Automated Solid-Phase Extraction (SPE) of Wastewaters and Surface Waters Using the Thermo Scientific Dionex AutoTrace 280 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 polychlorinated biphenyls (PCBs) in municipal and industrial wastewater.

Unlike the drinking water methods, however, analysis of wastewaters and the streams they flow into, need to contend with particulates. The Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction (SPE) 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 blockages.

Dionex AutoTrace 280 SPE Instrument for Automated SPE

Dionex AutoTrace 280 SPE 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

Thermo Scientific™ Dionex™ SolEx™ SPE C18, 6 mL Cartridge, with 0.5 g of packing (P/N 074417)

No.	Process six samples using the following procedure:
1	Wash syringe with 2 mL of CH_3OH.
2	Rinse column with 5 mL of EtOAc into SOLVENT WASTE.
3	Rinse column with 5 mL of DCM into SOLVENT WASTE.
4	Condition column with 10 mL of CH_3OH into SOLVENT WASTE.
5	Condition column with 10 mL of water into AQUEOUS WASTE.
6	Pause and Alert operator, resume when Continue is pressed.
7	Load 550 mL of sample onto column.
8	Dry column with gas for 10 min.
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.

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Sample Elute Procedure

No.	Process six samples using the following procedure:
1	Collect 5 mL fraction into sample tube using EtOAc.
2	Manually rinse sample container with 7 mL to COLLECT.
3	Manually rinse sample container with 10 mL to COLLECT.
4	Collect 2 mL fraction into sample tube using DCM.
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.

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 EPA Method 608 or Detection Limit requirements.

Wastewaters and surface water often contain high levels of suspended solids. The Dionex AutoTrace 280 SPE instrument can process up to six samples. If any sample plugs the Dionex SolEx 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 Dionex SolEx SPE cartridge, simply load the Blocked Shocker program and run on the effective channel.

Blocked Shocker Program

No.	Process six samples using the following procedure:
1	Collect 3 mL fraction into sample tube using EtOAc.
2	Manually rinse sample container with 15 mL to COLLECT.
3	Collect 2 mL fraction into sample tube using DCM.
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 the Dionex SolEx 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 Dionex SolEx 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 Dionex SolEx 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 a Dionex SolEx 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 Dionex SolEx 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 a gas chromatograph with dual 0.32 mm ID, 30 m long capillary columns, Rtx®-CLPesticides and Rtx-CLPesticidesII from Restek®.

Acknowledgements

Data and study submitted by: David Larabee-Zierath, PhD of the University Hygienic Laboratory, Iowa's Environmental and Public Health Laboratory, Iowa City, IA.

Table 1. Iowa river water, estimated total suspended solids: 70 mg/L

	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

	S4785.3	S4785.5	S4785.6	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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