SHIMADZU
Excellence in Science

Application News

No. GC-2106

Gas Chromatography

Determination of Haloacetic Acids (HAA9) and Dalapon in Drinking Water According to EPA Method 552.3 on Dual Columns from a Single Injection

■ Abstract

Haloacetic acids (HAAs) are known carcinogens that may occur as disinfection byproducts in drinking water. Currently, five HAAs are regulated under the Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR) and occurrence of four more HAAs is being monitored under the Unregulated Contaminant Rule 4 (2018-2020)[1]. EPA Method 552.3[2] is approved for the monitoring of the regulated HAAs (HAA5), the additional four HAAs (HAA9) and dalapon. This publication demonstrates the performance of the Shimadzu Nexis GC-2030 with dual ECDs and a single split/splitless injector for the analysis of the ten target compounds included in EPA Method 552.3 using helium as carrier gas. Precision was under 5% for mid-range concentration standard and under 16% for lowest concentration, and accuracy was within the acceptable range of 50-150% of expected values for lowest concentration (62-88%) and 70-130% of expected values for all other concentrations (95-112%). The results obtained with the Shimadzu Nexis GC-2030 with dual ECDs meet and exceed the quality assurance criteria outlined in EPA Method 552.3.

■ Introduction

Haloacetic acids (HAAs) are known carcinogens that may occur as disinfection byproducts in drinking water. Currently, five HAAs are regulated under the Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR) and there is a Maximum Contaminant Level of 60 ppb for the sum of these five compounds (MCAA, MBAA, DCAA, TCAA, DBAA). The occurrence of four more HAAs (BCAA, BDCAA, CDBAA, TBAA) is being assessed under Unregulated Contaminant Rule 4 (UCMR4). HAA5 are regularly monitored by water utilities to comply with federal regulations. Requirements for the analysis of HAA9 beyond the scope of UCMR4 will be determined once the rule is completed; however, some utilities already monitor them as means of process control during water treatment. EPA Method 552.3 is approved for the monitoring of regulated HAAs (HAA5), four additional HAAs (HAA9) and dalapon[1].

Table 1: List of HAAs included in EPA Method 552.3

Compound	Acronyms	HAA Group	
Monochloroacetic acid	MCAA	HAA5	HAA9
Monobromoacetic acid	MBAA	HAA5	HAA9
Dichloroacetic acid	DCAA	HAA5	HAA9
Trichloroacetic acid	TCAA	HAA5	HAA9
Dibromoacetic acid	DBAA	HAA5	HAA9
Bromochloroacetic acid	BCAA		HAA9
Bromodichloroacetic acid	BDCAA		HAA9
Chlorodibromoacetic acid	CDBAA		HAA9
Tribromoacetic acid	TBAA		HAA9

In this application, HAA9 and dalapon were analyzed according to EPA Method 552.3 using a Shimadzu Nexis GC-2030 with two ECD detectors. EPA Method 552.3 requires the confirmation of analyte identification via sample analysis in two dissimilar columns (ex. Rtx-1701 and Rxi-5Sil MS). Normally, two independent injections of the same sample would be needed to complete analysis on both the analytical and confirmation columns. In this analysis, a two-way injection port adaptor was installed to enable equal splitting of sample between the analytical column and the confirmation column. There are several advantages to using a two-way injection port adaptor instead of a press-tight Y-connection or a three-way union. First, the columns are independently installed with traditional graphite ferrules, so they can be easily replaced one at a time. Second, both columns are inserted into the injection port liner without extra parts or connections to alleviate concerns around dead volume or sealing issues. Lastly, setting flow and pressure parameters on the two columns connected to the two-way adaptor is the same as a single column connected to a regular injection port, requiring minimal method development. This single injection/single run configuration meets the EPA requirements for identification, quantification and confirmation of HAAs and dalapon.

■ Materials and Methods

Reagents

ECD grade tert-butyl methyl ester (MTBE) was purchased from Sigma (Cat. No. 1019951000). The internal standard (IS) stock solution (1,2,3-trichloropropane, Cat. No. 31648) was purchased from Restek. The haloacetic acid methyl ester mix was purchased from AccuStandard (Cat. No. M-552.3) and diluted to indicated concentrations in MTBE with containing 1 ppm internal standard.

