An automated approach for the analysis of VOCs in drinking and surface water by using the TriPlus RSH SMART VOC sample prep station

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Abstract

Purpose: Volatile organic chemicals (VOCs) are ubiquitous pollutants usually present at trace concentrations in a variety of complex matrices therfore they require to be extracted and pre-concentrated prior the analysis. Moreover, because of their chemical properties, they are prone to evaporate or degrade having limited stability for analysis.

Methods: In this study the performance of a dedicated robotic autosampler for the execution of an automated sample preparation workflow for VOC analysis are demonstrated.

Results: Reliable quantitative analysis for drinking and surface water samples was achieved in compliance with current regulations. The automated workflow ensured sample integrity reducing variability and possible risk of re-run sequences. Additonally, it provided labor-time saving, removed possible cross-contaminations and maximized the productivity of the laboratory

Introduction

Volatile organic compounds (VOCs) are considered ubiquitous pollutants in the environment therefore their presence is strictly regulated. One of the main challenges in VOC analysis is the sample preparation as these compounds are usually present at trace concentrations in a variety of complex matrices. Headspace is a straightforward approach that allows for the extraction of volatile and very volatile compounds from non-volatile matrix in a fast and simple way, without the need for time-consuming sample preparation. When dealing with HS sampling, the sample preparation is minimal, typically consisting of transferring the water sample into a HS vial and adding the ISTDs to a batch of samples before starting the analytical sequence (sample incubation followed by GC analysis). However, with this approach, sample vials may remain on the autosampler tray for hours, especially in case of long sequences, with possible impact on sample integrity and overall data repeatability, affecting quantitative analysis. With the Thermo ScientificTM TriPlusTM RSH SMART VOC sample prep, reagents can be added immediately before the sample incubation by using a dedicated dual head configuration (Figure 1). One head is equipped with a liquid tool to dispense the reagents (e.g., ISTD or calibration standard) into the sample vial, whereas the second head moves the vial into the incubator for headspace analysis.

Materials and methods

Standard and sample preparation

Multi-component standard stock solutions were placed in the autosampler tray and automatically diluted in 20 mL screw top headspace vials previously filled with tap water (10 mL), and containing solid sodium thiosulphate, to create the calibration curve and the quality check standards (QCs).

Tap water samples and surface water samples were collected from different locations around the Milan metropolitan area. Solid sodium thiosulphate was added immediately after sample collection in the field. Samples were prepared for analysis by transferring 10 mL of the collected water into 20 mL screw top headspace vials. An aliquot (10 µL) of the internal standard and surrogate solution was then automatically added by the autosampler to each sample immediately before vial incubation.

Test Method(s)

A TriPlus RSH SMART VOC sample prep station was installed on top of a Thermo Scientific[™] TRACE 1610 GC, equipped with a Thermo Scientific[™] iConnect[™] split/splitless injector working in HeSaver-H₂Safer mode, and coupled to a Thermo Scientific[™] ISQ[™] 7610 single quadrupole mass spectrometer.

Data Analysis

The Thermo Scientific[™] Chromeleon[™] 7.3 Chromatography Data System (CDS) ensured a streamlined automated workflow covering on-line sample preparation, sequence setup, data acquisition, and reporting. The Chromeleon Environmental Analysis Extension Pack for U.S. EPA-based environmental applications provides a comprehensive set of GC-MS eWorkflow™ procedures for quick sequence setup and reporting templates to make data review and reporting easier.



Results

Linearity

Two matrix-matched calibration curves in tap water ranging from 0.1 to 100 ng/mL were automatically diluted by the TriPlus RSH SMART VOC sample prep station and used to evaluate the system repeatability for calibration curve preparation. All target analytes showed a linear trend with coefficient of determination $(R^2) > 0.990$, relative response factor (RRF) %RSD < 20% and calculated amount within 20% the expected values. Full range calibration curves (0.1-100 ng/mL) for benzene, dibromomethane, and 1,2,4trimethylbenzene as well as an extracted ion chromatogram (XIC) showing the quantifier and gualifier ions for a tap water sample spiked at 0.1 ng/mL are reported as an example in Figure 2. The SIM trace showing all the target compounds in a tap water sample spiked with VOC mix at 0.1 ng/mL is also presented in Figure 2.

