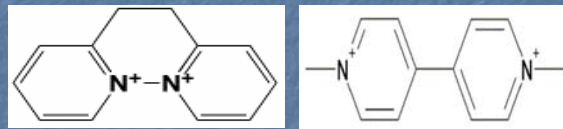


Evolution of Paraquat and Diquat Extraction and Analysis from Vegetation, Soil, and Water

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Diquat and Paraquat



- > Bipyridylium Herbicides
- > Broad Spectrum
- > Preharvest desiccators
- > Inactivated and immobilized by soil contact
- > Disrupts Photosystem I which is located in the chloroplast

Established Extraction Method

- > Weigh sample 50g of sample
- > Reflux in 100mL 50% H₂SO₄ for 4 hours
- > Filter samples using plastic Buchner funnel
- > Dilute up to 250mL
- > Dilute 10mL aliquot up to 250mL
- > Titrate to pH range of 10.5 to 10.7

Established Extraction Method SPE Conditioning

- > Condition C8 SPE
 - > 5mL DI water
 - > 5mL methanol
 - > 5mL DI water
 - > 5mL of cetyl trimethyl ammonium bromide with 0.5% ammonium hydroxide
 - > 5mL DI water
 - > 5mL methanol
 - > 5mL DI water
 - > 5mL 1-hexanesulfonic acid with 2% ammonium hydroxide

Established Extraction Method SPE Separation

- > Pass sample through SPE
- > Wash with 5mL DI water
- > Wash with 5mL methanol
- > Dry the column
- > Elute with two 2.5mL portions of 13.5mL o-H₃PO₄ and 10.3mL diethyl amine brought up to 1L with DI water
- > Add 100uL of 1-hexanesulfonic acid ion-pairing solution

Extraction Method Problems

- > Low spike recoveries
- > Need pH over 10.5, but analytes degrade over 10.7
- > Large amount of crystal formation

SPE Method Considerations

- Assume that acid extraction is not the problem
- Evaluate SPE method by doing water spikes
- Low recoveries

Waters' SPE Method

- Paraquat and Diquat in Tap Water Method
- Neutralize a diluted aliquot of the acid extract
- Uses moderate cation exchange (MCX) SPE instead of a stripped C8

Findings from MCX SPE Method

- Good recoveries for water spikes
- Adjust pH to 7-8 versus 10.5-10.7
- Lower pH reduces crystallization
- Column conditioning much more efficient

Sample Preparation



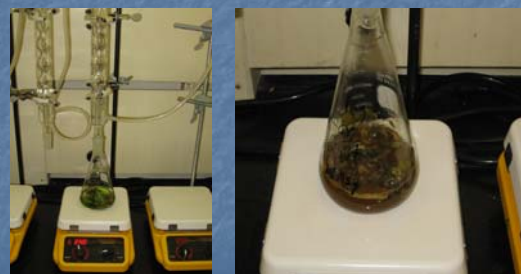
- Homogenize sample
- Weigh ~25g into 500mL glass volumetric flask
- Add spike mix to QC spikes

Acid Extraction

- Add stir bar to sample flask
- Add 100mL of a 50% H_2SO_4
- Connect condensers and start water flow
- Set Digital hot plates to 240°C
- Do something constructive for 4 hours



Acid Extraction

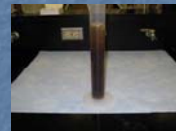


Acidified Sample Filtration



- > Transfer acid extraction to a 250mL centrifuge tube
- > Rinse flask three times using a total of 50mL of DI water
- > Centrifuge 10 minutes
- > Filter into plastic filter flask using plastic Buchner funnel
- > Add ~25mL DI water and shake pellet
- > Centrifuge and filter
- > Repeat

Partition Volume



- > Transfer extract to 250mL plastic graduated cylinder
- > Bring up to 250mL with DI water
- > Transfer to a 250mL centrifuge tube
- > Important in calculations

Titration



- > Aliquot 25mL into plastic beaker using a plastic pipette
- > Dilute to ~200mL
- > Titrate using 50% NaOH to pH ~2.5
- > Then titrate using 10% NaOH to pH 7-8
- > Use 10% HCl if pH goes higher than 8
- > Do not go higher than pH 10.7
- > Filter

MCX SPE Sample Concentration



- > Condition MCX by passing 5mL of methanol followed by 5mL DI water
- > Pass all of the sample through the SPE
- > Stop the flow when a few millimeters of sample remains
- > Add 5mL of methanol to the SPE

MCX SPE Sample Concentration



- > Allow the column to air dry for about 1 minute

MCX SPE Sample Elution



- Add 100uL of 800mM 1-hexanesulfonic acid ion-pairing solution to a 15mL plastic centrifuge tube
- Elute with 4.9mL of a 1M NH₄Cl solution that is 1:1 water:methanol
- Final ion-pairing concentration is 16mM

Analytical Method

- OctaDecylSilane (ODS) column
- Mobile Phase
 - Buffer 90%
 - 13.5mL o-H₃PO₄
 - 10.3mL diethyl amine
 - 3.0g 1-hexanesulfonic acid
 - In 1L DI water
 - Methanol 10%
- PDA detector
 - 257nm Paraquat
 - 308nm Diquat

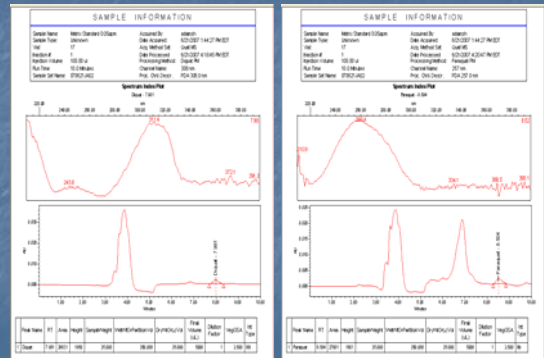


Standard Preparation

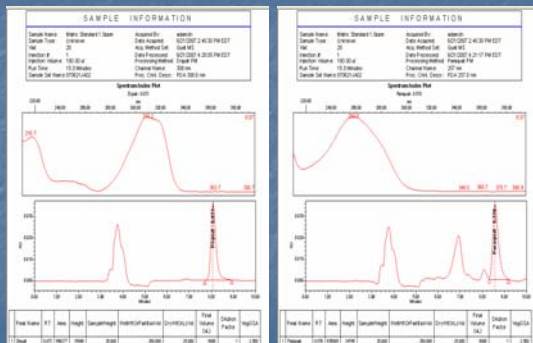


- Neat standards are salts, factor out anions and water weight
- Plastic volumetric flasks
- Made in elution solution
- 16mM 1-hexanesulfonic acid
- Spiking standard made in water

Matrix Standard Chromatogram



Matrix Standard Chromatogram



EPA Risk Levels/Tolerances (ppb)

Matrix	Diquat	Paraquat
Water (risk levels)	80	160
Soil (risk levels)	170000	350000
Vegetation (tolerances)	20	50
MDL (water)	4.0	4.0
MDL (soil and vegetation)	400	400

Extraction Method Comparison

- > Original Method
 - > Difficult to titrate due to tight pH range and degradation concerns
 - > SPE chemically stripped and then rebuilt
 - > Recoveries range between 30-60%
- > Current Method
 - > Large titration range well below degradation pH
 - > SPE designed to capture positively charged ions
 - > Recoveries range between 75-105%

Future Goals

- > Lower the MDL
 - > Approach toxicological significant concentrations
 - > Larger sample weights
 - > Smaller partitioning volume
 - > Larger aliquot volume
 - > Lower standard concentrations
- > Check digestion time

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