

Trihalomethanes Identification in Drinking Water using SPME-GC-TMS

Trihalomethanes (THMs) in drinking water were rapidly sampled and concentrated using solid phase microextraction (SPME) followed by on-site analysis with a TRIDION™-9 portable gas chromatograph-toroidal ion trap mass spectrometer (GC-TMS). The SPME-GC-TMS method can be used to effectively extract, concentrate, separate and detect THMs quickly and reliably at concentrations less than regulatory levels as specified by the U.S. EPA Primary Drinking Water Standards.

Introduction

Four trihalomethanes (THMs), Chloroform, Bromodichloromethane, Dibromochloromethane, and Bromoform in drinking water are routinely monitored using U.S. EPA Method 524.2¹. This analytical method calls for on-site sample collection, sample storage at 4°C, and transport of the sample back to a fixed base laboratory for gas chromatograph mass spectrometry (GC-MS) analysis. The CUSTODION™ SPME syringe and the TRIDION-9 gas chromatograph-toroidal ion trap mass spectrometer (GC-TMS) can be used for rapid on-site sample extraction² and analysis for sample pre-screening prior to sending samples to a fixed-based laboratory for confirmatory analysis. On-site sample collection and extraction using SPME will minimize target analyte losses when compared to traditional techniques that risk analytes loss during storage and transport. Thus, on-site chemical analysis and detection of THMs can not only be more timely, but also more accurate.

Sampling Equipment

The CUSTODION SPME syringe consists of a 1cm length of silica fiber coated with 50-100 µm of a liquid polymer film, solid sorbent or combination. The SPME fiber is housed in a durable syringe that can be operated with a single hand. Much like a retractable ball point pen, the push button trigger on top of the syringe allows the SPME fiber to be extended and retracted into and out of a protective metal sheath. The SPME fiber can trap target analytes from air, headspace, liquids or dissolved solid samples.

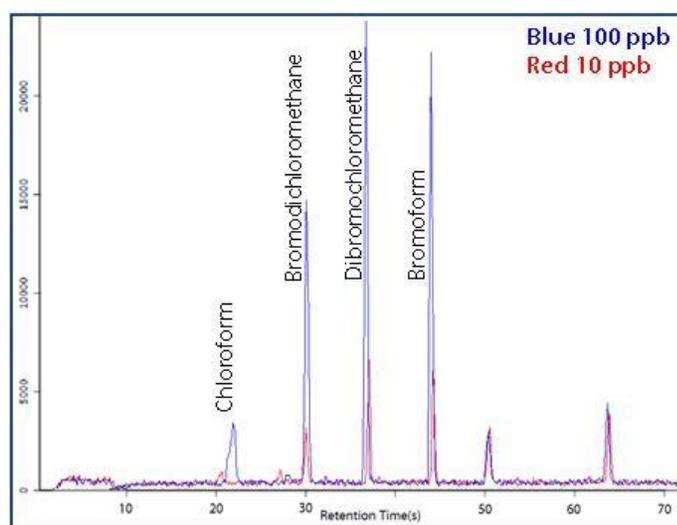


Figure 1. Chromatogram of low level detection of THMs in drinking water. Compound identification: Chloroform, Bromodichloromethane, Dibromochloromethane, and Bromoform.

A 65 µm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) SPME phase was used to evaluate the extraction and analysis of four THMs (Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform) specified in EPA Method 524.2. The compounds were extracted from spiked drinking water samples ranging from 10 – 500 ppb for each THM.

Sample Preparation and Analysis

THM spiked samples were prepared by diluting neat compounds (Sigma Aldrich, St. Louis, MO) to 500 ppb in drinking water. The individual THM standards were then combined and diluted to the required concentrations, which ranged from 1 ppb up to 100 ppb. Samples were shaken by hand for ~10 seconds, and the CUSTODION-12 SPME fiber was exposed to the headspace for ~50 seconds at ambient temperature (~24°C). The extraction method (including shaking) was repeated 5 times.

After a total of ~5 minutes of headspace sampling, the SPME fiber was introduced into the injection port on the TRIDION-9 GC-TMS where the THMs were desorbed from the fiber into a low thermal mass capillary GC column. The GC temperature was then rapidly programmed from 40° to 280°C at 2°C/s resulting in a total run time of 2.5 minutes. The low thermal mass GC was directly interfaced to a toroidal ion trap mass spectrometer (TMS), which has a mass range from 45-500 Da. Overall, this method is rapid with a total SPME sampling time of ~5 minutes and GC-TMS analysis time of ~3 minutes.

Experimental Conditions

Sampling:	Solid phase microextraction (SPME)
SPME Phase:	Divinylbenzene/Polydimethylsiloxane (DVB/PDMS, 65 µm)
GC Inj. Temp:	270°C
GC Column:	MXT-5, 5 m x 0.1 mm, 0.4 µm d _f
GC Carrier Gas:	Helium, 0.2ml/min, constant pressure
GC Column Temp:	40-280°C at 2°C/s
Transfer Line:	270°C
Injection Split Ratio:	20:1
Mass Analyzer:	Toroidal ion trap (TMS)
TMS Mass Range:	45-500 Da
Ionization Mode:	In-trap electron impact
Detector:	Electron multiplier
Vacuum:	Roughing and turbo molecular pumps
Resolution:	Less than unit mass to 230 amu, nominal unit mass to 500 amu

Results and Discussion

Figure 1 shows the GC-TMS separation of the THMs spiked into a drinking water sample. All four THMs were detected and positively identified by the TRIDION-9 compound library at both 100 and 10 ppb (v/v).

SPME-GC-TMS is a useful method for on-site sample screening prior to transport for laboratory THM analysis by GC-MS. Samples containing THMs at high concentrations can be screened using the TRIDION-9 and then diluted to an appropriate concentration level prior to laboratory GC-MS analysis to avoid sample carryover and/or contamination of the instrument. This can minimize re-analysis of samples and reduce down time.

The current U.S. EPA Primary Drinking Water Standard requires a maximum total cumulative concentration limit of no more than 80 ppb for the four THMs. At a detection level for the individual THMs of 10ppb as shown in Figure 1, the SPME-GC-TMS method can be used for point source analysis to rapidly determine regulatory compliance of drinking water and ground water samples in the field. The CUSTODION SPME syringe and TRIDION-9 GC-TMS provide a fast, easy, accurate and reliable method for sample extraction and on-site analysis.

References

1. Zhang, Zhouyao; Pawliszyn, Janusz. *Analysis for organic compounds in environmental samples by headspace solid phase microextraction*. Journal of High Resolution Chromatography (1993), 16(12), 689-92.
2. Deok-Hee Choa, Sung-Ho Kongb and Seong-Geun Oh, *Analysis of trihalomethanes in drinking water using headspace-SPME technique with gas chromatography*, Water Research (2003), 37 (2), 402-8.

Acknowledgements

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