Instrumentation

A Shimadzu GC-2030 with a dual line split/splitless injector, dual ECD Exceed detector and dual autosampler was used for analysis of HAA5, HAA9 and dalapon according to EPA Method 552.3 using helium as carrier gas. Methylated forms of HAAs, dalapon and surrogate as well as the internal standard were analyzed on the GC system. Analysis conditions are outlined in Table 2. LabSolutions software was used for data acquisition and processing. Concentrations reported in section "Results and Discussion" represent the concentration in the water samples, before extraction and methylation (derivatization).

■ Results and Discussion

Using a Shimadzu GC-2030 with a dual inlet, detector and autosampler, nine methylated haloacetic acids and dalapon were analyzed simultaneously on an analytical column (SH-Rtx-1701) and a confirmation column (SH-Rxi-5Sil MS) according to EPA 552.3 Method using helium as the carrier gas. The list of analytes, identification number (for reference purposes) and their retention times on each column are shown in Table 3.

Results discussed in the subsequent sections demonstrate the system suitability of Shimadzu Nexis GC-2030 with ECD Exceed in accordance with the quality assurance and quality control criteria outlined in EPA Method 552.3, including accuracy and precision.

Table 2: Instrument Configuration and Analytical Conditions

GC System	Shimadzu GC-2030 with SPL, 2-way splitter, dual ECD-2030 Exceed and AOC-20 Plus autosampler
Column	SH-Rtx-1701, 30m x 0.25mm x 0.25µm (line 1) SH-Rxi-5Sil MS, 30m x 0.25mm x 0.25µm (line 2)
Injector Mode	Split at 1:1 ratio increases to 10 after 0.5 min
Injection Volume	1.5 µL
Carrier Gas	Helium
Flow Mode	Constant pressure at initial linear velocity of 40cm/sec
Column Temp.	35°C, 10min – 3°C/min – 65°C – 10°C/min – 85°C – 20°C/min – 205°C, 5min
Injection Port Temp.	210°C
Detector Temp. and Current	290°C, 2nA
Detector Gases	N_2 45 mL/min

Table 3: List of compounds analyzed, Identification number and retention time in analytical and confirmation columns.

Compounds	Peak No.	Ret. Time (min)	
		SH-Rtx-1701	SH-Rxi-5Sil MS
MCAA	1	11.13	5.95
MBAA	2	15.96	9.88
Dalapon	3	16.44	12.50
DCAA	4	16.83	10.86
TCAA	5	20.20	16.48
1,2,3-trichloropropane (internal standard)	6	21.72	17.18
BCAA(*)	7	21.91	16.93
2-bromobutanoic acid (surrogate)	8	22.23	18.90
BDCAA(*)	9	23.78	22.04
DBAA	10	24.10	21.78
CDBAA(*)	11	25.47	24.42
TBAA(*)	12	26.69	25.85

(*) Compounds included in HAA9 group

Method interferences: solvents

Prior to analyzing any sample, materials used in this analysis must be demonstrated to be free of interferences. Area counts of target analytes or other method interferences must be 1/3 of the minimum reporting limit (MRL)[2]. In this work, 1 ppb was the lowest concentration evaluated. The signal-to-noise ratio (S/N) was above 20 for all compounds at this concentration, exceeding the method requirement of S/N ≥ 5.

The analytes for this project were purchased already derivatized, hence, sample preparation consisted in the dilution of standards with MTBE.

A fresh aliquot of solvent was analyzed at the beginning of each analytical batch during the performance tests for the analysis of HAA9 and dalapon.

Figure 1 shows the overlaid chromatograms from the solvent blank and 1 ppb standard acquired with the analytical column (Rtx-1701; Figure 1a) and confirmation one (Rxi5Sil-MS; Figure 1b). Only two peaks within the range of where haloacetic acids elute were detected in the solvent blank on both columns (noted with an asterisk in the figure). These peaks are not target analytes or interfere with their quantification.

