Modified EPA Method 549.2

Diquat and Paraquat from Drinking Water

This method is a modified summary of the SPE extraction contained in section 11.2 "Cartridge Extraction" of US EPA method 549.2.

VIP Note: EPA 549.2 specifies a 5 mL MeOH wash at step 11.2.5. It is this authors' belief that the MeOH wash will prematurely elute the diquat/paraquat – hexanesulfonic acid (Solution B) Ion Pair. This may result in low / irreproducible recoveries and is likely the cause of "significant variability between brands of C8 LSE media, and also between lots of the same brand of LSE media" as reported by the method itself. Please direct any questions regarding this modification to Marc Boggeri, SPE Technical Manager, Phenomenex, Inc. (310) 212-0555.

1. Principle

EPA 549.2 relies upon unusual ion pairing conditions that convert the reverse phase C8 into a solid support for the ion-paring reagent, 1-hexanesulfonic acid (solution B). Also, during conditioning cetyl trimethyl ammonium bromide (solution A) is used to deactivate residual silanol on the surface of the silica particle.

Note: Paraquat and Diquat adsorb onto untreated glass surfaces. For this reason it is recommended to use plastic labware or to silanize all glass products that come into contact with the sample.

2. Materials

Strata SPE Cartridge: C8 1g/6mL , Part Number: 8B-S005-JCH

Note: method specifies 500 mg cartridge, but Phenomenex recommends a 1 gram cartridge as it offers an extra margin of safety due to its larger retention capacity.

Solution A: Dissolve 0.5 g of cetyl trimethyl ammonium bromide and 5 mL of concentrated ammonium hydroxide in 500 mL of deionized water and dilute to 1 liter in a volumetric flask.

Solution B: Dissolve 10 g of 1-hexanesulfonic acid, sodium salt and 10 mL of concentrated ammonium hydroxide in 250 mL of deionized water and dilute to 500 mL in a volumetric flask.

Elution Solution: Add 13.5 mL of orthophosphoric acid and 10.3 mL of diethylamine to 500 mL of deionized water and dilute to 1 liter in a volumetric flask.

3. Specimen Preparation

Adjust sample pH to 7.0 –9.0 with 10% w/v NaOH or 10% v/v HCl.

4. Method

- ***Condition:*** *Sequentially pass through the cartridge:*

  1. 1 column volume of DI Water
  2. 1 column volume of Methanol
  3. 1 column volume of DI Water
  4. 1 column volume of Solution A. Allow to slowly percolate through the sorbent bed under low vacuum. (1 column volume in 1 - 2 minutes)
  5. 1 column volume of DI Water
  6. 2 column volume of Methanol
  7. 1 column volume of DI Water
  8. 1 column volume of Solution B. Allow to slowly percolate through the sorbent bed under low vacuum. (1 column volume in 1 - 2 minutes) Allow 1-2 mm of Solution B to remain on top of the sorbent.

- ***Load:***

  Pass the sample through the cartridge. Maximum sample flow rate 6 mL per minute.

  Note: Large volume samples may be processed by using an adapter cap (P/N AHO-7191) and 60 mL solvent reservoir (P/N AHO-7189), or by attaching a solvent vacuum line to the sample collection bottle. Please refer to the Phenomenex document entitled " Processing Large Volume Samples by SPE".

- ***Wash:***

  1. 1 column volume of DI Water
  2. VIP Note: EPA 549.2 specifies a 5 mL MeOH wash at this step. It is this authors' belief that the MeOH will prematurely elute the diquat/paraquat – hexanesulfonic acid (Solution B) Ion Pair. This will result in low or irreproducible recoveries or as the method itself specifies, significant "variability between brands of C8 LSE media, and also between lots of the same brand of LSE media".
  3. Dry the cartridge under full vacuum for a minimum of 60 seconds to insure removal of aqueous wash.

- ***Elute:***

  1. Place a collection container inside the manifold.
  2. Pass 2 x 2.5 mL of Elution Solution through the cartridge at a rate not to exceed 3mL/min.

5. Analysis

A. Fortify eluent with 100 µL of ion-pair "concentrate". Concentrate is made by dissolving 3.75 g of 1-hexanesulfonic acid in 25 mL of the Elution Solution.

B. HPLC column: Phenomenex Spherisorb C8, 3µ 100mm x 4.6mm or Phenomenex Sphereclone C8, 3µ 100mm x 4.6mm. Analyze by HPLC / DAD per Table 1, EPA 549.2.

Note: This information is designed to serve as a convenient summary of the solid phase extraction protocol contained in the referenced US EPA method. Phenomenex makes no guarantee regarding the accuracy or completeness of the method. Please contact the US EPA for a copy of the original, complete method.