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Fast determination of haloacetic acids in drinking water

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Introduction

As a result of current government proposals and developments, haloacetic acids (HAA) are in the focus of modern water analysis. The established methods use gas chromatography with electron capture detection (GC-ECD) or mass spectrometry (GC-MS). However, the drawback of these methods is the need for time-consuming derivatization and multiple extraction steps. Can the analysis be simplified? Can sensitive and rapid detection be achieved without sample pretreatment? In this paper, these questions are answered based on current developments in IC-MS/MS.

Discussion

Right2Water

In response to the "Right2Water" initiative, supported by 1.6 million Europeans, the European Commission proposed a revision of the Drinking Water Directive in January 2018.[1] The obligatory and extended list of criteria contains 18 new or revised entries, including chlorate and HAAs.[2]

Organic molecules present in the feedwater of drinking water production, as well as naturally occurring or anthropogenic bromide and iodide, react with chlorine-containing disinfectants to form halogenated intermediates from which the HAAs originate as by-products.

However, the U.S. Department of Health and Human Services[3], as well as other authors[4-7], evaluated the available scientific data as being insufficient to establish a safe link between human cancer and individual HAA, subclasses and the class of HAAs. Other studies on by-products of water disinfection indicate a potential cancer risk from chlorinated water and underline the relevance of animal cancer studies for humans.[3]

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Accordingly, the Annex to the EU proposal lists nine representative HAAs (9HAA) whose total content may not exceed 80 µg/L: monochloro (MCAA), dichloro (DCAA) and trichloroacetic acid (TCAA), mono- (MBAA) and dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromo-chloroacetic acid (DBCAA), and tribromoacetic acid (TBAA).

Analytics

Common gas chromatographic methods are based on liquid-liquid extraction and derivatization of HAAs either with diazomethane[8] or with methanol[9] in conjunction with electron capture detectors or mass spectrometers. These methods verify five of the nine proposed HAAs. They are labor-intensive and time-consuming. Also, diazomethane can only be used in Sweden with the permission of the proper authority because of its listing as a carcinogenic air pollutant in the workplace.[10]

Consequently, there is an increasing interest in simplified analytical methods for the determination of 9HAA. The low pKa values of HAAs[11] suggest the use of anion exchange chromatography.

IC-MS/MS

Currently, only one validated EPA method based on IC describes the separation of 9HAA in drinking water.[12] To minimize unwanted sensitivity losses in MS (ion suppression), the authors describe mandatory requirements for the chromatographic separation: The target components must be separated from the common anions in the drinking water, the samples must be directly injected. Filtration and sample pretreatment by solid phase extraction are not permitted. The effluent of the chromatographic system needs to be low conductive, and the EPA method specifies a value of less than 2.5 µS/cm. The separation is accomplished using a polymeric, high-capacity separation phase (Thermo Scientific™ Dionex™ IonPac™ AS24). Before conductivity and MS-detection, a continuously electrolytically regenerated suppressor (Thermo Scientific™ Dionex™ ASRS™) is used, converting the eluent (KOH) into water and the eluting anions into their corresponding acids, thus improving the sensitivity and selectivity of both detectors. Applying these experimental conditions the trace determination of 9HAAs is facilitated even in the presence of high concentrations of the main anions like 320 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate, and 20 mg/L nitrate (LSSM)[12]. The cycle time of the described EPA method is 56 min.