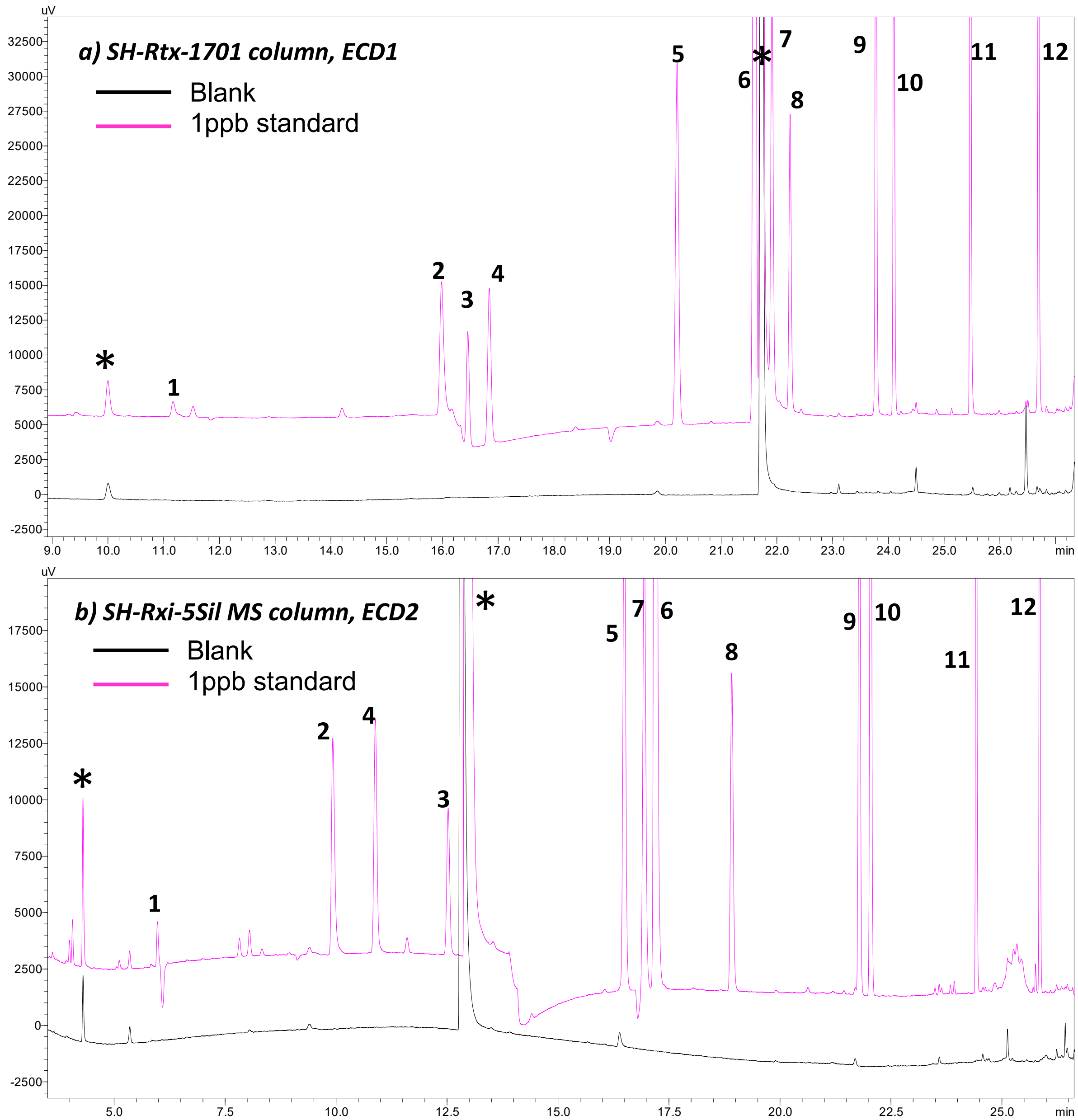

Figure 1: Chromatograms of MTBE blanks and 1 ppb HAA Methyl Ester Mix on a) analytical column (SH-Rtx-1701) and b) confirmation column (SH-Rxi-5Sil MS). The results shown in confirmed the suitability of our system for demonstrating its performance for the analysis of HAA9 and dalapon.

