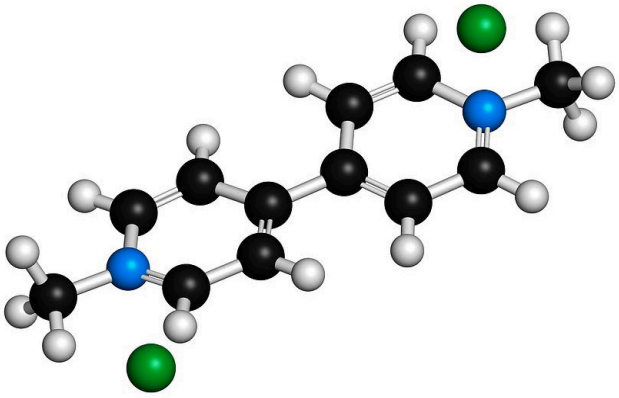
Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection*



UCT Part Numbers

EEC08156
500 mg C8,
6 mL cartridge

Or

ECUNI549
500 mg C8, 83 mL
Universal cartridge

Analyte	CASRN
Diquat 1,1′-ethylene-2,2′-bipyridium dibromide salt	85-00-7
Paraquat 1,1′-dimethyl-4,4′-bipyridium dichloride salt	1910-42-5

Initial Preparation

- Since diquat and paraquat are ionic analytes there is the potential for adsorption on glass surfaces.
- **Use only plastic labware.** Labware must be thoroughly washed and dried before use.
- Adjust a 250 mL of sample to pH 7 - 9 with 10 % aqueous sodium hydroxide or 10% aqueous hydrochloric acid solution depending upon initial pH.
- Assemble a C8 extraction cartridge in an appropriate manifold apparatus.
- If the sample contains particulates, filter through 0.45 µm Nylon membrane filter.
- **Ammonium hydroxide is volatile. Make fresh solutions daily from relatively new ammonium hydroxide stock.**

Sample Clean-up

- Clean-up procedures may not be necessary for a relatively clean sample matrix.
- If the sample contains particulates the entire sample should be passed through a 0.45 mm Nylon of PTFE membrane filter into a plastic container before starting extraction.

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Stock Standards Solutions

Diquat dibromide and Paraquat dichloride Stock Solutions (1000 mg/L)

1. Dry diquat (diquat dibromide monohydrate) and paraquat (paraquat dichloride tetrahydrate) salts in an oven at 110°C for three hours. Cool in a desiccator.
2. Repeat process to a constant weight.
3. Weigh 0.1968 g of dried diquat salt and 0.1770 g of dried paraquat salt.
4. Transfer to a silanized glass or polypropylene 100 mL volumetric flask. Add approximately 50 mL of deionized water then dilute to the mark with deionized water.

Calibration

In order to closely match calibration standards to samples, process standards by the following method:

- Condition a cartridge according to section 1 below.
- Pass 250 mL of reagent water through the cartridge and discard the water.
- Dry the cartridge by passing 5 mL of methanol through it. Discard the methanol.
- Pass 4.0 mL of the eluting solution through the cartridge and catch in a 5 mL silanized volumetric flask.
- Fortify the eluted solution with 100 µL of the ion-pair concentrate and with 500 µL of the stock standard and dilute to the mark with eluting solution. This provides a 10:1 dilution of the stock.
- Use serial dilution of the calibration standard by the same method to achieve lower concentration standards.

Procedure:

The cartridge must be conditioned properly before extraction.

1. Condition Cartridge

a) Place C8 cartridge(s) on a vacuum manifold system.
b) Draw the following solutions through the cartridge in the stated order. The flow rate through the cartridge should be approximately 10 mL/min.