Optimizations

The economics of a modern analysis laboratory can be improved by reducing the time required to determine a sample. Faster chromatography can be achieved, for example, by changing the column properties. With this in mind, the Thermo Scientific™ Dionex™ IonPac™ AS31 column was developed. On this column, the separation of the 9HAA with an electrolytically generated hydroxide gradient is achieved in less than 35 min. This results in a time savings of more than 30% (Figure 2).[13] Under these conditions, the main components chloride, sulfate, and bicarbonate/carbonate elute from the Dionex IonPac AS31 column in one peak without impairing the resolution of the HAAs. Figure 2 shows only the conductivity detection. The use of a continuously electrolytically regenerated suppressor is a prerequisite for the continuous desalination of the highly alkaline eluent, allowing connection of the IC to MS detectors. At the same time, the device configuration is clearly defined, and the traceability of the analytical measurement is ensured. Modern ion chromatographs, therefore, have automatic logging of the consumables used in the device, so that configuration information can readily be extracted at any time from the analytical raw data.[14,15] Figure 3 shows the detection of 9HAAs, 2,2-dichloropropionic acid (dalapon), and bromate in the targeted selected ion monitoring mode of the mass spectrometer. The quantities added to the drinking water matrix (LSSM, see Reference 12) were 4 µg/L, each. The determination of such trace levels and below is possible. The grayed segments in the figure represent the retention time windows during which the main components elute, and the chromatographic effluent is diverted to waste via the switching valve shown in Figure 1. This matrix diversion facilitates the trace determination of HAAs by further reducing potential ion suppression effects in the MS.

Various methods for the liquid chromatographic analysis of 9HAAs are found in the literature. Some selected examples describe HILIC MS/MS[16] or IC-MS/MS with KOH/K_2CO_3 eluents in conjunction with discontinuously regenerated packed bed suppressors,[17] RP-MS/MS,[18] or IC-HRMS in conjunction with SPE[19]. In most of these articles, obligatory demands of the validated EPA-method for the determination of 9HAAs are not met.

As long as no validated ISO methods are available for the analysis of 9HAAs with IC/LC, it is suggested to follow the EPA evaluation procedure and prerequisites when testing any newly developed method.[12]