Calibration Curve

EPA Method 552.3 requires at least five calibration standards for preparing the initial calibration curves, with the lowest calibration standard at or below the MRL[2]. In this study, a seven-point calibration was used.

The HAA methyl ester mix was diluted to prepare the six calibration standards with concentrations ranging from 1 to 50 µg/L (in water sample). Internal standard calibrations fitted quadratically with 1/A weighting without forcing through zero were built for all targets, in accordance with acceptable options included in EPA Method 552.3.

The HAA9 and dalapon calibration curves are shown in Figure 2 in the analytical (Figure 2a) and confirmation (Figure 2b) columns.

To procced with the analysis of samples, accuracy of the calibration curve needs to be demonstrated. Per criteria outlined in EPA Method 552.3, the analyte concentrations should be within 70-130% of the expected values, except for the lowest calibration level, for which results within 50-150% of expected values are accepted[2]. As shown in Table 4, all concentrations measured were within ± 28% of expected values. Hence, all results met and exceeded the accuracy ranges established by EPA, including the lowest calibration level (1 ppb).

a) SH-Rtx-1701

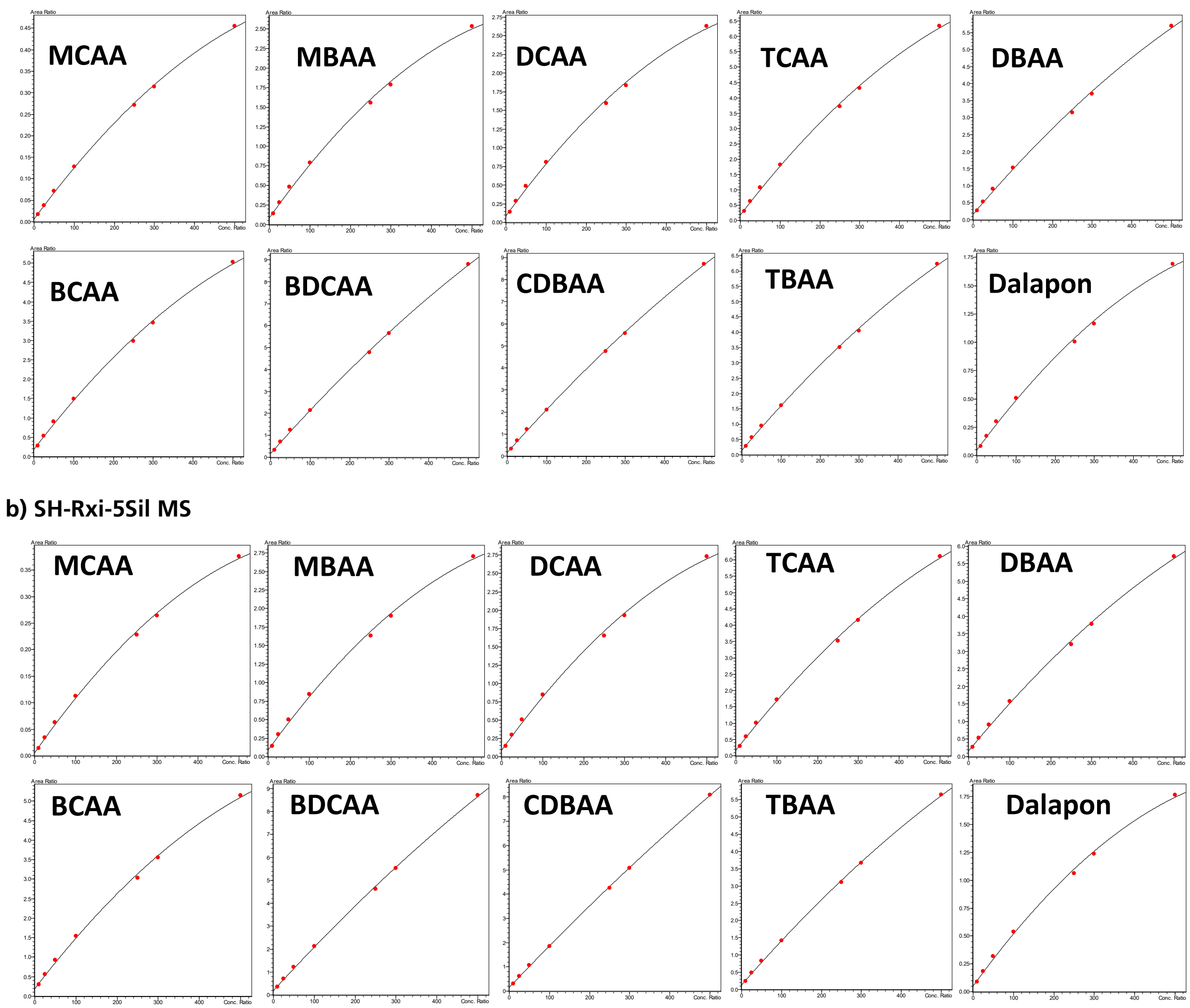

Figure 2: Seven-point calibration curves for HAA9 and dalapon on a) analytical column (SH-Rtx-1701) and b) confirmation column (SH-Rxi-5Sil MS).

Table 4: Calibration curve accuracy: Percent difference of measured concentrations from expected concentrations.

Expected conc.	1 ppb		2.5 ppb		5 ppb		10 ppb		25 ppb		30 ppb		50 ppb	
	ECD1	ECD2	ECD1	ECD2	ECD1	ECD2	ECD1	ECD2	ECD1	ECD2	ECD1	ECD2	ECD1	ECD2
MCAA	88.2	84.2	104.1	106.5	107.1	108.2	102.3	104.4	97.8	96.3	98.0	97.5	101.6	102.6
MBAA	72.7	72.6	109.8	110.7	112.4	110.7	104.3	105.3	96.2	95.4	96.5	97.3	103.2	102.9
