

EPA Method 552.1 – Haloacetic Acid and Dalapon by Automated Solid Phase Extraction

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Introduction

Method 552.1 is an ion exchange procedure used for determining haloacetic acids and dalapon in drinking water and drinking water sources. Since this is an ion exchange procedure, the potential interferences are other naturally occurring ions in water sources. Sulfate and thiosulfate are effective counter ions that compete with the analytes for the ion exchange sites on the solid phase extraction (SPE) disk. Sulfate ions in concentrations greater than 200 mg/l will effectively displace the haloacetic acids from the SPE disk during the extraction process. Reduced recoveries may also be observed in very high ionic strength waters (i.e. 400 mg/l NaCl). Therefore, the success of the extraction efficiency depends on the sample being relatively free of ionic species.

This paper presents data demonstrating the capability of the Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems for performing the sample extraction. Automated SPE reduces solvents, eliminates emulsions, reduces exposure to solvents, improves recoveries and consistency of results, and increases productivity and reduces labor costs.

Instrumentation

- Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems
- Heating Block
- Empore[™] 47 mm Anion Exchange Disk
- HP 5890 GC, ECD, 7673A autosampler,

Method Summary

I. Calibration Standards

- 1) Primary dilution standard prepared from AccuStandard M-552.1A and M-552.1-SS stock solutions in CH₃OH.
- 2) Six different levels of standard concentrations for each analyte prepared from pipeting the appropriate volumes of primary dilution solution.
- 3) Standards extracted with Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems.
- 4) After extraction, solvent partition step performed on all standards.
- 5) Calibration run on GC.

II. Initial Demonstration of Capability (IDC)

- 1) Five replicate, 100 mL volumes of DI water acidified to pH 5

with HCl.

- 2) 200 µl of the primary dilution solution added to each bottle to obtain Level 2 analyte concentrations.
- 3) Spiked DI water samples extracted with Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems.
- 4) After extraction, perform solvent partition.
- 5) Analyze on GC.

III. Method Detection Limit (MDL)

- 1) Nine replicate, 100 mL volumes of DI water acidified to pH 5 with HCl.
- 2) 100 µl of the primary dilution solution added to each bottle to obtain Level 1 analyte concentrations.
- 3) Extracted with Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems.
- 4) After extraction, perform solvent partition.
- 5) Analyze on GC.

Results

The pH of the DI water was adjusted using HCl rather than H₂SO₄, to avoid the introduction of sulfate ions. It is also recommended to use a 1% solution of ammonium chloride, NH₄Cl (1 g / 100 mL), rather than granular ammonium chloride because the chloride ions will compete with the active sites of the SPE disk and reduce the recoveries of the haloacetic acids. The Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems were also flushed with DI water between samples to remove any traces of acid left behind from the previous extraction run.

Each laboratory is responsible for operating a formal quality assurance program. For Method 552.1, the minimum requirements include an initial demonstration of laboratory capability (IDC), MDL study, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified matrices, and QC samples.

The capability of the Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems for the extraction of haloacetic acids and dalapon in drinking water was demonstrated by performing the IDC, MDL study, and tracking of the surrogate and internal standard recoveries. All results are presented in Appendix I. Table 1 shows the extraction method programmed into the SPE-DEX[®] Controller used to run Method 552.1.

Table 1: Extraction method programmed into the SPE-DEX[®] Controller

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	3:00 min	30 sec
Prewet 2	HCl/Methanol	1:30 min	1 sec
Prewet 3	Reagent Water	30 sec	1 sec
Prewet 4	NaOH/Reagent Water	1:30 min	1 sec
Prewet 5	Reagent Water	30 sec	2 sec
Prewet 6	Reagent Water	30 sec	0 sec
Process Sample			
Wash 1	Methanol	30 sec	1:00 min
Wash 2	Methanol	30 sec	1:00 min
Air Dry			2:00 min
Rinse 1	H ₂ SO ₄ /Methanol	4:00 min	2:00 min
Rinse 2	H ₂ SO ₄ /Methanol	2:00 min	2:00 min

Conclusions

The data in Appendix I meet the EPA criteria for Method 552.1 and demonstrate the capability of the Horizon Technology SPE-DEX[®] 4790 Automated Extractor Systems to perform the extraction process. Automated SPE reduces solvents, eliminates emulsions, reduces exposure to solvents, improves recoveries and consistency of results, and increases productivity and reduces labor costs.