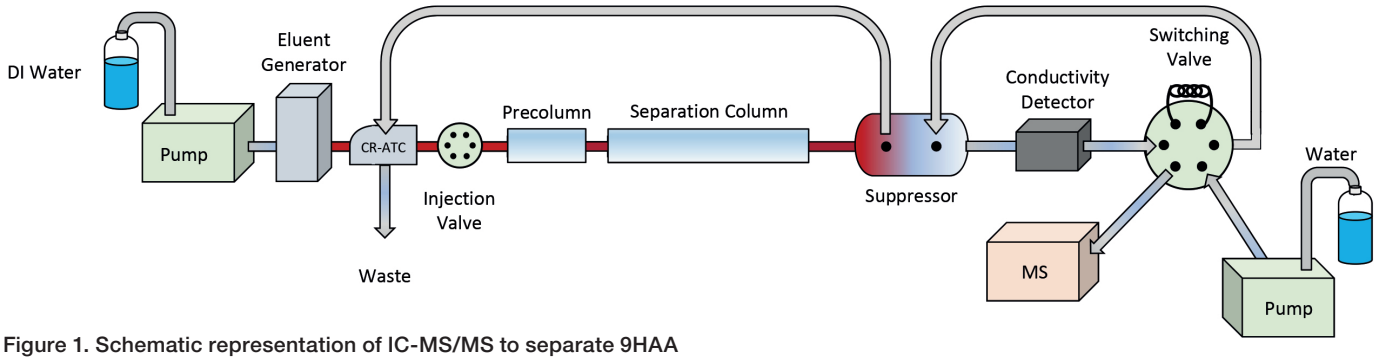
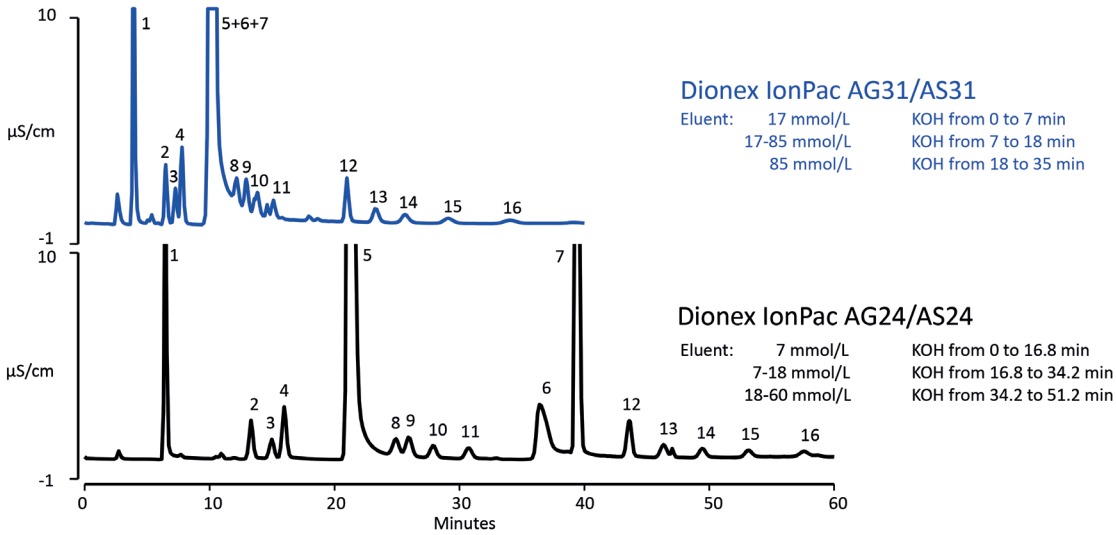
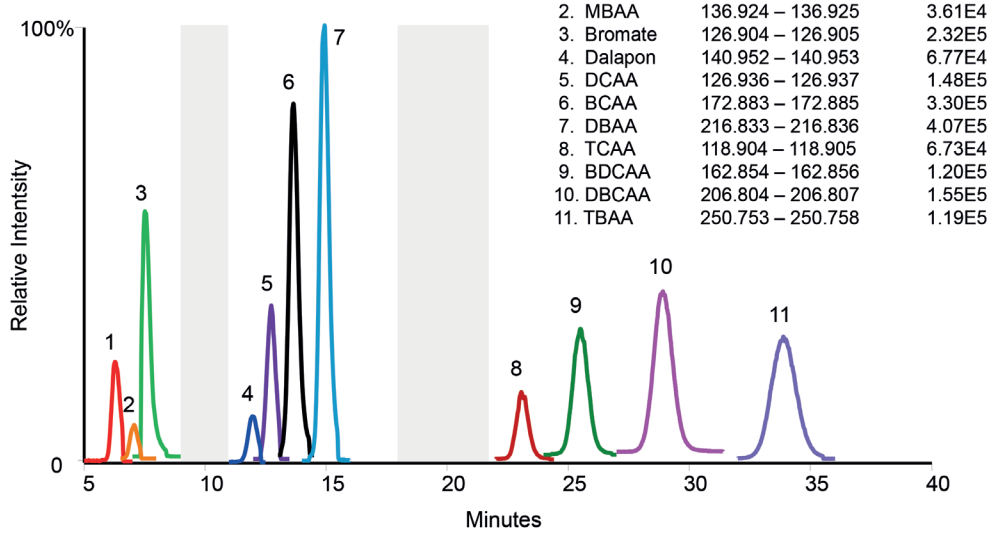


Figure 1. Schematic representation of IC-MS/MS to separate 9HAA



Peak		mg/L
1	Fluoride	NQ
2	MCAA	1.0
3	MBAA	1.0
4	Bromate	1.0
5	Chloride	NQ
6	Sulfate	NQ
7	Carbonate	NQ
8	Dalapon	1.0
9	DCAA	1.0
10	BCAA	1.0
11	DBAA	1.0
12	Nitrat	NQ
13	TCAA	1.0
14	BDCAA	1.0
15	DBAA	1.0
16	TBAA	1.0