Note: Do not to let the cartridge go dry once starting the addition of solutions

c) Add 5 mL of reagent water to the cartridge and draw through to waste.
d) Add 5 ml of methanol to the cartridge and soak for about one minute.
e) Apply vacuum to draw most of the methanol through the cartridge. Leave a thin layer on top of the frit.
f) Add 5 ml reagent water to the cartridge.
g) Apply vacuum and draw most of the water through the cartridge. Leave a thin layer of water on the frit.
h) Apply 5 mL of conditioning **Solution A** to the cartridge.

Solution A: Dissolve 0.500 grams cetyl trimethyl ammonium bromide and 5 mL of ammonium hydroxide in 500 mL of reagent water. Dilute to 1000 mL

i) Draw a small amount through the cartridge leaving a thin layer on the frit.
j) Soak for one minute.
k) Use 5 mL of reagent grade water to rinse the Solution A from the cartridge. Allow a thin layer of water to remain on the cartridge frit.
l) Rinse the cartridge with 10 mL of methanol.
m) Rinse the cartridge with 5 mL of reagent grade water.
n) Condition the cartridge with 20 mL of **Solution B**.
o) **Solution B:** Dissolve 10 g 1-hexanesulfonic acid sodium salt and 10 mL of ammonium hydroxide in 250 mL of DI water then dilute to 500 mL.
p) Retain **Solution B** in the cartridge to keep it activated. **Do Not Rinse.**

2. Sample Extraction

a) Determine the pH of the sample. Adjust to 7.0 – 9.0 with 10% NaOH or 10% v/v HCl before extracting.
b) Using a volumetric flask add 250 mL of the water sample to the reservoir and start the vacuum at a rate of 3 to 6 mL per minute.
c) Draw the sample through the cartridge draining as much water from the sample bottle as possible.
d) Rinse the cartridge with 5 ml of HPLC grade methanol.
e) Draw vacuum through the cartridge for 1 minute to dry.
f) Remove the filtration assembly and insert a silanized 5 mL volumetric (plastic vessel is preferred) flask for collection of the eluate.

3. Cartridge Elution

a) Add 4.5 ml of Cartridge Eluting Solution to the cartridge.
b) Allow to soak for one minute.

Cartridge Elution Solution: Dissolve 13.5 mL of orthophosphoric acid and 10.3 mL of diethylamine in 500 mL of DI water, then dilute to 1 liter

c) Elute at 1-2 mL (drop by drop) per minute drawing all solution through the cartridge.
d) Using cartridge **Ion-pair solution**, add 100 µL to the flask.

Ion-pair Concentrate: Dissolve 3.75 grams of 1-hexanesulfonic acid in 15 mL of the **Cartridge Elution Solution** and dilute to 25 mL in a volumetric flask with additional **Cartridge Elution Solution**

e) Bring the eluate to a known volume of 5 mL using **Cartridge Elution Solution.**
f) The extract is now ready for HPLC analysis as shown below.

4. HPLC Analysis

Mobile Phase – Prepare mobile phase by adding reagents 1-4 to 500 mL DI water:

a) 13.5 mL of orthophosphoric acid
b) 10.3 mL of diethylamine
c) 3.0 g of 1-hexanesulfonic acid, sodium salt
d) Mix and bring to a final volume of 1 L with DI water

HPLC Conditions
Column: Phenomenex Spherisorb, 3F, 4.6 mm x 100 mm or equivalent
Column Temperature: 35° C
Flow Rate: 2.0 mL/min., Ion-Pair Mobile Phase
Injection Volume: 200 µL
Photodiode Array Detector Settings
Wavelength Range: 210 - 370 nm
Sample Rate: 1 scan/sec.
Wavelength Step: 1 nm
Integration Time: 1 sec.
Run Time: 5.0 min.
Quantitation Wavelengths: Diquat 308 nm, Paraquat 257 nm

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References:

[1] *EPA Method 549.2 Revision 1.0, Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection, J.W. Munch (USEPA) and W.J. Bashe (DynCorp/TAI) - Method 549.2, Revision 1.0 (1997),National Exposure Research Laboratory, Office Of Research And Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

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