DCAA	72.5	72.8	110.7	111.1	111.8	111.1	104.2	104.7	96.2	95.3	96.9	97.7	102.8	102.8
TCAA	78.5	80.0	107.6	107.7	109.7	107.9	103.6	103.4	96.9	96.2	97.4	98.8	102.0	101.5
DBAA	75.5	74.9	107.9	108.3	110.5	110.0	103.2	104.0	96.8	96.0	97.7	98.2	102.0	101.9
BCAA	83.9	83.3	107.7	106.0	107.6	107.9	99.9	101.9	98.3	97.3	99.0	99.0	100.8	101.0
BDCAA	74.0	77.8	109.5	107.2	111.1	109.4	103.5	104.3	96.6	96.1	97.7	98.3	101.7	101.7
CDBAA	86.0	86.7	107.4	106.8	105.9	105.7	99.7	99.5	99.0	98.4	98.8	99.7	100.7	100.5
TBAA	80.4	83.6	108.9	107.3	108.1	107.0	101.0	100.6	98.7	98.2	97.6	99.0	101.2	100.8
Dalapon	75.3	75.8	109.1	109.3	111.3	110.4	104.6	104.9	96.2	95.6	96.9	97.5	102.7	102.7

Additionally, although not required by EPA in Method 552.3, coefficients of determination were calculated for all target analytes. As shown in the results in Table 5, fittings with $r^2 > 0.997$ were obtained for all analytes.

Table 5: Coefficient of determination (r^2) of the calibration curves.

Compounds	r^2	
	SH-Rtx-1701	**SH-Rxi-5Sil MS**
MCAA	0.9992	0.9985
MBAA	0.9974	0.9975
Dalapon	0.9977	0.9978
DCAA	0.9975	0.9975
TCAA	0.9984	0.9987
BCAA	0.9983	0.9982
BDCAA	0.9993	0.9991
DBAA	0.9981	0.9984
CDBAA	0.9995	0.9995
TBAA	0.9990	0.9993

Accuracy and precision

Accuracy and precision must be also demonstrated prior to analyzing samples by EPA Method 552.3, especially in instances when a full initial calibration curve is not analyzed, based on the results from a mid-range level quality control sample [2]. For this purpose, a 10 ppb standard (mid-range in calibration curve) was analyzed in replicates in five consecutive analytical batches over five days (total n=20). The concentration of the analytes, summarized in Table 6, was within 5% of the expected value for all analytes, meeting and exceeding EPA's accuracy criteria (mean recovery within ±20%). Also, as shown in Table 6, RSD for all analytes were less than 5%, exceeding the EPA requirement for precision (≤ 20% RSD).

