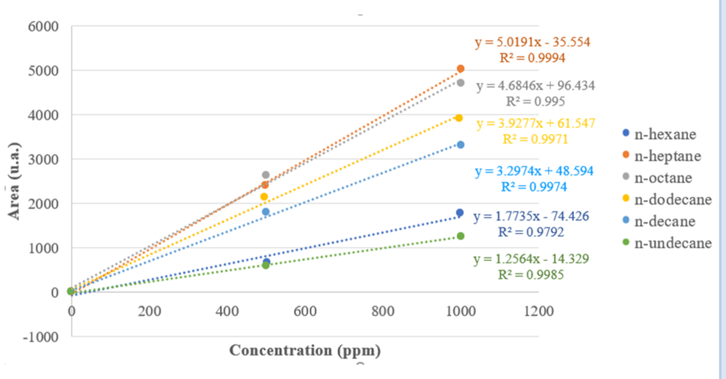

Figure 7: Linearity curve of six alkanes (from C6 to C11) in a water/TEG mixture (35/65 v/v) in the range 0 – 1000 ppm

CONCLUSION AND PERSPECTIVES

We presented **three different analytical methods** for continuous and automatic measurement of **VOCs in liquids**. The first system is designed for the quantification of **trace-level of VOCs in water** and is perfectly suited for the analysis of drinking water. The other two systems are necessary for industrial applications where **very high concentrations need to be measured**. When the sample mainly consists of water, the Purge and Trap system with specific dilution module is preferred for two reasons: first, the analytical performances are better for purge systems than headspace (linearity and stability). Then the headspace can be very sensitive to matrix effect because the solubility of VOCs will be affected. Nevertheless, when the sample consists in organic molecules (alcohol, oil) it is necessary to use the headspace sampling system. All three systems have been tested using **embedded gas generators**. Therefore, only power supply is needed to operate the system 24 hours, 7 days a week. This design makes the system perfectly suitable for **measurement in industrial contexts**.

REFERENCES: [1]Yu, B., Yuan, Z., Yu, Z., and Xue-song, F. (2022). BTEX in the environment: An update on sources, fate, distribution, pretreatment, analysis, and removal techniques. Chemical Engineering Journal 435, 134825. https://doi.org/10.1016/j.cej.2022.134825.
[2] Sridhara Chary, N., Fernandez-Alba, A,R. (2012). Determination of volatile organic compounds in drinking and environmental waters. Trends in Analytical Chemistry, Vol. 32. https://doi.org/10.1016/j.trac.2011.08.011