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Application Brief 875

Modification of EPA Method 608 for Automated Solid Phase Extraction (SPE) of Wastewaters and Surface Waters Using the Dionex AutoTrace Instrument

INTRODUCTION

EPA Method 525.2, Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry, can be used as a basis for developing a liquid-solid Extraction method for EPA Method 608, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Organochlorine Pesticides and PCBs.

Unlike the drinking water methods, however, analysis of wastewaters and the streams they flow into, need to contend with particulates. The Dionex AutoTrace instrument has features that allow analysis of samples even with high amounts of suspended solids.

The loading pumps are able to load samples at a given rate even as the bed begins to block. If the bed does get completely blocked, the sample is still in the original container where it can be retrieved for further processing without loss. The solvent delivery syringe is able to deliver solvent under sufficient positive pressure to overcome severe blockage.

SAMPLE PRETREATMENT

2.5 mL of methanol is added to 500 mL of sample. Surrogates, tetrachloro-m-xylene (TCX), and decachlorobiphenyl (DCBP) are added to monitor extraction efficiency.

SPE Cartridge Used:

ISOLUTE C18 (EC) 500 mg in a 6 mL cartridge with a polyurethane plug prefilter, part number 221-0050-CD

AUTOTRACE EXTRACTION PROCEDURE

Process 6 Samples using the following procedure:

Step 1: Wash syringe with 2 mL of CH_3OH.
Step 2: Rinse column with 5 mL of EtOAc into SOLVENT WASTE.
Step 3: Rinse column with 5 mL of DCM into SOLVENT WASTE.
Step 4: Condition column with 10 mL of CH_3OH into SOLVENT WASTE.
Step 5: Condition column with 10 mL of Water into AQUEOUS WASTE.
Step 6: Pause and Alert operator, resume when Continue is pressed.
Step 7: Load 550 mL of sample onto column.
Step 8: Dry column with gas for 10 min.
Step 9: END

Solvent 1: Water (reagent grade)
Solvent 2: CH_3OH (methanol)
Solvent 3: EtOAc (ethyl acetate)
Solvent 4: DCM (dichloromethane)
Solvent 5: Unused (load with methanol)

Cond Flow: 40 mL/min
Load Flow: 20 mL/min
Rinse Flow: 40 mL/min
Cond Air Push: 15 mL/min
Rinse Air Push: 20 mL/min
Elute Air Push: 5 mL/min

Step 6 is added so that the conditioning steps can be started before final preparations of the samples are finished without worry that the instrument will try to load samples before the operator is ready.

SAMPLE ELUTE PROCEDURE

Process 6 Samples using the following procedure:

Step 1: Collect 5 mL fraction into sample tube using EtOAc.
Step 2: Manually Rinse sample container with 7 mL to COLLECT.
Step 3: Manually Rinse sample container with 10 mL to COLLECT.
Step 4: Collect 2 mL fraction into sample tube using DCM.
Step 5: END

Solvent 1: Water (reagent grade)
Solvent 2: CH_3OH (methanol)
Solvent 3: EtOAc (ethyl acetate)
Solvent 4: DCM (dichloromethane)
Solvent 5: Unused (load with methanol)

Cond Flow: 40 mL/min
Load Flow: 3 mL/min
Rinse Flow: 40 mL/min
Cond Air Push: 15 mL/min
Elute Flow: 20 mL/min
Rinse Air Push: 20 mL/min

Note change in Load Flow rate.
Elute Air Push: 5 mL/min

At Step 2, add 5 mL of ethyl acetate to sample container, at Step 3 add 5 mL of dichloromethane to sample container.

All channels that succeed in delivering solvent from its sample container are now finished. The channel's tension is released and the extracts removed, dried and concentrated to 1 mL according to EPA Method 525.2, paragraph 11.1.5.

Wastewaters and surface water often contain high levels of suspended solids. The selection of ISOLUTE Depth Filters can trap particulate above the reservoir. The AutoTrace system can process up to six samples. If any sample plugs the SPE Cartridge, simply release the tension on that channel to prevent further processing and continue to process the remaining samples during loading.

For any Channel that does not push the contents through the SPE cartridge, simply load the Blocked Shocker program and run on the effective channel.