Table 6: Repeatability (%RSD, n=20) of 10 ppb (mid-range) standard over five days.

Compounds	SH-Rtx-1701		SH-Rxi-5Sil MS	
	Mean % recovery	**%RSD**	**Mean % recovery**	**%RSD**
MCAA	97.14	1.97	100.55	1.52
MBAA	97.89	2.61	97.75	2.71
Dalapon	98.61	2.58	98.07	2.60
DCAA	99.04	2.48	98.31	2.97
TCAA	98.70	3.14	99.04	2.71
BCAA	100.25	2.99	100.57	2.77
BDCAA	97.71	3.96	97.586	3.57
DBAA	102.849	2.99	100.979	2.31
CDBAA	97.536	3.86	95.726	4.28
TBAA	98.628	3.99	95.996	4.60

Data was further evaluated for accuracy and precision at the MRL (1 ppb) over three days (n=6). As shown in Table 7, %RSD for all compounds at 1 ppb were less than 16%, exceeding the EPA's precision requirement (≤ 20% RSD). For the lowest standard of the calibration curve, measured concentration must be within ±50% of the expected value; all HAA9 and dalapon met this criterion and, furthermore, accuracy was within ±35% for most of the compounds.

Table 7: Repeatability (%RSD, n=6) of 1 ppb (lowest concentration) standard over three days.

Compounds	SH-Rtx-1701		SH-Rxi-5Sil MS	
	Mean % recovery	**%RSD**	**Mean % recovery**	**%RSD**
MCAA	82.25	6.75	75.16	5.81
MBAA	64.37	12.76	62.69	12.49
Dalapon	65.76	10.56	62.33	13.96
DCAA	67.83	7.88	64.44	12.56
TCAA	73.14	9.26	69.45	11.87
BCAA	66.83	11.75	61.61	15.78
BDCAA	80.68	6.03	77.50	7.58
DBAA	69.00	11.01	65.73	13.28
CDBAA	82.22	5.44	80.32	5.96
TBAA	74.45	6.24	72.13	7.80

■ Conclusion

The Shimadzu Nexis GC-2030 with a split/splitless injector and dual ECDs was employed to analyze HAA9 and dalapon according to EPA Method 552.3 and using helium as carrier gas. The injection port split-flow set up allowed users for the simultaneous quantitation of compounds on the analytical column and the confirmation column from one injection, increasing the throughput and saving samples.

The results obtained, in terms of accuracy and precision, met and exceeded EPA quality assurance requirements, hence, demonstrated the excellent performance and robustness of the system.

■ References

1. EPA the Fourth Unregulated Contaminant Monitoring Rule (UCMR4) Fact Sheet for Assessment Monitoring – Haloacetic Acid (HAA) (2016)
2. EPA Method 552.3, Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Dectection, EPA 815-B-03-002 (2003)

■ Consumables

Part Number	Description	Unit	Instrument
221-76650-01	Septa, Green, Premium Low Bleed	Pk of 25	GC-2030
227-35007-01	Split Liner with Wool, GC-2030	Pk of 5	
221-32126-05	Graphite ferrules, for 0.25mm-0.32mm ID columns	Pk of 10	
221-34618-00	Syringe, 10 µL, fixed needle	each	AOC-20i/s
220-97331-31	Sample Vials, 1.5 mL Amber Glass with Caps & Septa	Pk of 100	
220-97331-47	Sample Vials, 1.5 mL Amber Glass with Caps & Septa	Pk of 1000	
220-97331-62	200 µL Glass Inserts for 1.5mL Vials	Pk of 100	
220-97331-23	Wash Vials, 4 mL Amber Glass with Caps & Septa	Pk of 100	
221-76185-30	SH-Rtx-1701 Cap. Column, 30 x 0.25 x 0.25	each	Column (primary)
221-75954-30	SH-Rxi-5Sil MS Cap. Column, 30 x 0.25 x 0.25	each	Column (confirmation)

First Edition: March 2021

SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com