Figure 2. Examples of full range calibration curves (0.1–100 ng/mL (A), XIC showing the quantifier and qualifier ions for a tap water sample spiked at 0.1 ng/mL (B), and SIM trace showing the target compounds in a tap water sample spiked with a VOC mix at the lowest calibration point (0.1 ng/mL), ISTD (20 ng/mL) and surrogates (25 ng/mL) (C)







Method detection limits (MDLs)

samples spiked with VOC solution at 0.5 ng/mL, ISTD (20 ng/mL) and surrogate mix (25 ng/mL). Calculated MDLs were < 0.20 ng/mL, with calculated absolute peak area %RSD < 20% for all compounds (Figure 3). Figure 3. Calculated MDLs (ng/mL) for the investigated VOCs

MDLs and precision were assessed using n=10 replicates of matrix-matched water



Inter-day repeatability

Analytical testing laboratories need to process a high number of samples every day. The repeatability of the TriPlus RSH SMART VOC sample prep station and system performance for everyday analysis were evaluated over six days of continuous operation by preparing three batches of samples (n=44 samples each) consisting of blank matrix, a calibration set ranging from 0.1 to 100 ng/mL, matrix-matched QCs spiked with VOC standard solution at 10 ng/mL bracketing series of n=5 samples of tap and surface water samples collected in different locations in the Milan area. The precise mechanical control of the TriPlus RSH SMART VOC sample prep station ensured reproducible addition of both the ISTD / surrogate solution as well as the VOC mix with QC calculated amount with respect to the batch ran on day 1 within 20% (Figure 4), calculated recovery within 70–130%, with the only exception of 1,2-dibromo-3 chloropropane for which the % recovery was 132% (Figure 5), and average ISTD / surrogate solution absolute peak area %RSD across the entire evaluation period < 20%. The analyzed sample results were compliant with the allowed threshold limits established by the current EU directives on the quality of water intended for human consumption and for the surface waters.

Figure 4. QC calculated amount deviation with respect to the batch ran on day 1

QC calculated amount deviation across n=3 batches within 20% 30 20 15 808008*808⁰⁰⁰⁰ 08⁰ 0800 08⁰ 0800 80 00⁰ Batch 1 Batch 2 Batch 3

evaluation period of six working days



Surr Dibromofluoromethane (%RSD=8.5) ISTD 1.4-Difluorobenzene (%RSD=6.6) ■ ISTD Chlorbenzene D5 (%RSD=6.5) BFB 1-Bromo-4-fluorobenzene (%RSD=9.7)

Conclusions

The automated sample preparation capability of the TriPlus RSH SMART VOC sample prep station coupled to the ISQ 7610 GC-MS system provides an ideal solution for water testing laboratories looking to improve productivity and deliver confident results.

- set by the current EU regulation.
- dilution and ISTD addition workflows.
- toxic chemicals.
- acquisition, and reporting

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Figure 5. ISTD / surrogate peak area %RSD across the samples in the

Sample number

- ISTD Pentafluorobenzene (%RSD=5.9) Surr Toluene D8 (%RSD=9.1) ISTD 1,4-Dichlorobenzene D4 (%RSD=6.8)

Static headspace is a convenient solventless extraction technique for volatiles in water with almost no sample preparation required that ensures results in compliance with the thresholds

Unattended operations of up to 210 samples can be achieved with the automated calibration

The automated addition of fresh reagent just before the incubation increases the stability of ISTD / surrogates mix, therefore improving the accuracy of the quantitation of target analytes during data reprocessing for highly reliable quantitative analysis while reducing errors or possible cross contaminations and maximizing the productivity of the laboratory. Additionally, it allows saving valuable analyst time and improving safety by limiting the user's exposure to

The integrated control for both autosampler and GC-MS in a single CDS ensures a streamlined automated workflow from on-line sample preparation to sequence setup, data