SHIMADZU

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Ensuring drinking water quality through a single method of VOCs analysis and taste- and odor-causing substances

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1. Introduction

Monitoring contaminants in drinking water is essential to protect public health. A recurring issue is the presence of off-flavor (musty and earthy odor), mainly caused by the compounds 2-methylisoborneol (2-MIB) and geosmin, produced by cyanobacteria and actinobacteria. Brazilian regulations, such as *CONAMA* Resolution No. 357 and *Portaria* GM/MS 888/21, define limits for volatile organic compounds (VOCs), but lack of limits for musty/earthy odor substances. Regarding to the method, the US EPA 524.4, from the United States Environmental Protection Agency (USEPA), proposes the analysis of VOCs by GC-MS coupled to Purge & Trap as sample introduction technique.

Table 1 – Compounds maximum residue levels (MRL)

Compound Name	Limit (ug/L)
Vinyl chloride	0.5
Methylene chloride	20
Chloroform; Dibromomethane; Dibromochloromethane; Bromoform	100
Carbon Tetrachloride; Trichloroethylene	4
Benzene; 1,2-Dichloroethane	5
1,4-Dioxane	48
Epichlorohydrin	0.4
Toluene	30
Tetrachloroethene	40
Chlorobenzene	20
Ethylbenzene	300
Sum of Xylenes	500
1,4-Dichlorobenzene	0.3
1,2-Dichlorobenzene	1

Considering the need for versatility, a unique method was developed that allows the simultaneous analysis of VOCs, 2-MIB, and geosmin in a single run.

2. Methods

- The P&T system was used, which is a dynamic headspace system, in which purge gas is passed through the water sample, and the volatile analytes are forcibly expelled with the purge gas and trapped by an appropriate adsorbent (**Fig 1**).
- The EST Analytical Evolution2 Purge & Trap concentrator and Centurion autosampler were interfaced to a Shimadzu GCMS-TQ8050 NX (**Fig 2**).

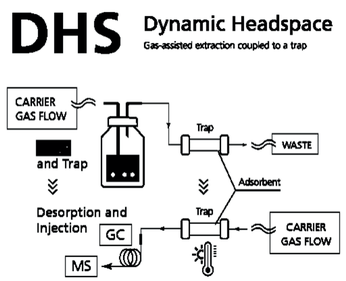

Fig. 1 Dynamic Headspace P&T.

- In accordance with the method EPA 524.4, the analysis was configured in Selected Ion Monitoring (SIM) mode. The compound 1-Bromo-4-Fluorobenzene (BFB) was used as the internal standard and nitrogen was used as the purge gas, due to the shortage and high cost of high purity helium.
- Therefore, helium was exclusively used as the carrier gas. Ultra-pure water samples were fortified with target compounds, covering a concentration range of 0.1 to 10 ppb, for 20 different compounds and a range of 5.0 to 50 ppb for the 1,4-Dioxane compound.
- To achieve high analytical sensitivity and a low LOQ for the odor-causing compounds, it was necessary to acquire in Multiple Reaction Monitoring (MRM) mode, the method operated in simultaneous SIM/MRM mode.

Fig. 2 EST Evolution2 P&T + Centurion + GCMS-TQ8050 NX.

3. Results and Discussion

- Using the P&T-GC-MS/MS system for single method analysis, the chromatographic runtime was 18 minutes. The substances were separated using a 0.25 mm × 30 m × 1.4 µm SH-I-624Sil MS capillary column. The chromatogram from a single injection of VOCs, 2-MIB, and geosmin is represented in **Fig 3**.

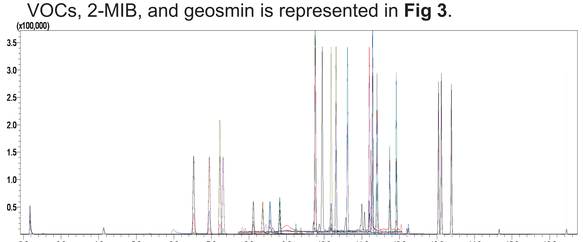

Fig. 3 Chromatogram VOCs + 2-MIB and Geosmin.

- The established limits of quantification (LOQ) for the VOCs compounds were set at 0.25 ppb, except for dioxane, 2-MIB, and geosmin, which had LOQs of 5.0 ppb and 10 ppt, respectively. Quadratic calibration curves were developed using six or seven concentration levels of the target compounds, yielding satisfactory results with coefficients of determination (R^2) exceeding 0.995 for all analytes.

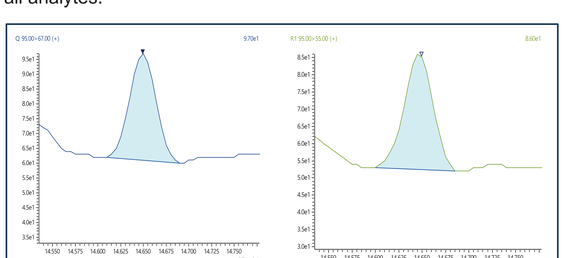

Fig. 4 Chromatogram of 2-MIB at a concentration of 10 ppt acquired in MRM mode.

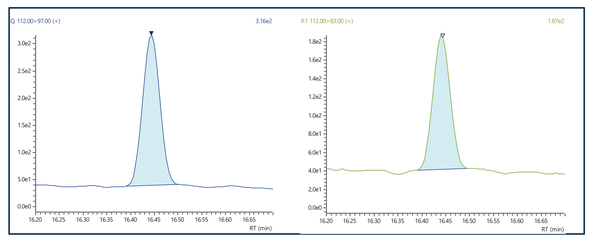

Fig. 5 Chromatogram of geosmin at a concentration of 10 ppt acquired in MRM mode.

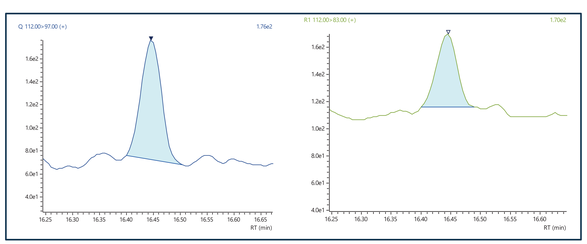

Fig. 6 Chromatogram of geosmin at a concentration of 1 ppt acquired in MRM mode.

4. Conclusion

The results obtained demonstrated the feasibility of using these instruments to monitoring drinking water quality through the most comprehensive methodology possible, in compliance with Brazilian regulations and EPA Method 524.4. This study stands out due to the lack of single, highly sensitive methods for comprehensive drinking water analysis that include all purgeable VOCs, especially when using nitrogen as the purge gas and taste and odor (T&O) compounds, as required by Brazilian standards. Specifically for 2-MIB and geosmin, the most commonly used analytical technique is solid-phase microextraction (SPME). However, integrating the analysis of all these compounds into a single analytical method is essential in terms of productivity, operational simplicity, and analytical sensitivity.

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