BLOCKED SHOCKER PROGRAM:

Process 6 Samples using the following procedure:

Step 1: Collect 3 mL fraction into sample tube using EtOAc.
Step 2: Manually Rinse sample container with 15 mL to COLLECT.
Step 3: Collect 2 mL fraction into sample tube using DCM.
Step 4: END

Do not add more solvent at Step 3, this program seeks to empty the sample container of solvent already contained.

If loading pump is still unable to deliver solvent through SPE cartridge, Blocked Shocker can be run twice more and the solvent forced through by the piston will suffice to extract the analytes from the SPE cartridge.

Once all channels that successfully loaded have been eluted, resume work on samples that blocked by starting at the Sample Load Program with a fresh SPE cartridge on a different channel, loading the remainder of the sample. Elute both cartridges as described above and combine the extracts into one.

Discussion

The solvent delivery piston is more able to force liquid through the SPE than is the loading pump. Sometimes, the resistance is caused by residual water surface tension in the SPE bed and forcing through some solvent with the syringe will enable the resistance to lessen for the loading pump. If the sample contains sufficient solids to plug an SPE cartridge, the likelihood that analytes have adsorbed to the wall of the container and not been transferred to the cartridge is reduced, thus the solvent delivered by Blocked Shocker can be assumed to contain all of the analytes present in the sample.

Table 1 shows recoveries from a run (n=4) where all samples eluted normally. Table 2 shows recoveries from another run (n=4) that experienced various problems. Replicate S4788.2 resisted elution by the loading pumps and was eluted with 3 repetitions of Blocked Shocker. Replicates S4788.3 and S4788.5 needed Blocked Shocker once and then succeeded in eluting using the loading pumps. Replicate S4788.6 blocked before loading all of the sample and was restarted on a second SPE cartridge, then both elutions were combined.

Analysis of Example Spike Recoveries

Analyze extracts on a gas chromatograph equipped with electron capture detectors. The following results were obtained using a CG/MS with dual 0.32 mm ID, 30 m long capillary columns, Rtx®-CLPesticides and Rtx-CLPesticidesII from Restek®.

500 mL of sample was spiked with 100 µL of surrogate solution with 5 ng/µL each of TCX and DCBP. Analytes were spiked in with 100 µL of 2.5 ng/µL solution. Extracts were fortified with 100 µL of 2.5 ng/µL solution of dibromooctofluorobiphenyl as an internal standard. Various river waters were spiked and analyzed, as shown in Tables 1 and 2 below.

Compound	Mean	Std. Dev.
SS:TCX	71.3	3.9
SS:DCBP	55.5	11.5
alpha-BHC	98.2	1.6
gamma-BHC	113.3	4.7
beta-BHC	125.0	22.9
delta-BHC	123.2	18.8
Heptachlor	90.1	2.9
Aldrin	69.9	4.9
Hepta.epoxide	104.1	13.8
DDE	77.7	13.3
Endosulfan I	119.3	18.5
Dieldrin	123.6	20.6
Endrin	121.1	21.4
DDD	106.8	24.0
Endosulfan II	119.8	26.5
DDT	72.1	16.7
Methoxychlor	125.8	38.8
Endosulfan sulfate	147.8	34.9

Table 1. GC/ECD analysis results of Iowa River Water. Estimated Total Suspended Solids, 70 mg/L.

Compound	Mean	Std. Dev.
SS:TCX	51.4	4.1
SS:DCBP	25.4	5.9
alpha-BHC	65.7	18.3
gamma-BHC	72.0	18.6
beta-BHC	70.2	17.2
delta-BHC	70.9	18.8
Heptachlor	45.8	10.3
Aldrin	39.4	8.6
Hepta.epoxide	62.8	13.9
DDE	37.5	8.8
Endosulfan I	69.7	13.7
Dieldrin	70.4	14.8
Endrin	61.1	12.4
DDD	49.6	10.0
Endosulfan II	66.1	10.9
DDT	21.8	4.0
Methoxychlor	45.3	14.8
Endosulfan sulfate	81.5	15.8

Table 2. GC/ECD analysis results of Cedar River Water. Estimated Total Suspended Solids, 64 mg/L.

CONCLUSION

The AB has shown that AutoTrace provides an automated solution to US EPA Method 608.

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