Appendix I

Table 2: Calibration Standards

Analyte	Level 1 (ppb)	Level 2 (ppb)	Level 3 (ppb)	Level 4 (ppb)	Level 5 (ppb)	Level 6 (ppb)
Monochloroacetic Acid	2.97	5.94	11.9	17.8	23.8	29.7
Monobromoacetic Acid	2.00	4.00	8.00	12.0	16.0	20.0
Dalapon	2.00	4.00	8.01	12.0	16.0	20.0
Dichloroacetic acid	2.98	5.95	11.9	17.8	23.8	29.8
2-Bromopropionic Acid	0.984	1.97	3.94	5.90	7.87	9.84
Trichloroacetic Acid	0.990	1.98	3.96	5.94	7.92	9.90
1,2,3-Trichloropropane (internal standard)	19.8	19.8	19.8	19.8	19.8	19.8
Bromochloroacetic Acid	1.99	3.97	7.94	11.9	15.9	19.9
Dibromoacetic Acid	0.985	1.97	3.94	5.91	7.88	9.85

Table 3: Initial Demonstration of Capability

	Monochloroacetic Acid (5.94 ug/l)		Monobromoacetic Acid (4.00 ug/l)		Dalapon (4.00 ug/l)		Dichloroacetic Acid (5.95 ug/l)		2-Bromopropionic Acid* (8.22 ug/l)		Trichloroacetic Acid (1.98 ug/l)		Bromochloroacetic Acid (3.97 ug/l)		Dibromoacetic Acid (1.97 ug/l)	
	ppb	%	ppb	%	ppb	%	ppb	%	ppb	%	ppb	%	ppb	%	ppb	%
IDC1	4.63	78	3.38	85	3.65	91	4.99	84	7.16	87	1.73	87	3.18	80	1.59	81
IDC2	4.86	82	3.58	90	3.97	99	5.48	92	7.45	91	1.88	95	3.44	87	1.69	86
IDC3	5.33	90	3.91	98	4.33	108	5.89	99	8.21	100	1.96	99	3.34	84	1.62	82
IDC4	5.23	88	3.99	100	4.13	103	5.68	95	7.78	95	1.86	94	2.76	70	1.43	73
IDC5	5.42	91	3.96	99	4.10	103	5.84	98	8.07	98	1.83	92	2.76	70	1.43	73
Mean		86		94		101		94		94		93		78		79
STDEV		0.0559		0.0658		0.0634		0.0602		0.0526		0.0439		0.0789		0.0579

* Includes Level 2 standard of 1.97 ppb plus the surrogate 6.25 ppb

Table 4: MDL Study

	Monochloroacetic Acid (2.97 ug/l)	Monobromoacetic Acid (2.00 ug/l)	Dalapon (2.00 ug/l)	Dichloroacetic Acid (2.98 ug/l)	2-Bromopropionic Acid (0.984 ug/l)	Trichloroacetic Acid (0.990 ug/l)	Bromochloroacetic Acid (1.99 ug/l)	Dibromoacetic Acid (0.985 ug/l)
MDL1	2.84	2.01	1.93	2.91	0.950	1.05	2.30	1.36
MDL2	1.91	1.53	1.25	1.94	0.662	0.830	1.88	1.21
MDL3	2.81	2.02	1.76	2.96	0.935	1.02	2.36	1.37
MDL4	2.59	1.87	1.73	2.80	0.889	1.01	2.34	1.39
MDL5	2.41	1.74	1.26	2.56	0.790	0.837	2.21	1.34
MDL6	2.70	2.16	2.10	2.93	0.987	1.10	2.15	1.25
MDL7	2.62	1.91	1.79	2.69	0.907	1.05	2.24	1.29
MDL8	2.05	1.73	1.68	2.32	0.728	0.977	2.19	1.28
MDL9	2.34	1.83	1.59	2.30	0.808	0.922	1.70	1.04
Mean	2.47	1.87	1.68	2.60	0.851	0.977	2.15	1.28
STDEV	0.3265	0.1875	0.2804	0.3515	0.1097	0.0955	0.2212	0.1082
Students t	2.896	2.896	2.896	2.896	2.896	2.896	2.896	2.896
MDL	0.95	0.54	0.81	1.02	0.32	0.28	0.64	0.31

Table 5: Internal Standard Peak Areas

	Run Designation	1,2,3-Trichloropropane Peak Area
Standards	Level 1	137,081
	Level 2	127,034
	Level 3	127,374
	Level 4	124,712
	Level 5	127,111
	Level 6	126,997
Initial Demonstration of Capability	IDC1	138,606
	IDC2	133,971
	IDC3	123,594
	IDC4	119,016
	IDC5	115,416
MDL Study	MDL1	122,805
	MDL2	124,255
	MDL3	121,991
	MDL4	115,357
	MDL5	126,295
	MDL6	120,202
	MDL7	134,567
	MDL8	137,852
	MDL9	137,188