Figure 2. Comparison of chromatographic selectivities. Instrument: Thermo Scientific™ Dionex™ ICS-6000. Columns and conditions: see illustration. Detection: Suppressed Conductivity (Thermo Scientific™ Dionex™ ADRS Anion Dynamically Regenerated Suppressor)



Peak	Mass Range (*m/z*)	Intensity
1. MCAA	92.975 – 92.976	9.59E4
2. MBAA	136.924 – 136.925	3.61E4
3. Bromate	126.904 – 126.905	2.32E5
4. Dalapon	140.952 – 140.953	6.77E4
5. DCAA	126.936 – 126.937	1.48E5
6. BCAA	172.883 – 172.885	3.30E5
7. DBAA	216.833 – 216.836	4.07E5
8. TCAA	118.904 – 118.905	6.73E4
9. BDCAA	162.854 – 162.856	1.20E5
10. DBCAA	206.804 – 206.807	1.55E5
11. TBAA	250.753 – 250.758	1.19E5

Figure 3. Separation and detection of the 9HAA, bromate and dalapon, 4 µg/L (each) in drinking water (LSSM, s. [12]). Dionex ICS-6000 system with Dionex IonPac AS31 column (15 ˚C), KOH gradient (Eluent Generator), 0.3 mL/min, 100 µL injection, Conductivity detection (Dionex ADRS). MS detection: Thermo Scientific™ Q Exactive™ HF-X Hybrid Quadrupole-Orbitrap™ mass spectrometer, Targeted SIM XIC.

Summary

IC can be used to directly determine the 9HAAs and bromate, chlorate and dalapone as listed in the EU proposal without sample preparation. Mass spectrometry detection provides the sensitivity and selectivity required to achieve reliable analytical results. In conjunction with "Reagent-Free IC" (RFIC), i.e., IC without manual preparation of eluents or regenerants, a high degree of automation is achieved, which yields high reproducibility of the separations and minimal labor in the laboratory. The use of a new stationary phase (Dionex IonPac AS31) reduces the run times by more than 39% in comparison to EPA Method 557, and all the key requirements for analytical validation as in EPA Method 557 are met. The method described in EPA Method 557 should be used as a reference for the evaluation of new methods.

