3M

Empore™ Extraction Disks

METHOD Summary

EPA Method 552.1

Summary

This method summarizes the extraction and elution of a 100 ml water sample, partitioning of the eluate into methyl t-butyl ether (MtBE) and derivatization of the analytes as specified in Section 11 of the EPA method. Some additional notes for successful sample preparation preface the actual method summary.

Description

EPA Method 552 Revision 1.0 (August 1992) is an ion exchange solid-phase extraction method for the Determination of Haloacetic Acids and Dalapon in Drinking Water using gas chromatography with electron capture detection. The method permits the use of solid phase extraction disks "as long as all the quality control criteria specified in Section 9.0 of the method are met" (Section 2.1 of Method 552.1).

Tips for Successful Sample Preparation

Minimize Sample Interferences

Ion exchange separations are susceptible to poor results in the presence of competing anions in the sample. Highly selective counter ions, such as sulfate ions, or an abundance of lower selectivity counter ions, such as chloride ions can negatively impact extraction of the haloacetic acids in solution by depleting the ion exchange capacity of the solid phase extraction disk. Strongly selective counter ions cannot be displaced by the lower selectivity carboxylic acids that are sought in this method.

- EPA Method 552.1 lists the use of sulfuric acid for sample pH adjustment. Hydrochloric acid is an alternative for consideration to avoid creating an excess of highly selective SO_4^{-2} ions in the sample.
- EPA Method 552.1 also recommends the use of NH_4Cl to stabilize collected water samples. The amount of NH_4Cl added is critical to minimize competition for binding sites.

Extract and elute at optimal pH levels

The carboxylic acids sought in EPA Method 552.1 must be in an ionic form in order to be effectively extracted by an anion exchange medium. The rule of thumb for anions is that the pH of the sample should be two pH units above the pKa of the acid for it to be fully ionic. [The pKa is the pH at which half the analyte in solution is charged and half is neutral]. The pKa values for the analytes in this method range from about 0.8 to about 2.9. Method 552.1 requires a sample pH of 5 ± 0.5 to ensure the carboxylic acids are fully ionized and able to be extracted. A partial list of individual pKa values is found below.

Allow adequate time for optimized reaction kinetics

The strong anion exchange disk possesses the same fast flow characteristics as other Empore disks. However, due to the kinetics of ion exchange reactions, a slower flow rate may be desirable. Evaluating recoveries at varying flow rates for sample extraction and elution allows the determination of optimal sample processing time for a given analyte and sample matrix. A minimum 30 seconds soaking time for the disk is recommended during the elution step. If possible, allow the eluting solvent to drip slowly through the disk and into the collection vial.

Use adequate elution solvent

Recoveries may improve using 2 x 5 ml aliquots of 10% H_2SO_4/methanol instead of a single 4 ml aliquot. However, the risk of GC column damage is present if strongly acidic sample is injected. Increasing the amount of sodium sulfate called for the in the method will aid in minimizing this risk.

Derivatization

- Inadequate cooling of the MtBE/MeOH solution after heating may cause variability in the partitioning, making the transfer of the MtBE layer more difficult.
- If MeOH or water solutions contaminate the MtBE, there is a possibility of acid being injected into the GC (see comments above).
- If water is transferred into the MtBE, esterification can be reversed.

Analyte	pKa
Monochloroacetic acid (MCAA)	2.81
Monobromoacetic acid (MBAA)	2.86
Dichloroacetic acid (DCAA)	1.25
Trichloroacetic acid (TCAA)	0.77
Dalapon	1.84

Method

STEP 1

Sample Preparation: A 100 ml sample is adjusted to pH 5.0 ± 0.5. Surrogate standard is added according to section 7.15.3 of the EPA method. Please refer to the section on minimizing sample interferences above.

STEP 2

Assemble Glassware: Place a 47 mm Empore™ Anion Exchange - SR Extraction Disk in a filtration glassware apparatus. Refer to Section 4 of EPA Method 552.1 for glassware cleaning protocol. To swell the resin and pre-wash the disk, place 10 mL acetone onto the disk surface (see Note). Allow disk to soak for about three minutes. Pull remaining acetone through the disk with vacuum to dry the disk. Repeat using 10 mls isopropyl alcohol.
NOTE: The disk will swell upon addition of acetone. This may cause cosmetic wrinkles; however, this will not affect the performance of the disk. An alternative method of pre-swelling the disk is to apply 2-4 mls acetone directly to the surface of the disk prior to clamping the glass reservoir into place.

STEP 3

Condition Disk:
NOTE: Do not allow the disk to become dry during or between any of the conditioning steps right through sample extraction. If the disk should become dry, repeat the conditioning process.

- Add 10 mls methanol to the reservoir. Draw a small amount (several drops) of methanol through the disk with vacuum; vent the system and allow the disk to soak for one minute. Draw most of the remaining solvent through the disk, leaving 3-5 mm of methanol to cover the surface of the disk.
- Add 10 mls 1M HCl/Methanol to the disk (refer to Section 7 of EPA Method 552.1). Draw a small amount of the acidic methanol through the disk with vacuum; vent the system and allow the disk to soak for thirty seconds. Draw most of the remaining solvent through the disk, leaving enough to cover the surface of the disk.
- Wash the disk with two successive10 ml aliquots of reagent grade water, drawing most of the water through the disk between washes but always leaving enough water to cover the surface of the disk.
- Add 10 mls 1N NaOH (aqueous). Draw a small amount through the disk with vacuum; vent the system and allow the disk to soak for thirty seconds. Draw most of the remaining NaOH through the disk, leaving enough to cover the surface of the disk.
- Wash the disk with two successive10 ml aliquots of reagent grade water, drawing most of the water through the disk between washes but always leaving enough water to cover the surface of the disk.

STEP 4

Extract Sample: Add the sample to the reservoir and apply vacuum until the entire sample is drawn through the disk. The disk should be allowed to dry at this point. Please refer to tips relating to reaction kinetics above.

STEP 5

Dry disk under vacuum for 5 minutes.

STEP 6

Wash disk: Add 10 mls methanol to the sample container and agitate to completely rinse all surfaces. Transfer this methanol to the reservoir with a pipette, rinsing down the sides in the process. Draw the methanol through the disk and discard. Repeat with a second 10 mL aliquot of methanol.

STEP 7

Elute Disk: With a receiving vial in place, add 4 mls 10% H_2SO_4/methanol (v/v) to the reservoir. Allow elution solvent to soak disk for at least 30 seconds. Apply vacuum and collect eluate in the vial. Please refer to tips relating to reaction kinetics above.

STEP 8

Derivatize: Add 2.5 mls MtBE to the vial, cap, and agitate for 5 seconds. Heat the vial for 1 hour at 50°C to methylate analytes. Cool vial and add enough 10% Na_2SO_4/H_2O (w/v) to produce two immiscible layers. Agitate for 15 seconds and let stand to allow phases to separate. Transfer MtBE to a volumetric flask. Wash the aqueous layer twice with 1 ml aliquots of MtBE, transferring the solvent to the volumetric flask. Add internal standard solution and bring to volume with MtBE.

STEP 9

Analyze by GC/ECD.

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