DIONEX

Application Note 815

Automated Solid-Phase Extraction of Wastewaters and Surface Waters Using the AutoTrace® SPE Instrument for EPA Method 608

INTRODUCTION

EPA method 608 uses liquid-liquid extraction by Separatory funnel combined with gas chromatography and electron capture detector for the analysis of organochlorine pesticides and PCBs in municipal and industrial waste water.

Unlike the drinking water methods, however, the extraction of wastewaters may contain particulates or suspensions that may block or clog SPE materials. The AutoTrace SPE instrument has features that allow extraction 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 from 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 blockages.

AUTOTRACE EXTRACTION PROCEDURES

2.5 mL of methanol is added to 500 mL of sample. Various river water samples (500 mL) were spiked 100 µL of surrogate with 5ng/µL each of Tetrachlorometaxylene (TCMX) and Decachlorobiphenyl (DCB). Analytes were spiked with 100 µL at 2.5 ng/µL.

SPE Cartridge Used:

C18 cartridge 500 mg in a 6 mL cartridge with a polyurethane plug prefilter, part number 221-0050-CD.

AutoTrace Instrument for Automated SPE

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 minutes

Solvents	Flow Rate	
Water (reagent grade)	Cond. Flow:	40 mL/min
CH_3OH (methanol)	Load Flow:	3 mL/min
EtOAC (ethyl acetate)	Rinse Flow:	40 mL/min
DCM (dichloromethane)	Cond. Air Push:	15 mL/min
Unused (load with methanol)	Elute Flow:	20 mL/min
	Elute Air Push:	5 mL/min

Step 6 is added so the conditioning steps can be started before final sample preparations are completed. This alleviates any concern that the instrument will load the sample 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

Solvents	Flow Rate	
Water (reagent grade)	Cond. Flow:	40 mL/min
CH_3OH (methanol)	Load Flow:	3 mL/min
EtOAC (ethyl acetate)	Rinse Flow:	40 mL/min
DCM (dichloromethane)	Cond Air Push:	15 mL/min
Unused (load with methanol)	Elute Flow:	20 mL/min
	Elute Air Push:	5 mL/min

Note change in Load Flow rate.

Manual Rinse Details

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 their sample containers are now finished. The channel's tension is released and the extracts removed, dried, and concentrated to an appropriate final volume as dictated by method 608 or Detection Limit requirements.

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 sample loading.

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

Do not add more solvent at Step 3. The purpose of this program is to empty the sample container of the rinse solvent.

If loading pump is still unable to deliver solvent through SPE cartridge, the Blocked Shocker program can be run twice more. 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 some solvent through 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

Samples were analyzed on a gas chromatograph equipped with electron capture detectors. The following results were obtained using an Agilent® 6890 with dual 0.32 mm ID, 30 m long capillary columns, Rtx®-CLPesticides and Rtx-CLPesticidesII from Restek®.

Table 1. Iowa River Water, Estimated Total Suspended Solids, 70 mg/L						
	S4785.2	**S4785.3**	**S4785.5**	**S4785.6**	**Mean**	**Std. Dev.**
SS:TCX	72.7%	68.0%	68.3%	76.1%	71.3%	3.9%
SS:DCBP	44.5%	70.2%	58.9%	48.6%	55.5%	11.5%
alpha-BHC	98.7%	96.0%	98.3%	99.9%	98.2%	1.6%
gamma-BHC	108.5%	119.2%	114.4%	110.9%	113.3%	4.7%
beta-BHC	107.4%	158.0%	122.4%	112.2%	125.0%	22.9%
delta-BHC	108.1%	150.0%	122.0%	112.7%	123.2%	18.8%
Heptachlor	86.5%	93.0%	91.8%	89.3%	90.1%	2.9%
Aldrin	63.2%	74.8%	71.8%	69.8%	69.9%	4.9%
Hepta.epoxide	94.4%	124.6%	97.8%	99.7%	104.1%	13.8%
DDE	67.3%	96.0%	78.9%	68.3%	77.7%	13.3%
Endosulfan I	102.8%	145.3%	118.8%	110.3%	119.3%	18.5%
Dieldrin	105.5%	152.6%	122.8%	113.3%	123.6%	20.6%
Endrin	104.6%	151.8%	119.3%	108.6%	121.1%	21.4%
DDD	87.6%	141.1%	105.3%	93.1%	106.8%	24.0%
Endosulfan II	99.6%	158.1%	116.4%	105.0%	119.8%	26.5%
DDT	80.5%	90.1%	65.6%	52.1%	72.1%	16.7%
Methoxychlor	129.6%	177.7%	108.8%	86.9%	125.8%	38.8%
Endosulfan sulfate	122.0%	198.5%	142.6%	128.0%	147.8%	34.9%

Table 2. Cedar River Water, Estimated Total Suspended Solids, 64 mg/L						
	S4788.2	S4788.3	S4788.5	S4788.6	Mean	Std. Dev.
SS:TCX	54.9%	46.8%	49.1%	54.9%	51.4%	4.1%
SS:DCBP	23.6%	19.0%	25.6%	33.2%	25.4%	5.9%
alpha-BHC	64.6%	48.4%	58.8%	91.2%	65.7%	18.3%
gamma-BHC	72.1%	53.7%	64.8%	97.6%	72.0%	18.6%
beta-BHC	68.5%	54.1%	63.9%	94.5%	70.2%	17.2%
delta-BHC	69.0%	53.0%	64.3%	97.2%	70.9%	18.8%
Heptachlor	49.0%	36.7%	38.6%	59.0%	45.8%	10.3%
Aldrin	40.2%	30.7%	35.6%	50.9%	39.4%	8.6%
Hepta.epoxide	62.5%	48.6%	58.3%	81.8%	62.8%	13.9%
DDE	37.3%	28.8%	34.2%	49.5%	37.5%	8.8%
Endosulfan I	70.7%	54.9%	65.3%	87.7%	69.7%	13.7%
Dieldrin	70.1%	55.0%	65.9%	90.4%	70.4%	14.8%
Endrin	63.1%	48.6%	55.3%	77.5%	61.1%	12.4%
DDD	50.8%	38.7%	46.2%	62.5%	49.6%	10.0%
Endosulfan II	68.6%	52.7%	64.1%	79.0%	66.1%	10.9%
DDT	23.5%	17.6%	19.4%	26.5%	21.8%	4.0%
Methoxychlor	47.7%	35.5%	32.7%	65.2%	45.3%	14.8%
Endosulfan sulfate	83.6%	63.8%	76.8%	101.7%	81.5%	15.8%

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