Bibliography

1. European Commission, "Proposal for a DIRECTIVE OF THE EUROPAN PARLIAMENT AND OF THE COUNCIL on the quality of water intended for human consumption (recast)," [Online]. Available: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM:2017:0753:FIN. [Accessed Feb 6, 2019].
2. European Commission, "Safer water drinking for all Europeans: Questions and Answers," 01 2018. [Online]. Available: http://europa.eu/rapid/press-release_MEMO-18-430_de.htm. [Accessed Feb 6, 2019].
3. U.S. Department of Health and Human Services, "Revised Draft: Report on Carcinogens Monograph on Haloacetic Acids Found as Water Disinfection By-Products," 2017. [Online]. Available: https://ntp.niehs.nih.gov/ntp/about_ntp/monopeerrvw/2017/july/haadraftmonograph20171030.pdf. [Accessed Feb 6, 2019].
4. World Health Organization, "Guidelines for drinking-water quality: Fourth edition incorporating the first addendum," 2017. [Online]. Available: https://apps.who.int/iris/bitstream/handle/10665/254637/9789241549950-eng.pdf;jsessionid=3FB9299F2F587AC79B6974B31C0B6FDA?sequence=1. [Accessed Feb 6, 2019].
5. World Health Organization (IARC Working group on the evaluation of carcinogenic risks to humans), "Some chemicals present in industrial and consumer products, food and drinking-water/IARC Monographs, Volume 101," [Online]. Available: https://monographs.iarc.fr/wpcontent/uploads/2018/06/mono101.pdf. [Accessed Feb 6, 2019].
6. World Health Organization (IARC Working group on the evaluation of carcinogenic risks to humans), "Trichloroethylene, tetrachloroethylene, and some other chlorinated agents/IARC Monographs, Volume 106," [Online]. Available: https://monographs.iarc.fr/wp-content/uploads/2018/06/mono106.pdf. [Accessed Feb 6, 2019].
7. Villanueva, C.M.; Kogevinas, M.; Cordier, S.; Templeton, M.R.; Vermeulen, R.; Nuckols, J.R.; Nieuwenhuijsen, M.J.; Levallois, P. "Assessing Exposure and Health Consequences of Chemicals in Drinking Water: Current State of Knowledge and Research Needs," *Environ. Health Perspect.,* No. 122, pp. 213-221, 2014.
8. International Organization for Standardization, ISO 23631:2006(E) — Determination of dalapon, trichloroacetic acid and selected haloacetic acids — Method using gas chromatography (GC-ECD and/or GC-MS detection) after liquid-liquid extraction and derivatization, 2006-05 ed., Beuth-Verlag, 2006.
9. U.S. Environmental Protection Agency, Method 552.3, Determination of Haloacetic Acids and Dalapon in Drinking Water Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection, 1 ed., O. o. G. W. a. D. Water, Ed., Cincinatti, 2003.
10. International Organization for Standardization, Corrigenda to DIN ISO 23631:2006-05, 11-2007 ed., Berlin: Beuth Verlag, 2007.
11. Hillen, E. "Halogencarbonsäuren," in *Römpp Chemie Lexikon,* 9th ed., J. Falbe and M. Regitz, Eds., Stuttgart; New York, Georg Thieme Verlag, 1995.
12. U.S. Environmental Protection Agency, Method 557: Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS), 1 ed., O. o. G. W. a. D. Water, Ed., Cincinatti, 2009.
13. Thermo Fisher Scientific Inc., "Dionex IonPac AS31," 2018. [Online]. Available: https://assets.thermofisher.com/TFS-Assets/CMD/manuals/man-155007-ionpac-as31-columns-man155007-en.pdf. [Accessed Feb 11, 2019].
14. Thermo Fisher Scientific Inc., "Dionex Integrion HPIC System Operator's Manual Revision 04," 2016. [Online]. Available: https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-22153-97003-IC-Integrion-Man2215397003-EN.pdf. [Accessed Feb 8, 2019].
15. Thermo Fisher Scientific Inc., "Dionex ICS-6000 Consumables Tracking Quick Start Guide," 2018. [Online]. Available: https://assets.thermofisher.com/TFS-Assets/CMD/manuals/qs-065759-ics-6000-cdm-qs065759-en.pdf. [Accessed Feb 8, 2019].
16. Chen,C.-Y.; Chang, S.-N.; Wang,G.-S. "Determination of Ten Haloacetic Acids in Drinking Water High-Performance and Ultra-Performance Liquid Chromatography – Tandem Mass Spectrometry," *J. Chromatogr. Sci.* Vol. 47, pp. 67-73, January 2009.
17. Wu, S.; Anumol, T.; Gandhi, J.; Snyder, S. A. "Analysis of haloacetic acids, bromate, and dalapon in natural waters by ion chromatography – tandem mass spectrometry," *J. Chromatogr. A* Vol. 1487, pp. 100-107, 03 01 2017.
18. Meng, L.; Wu, S.; Ma, F.; Jia, A.; Hu, J. "Trace determination of nine haloacetic acids in drinking water by liquid chromatography electrospray tandem mass spectrometry," *J. Chromatogr. A* Vol. 1217, pp. 4873-4876, 24 05 2010.
19. Gallidabino, M. D.; Hamdan, L.; Murphy B.; Barron, L. P. "Suspect screening of halogenated carboxylic acids in drinking water using ion exchange chromatography – high resolution (orbitrap) mass spectrometry (IC-HRMS)," *Talanta*, Vol. 178, pp. 57-68, 2018.

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