# Automated Solid-Phase Extraction (SPE) of Wastewaters and Surface Waters for Polyaromatic Hydrocarbons and Phthalates — Modification of EPA Method 625



## 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 625, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs).

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 if the bed begins to block. The solvent delivery syringe is able to deliver solvent under sufficient positive pressure to overcome most blockages. 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.

## Sample Pretreatment

2.5 mL of methanol and 2 mL of concentrated sulfuric acid is added to 500 mL of sample. Surrogates for EPA Method 625 are added and monitored for extraction efficiency. However, only 2-Fluorobiphenyl, 2,4,6-Tribromophenol and Terphenyl-d14 are expected to perform well.

### 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 CH3OH 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. If any sample completely plugs the Dionex SolEx SPE cartridge, release the tension on that channel to prevent further processing and proceed with elution steps on remaining channels.

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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 |
| Elute Air Push: | 5 mL/mtin |

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 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.

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.

Replicates (n=4) of two different river water samples were extracted by the above method. Similar samples from the same locations were used in a separate study looking at Organochlorine Pesticides. In the previous study, the use of the Blocked Shocker Program was needed. In this study it was not, possibly due to the sulfuric acid. The solvent delivery syringe is more able to force liquid through the SPE than is the loading pump.

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Table 1. GC/MS analysis results of Iowa river water, Iowa City, IA. Collected 9/13/02, estimated total suspended solids: 70 mg/L.

| Compound | Mean | Std. Dev. |
|---|---|---|
| SS:2-Fluorobiphenyl | 67.7 | 8.4 |
| SS:Terphenyl-d14 | 90.1 | 4.9 |
| SS:2,4,6-Tribromophenol | 104.1 | 4.0 |
| Acenaphthylene | 50.0 | 8.4 |
| Acenaphthene | 45.8 | 7.7 |
| Anthracene | 70.6 | 6.4 |
| Benzo[a]anthracene | 79.1 | 6.8 |
| Benzo[b]fluoranthene | 77.8 | 7.2 |
| Benzo[k]fluoranthene | 79.4 | 5.8 |
| Benzo[g,h,i]perylene | 75.5 | 8.4 |
| Benzo[a]pyrene | 79.1 | 7.0 |
| Chrysene | 93.0 | 5.3 |
| Dibenza[a,h]anthracene | 74.7 | 6.4 |
| Fluoranthene | 67.4 | 5.0 |
| Fluorene | 52.4 | 6.6 |
| Indeno[1,2,3-cd]pyrene | 76.8 | 7.5 |
| Naphthalene | 49.5 | 13.0 |
| Phenanthrene | 66.9 | 5.7 |
| Pyrene | 79.4 | 7.7 |
| Diethylphthalate | 90.3 | 3.0 |
| Dimethylphthalate | 85.2 | 3.1 |
| Di-n-butylphthalate | 90.5 | 3.6 |
| Di-n-octylphthalate | 94.9 | 13.6 |

Table 2. GC/MS analysis results of cedar river water, Rochester, IA. Collected 9/13/02, estimated total suspended solids: 64 mg/L.

| Compound | Mean | Std. Dev. |
|---|---|---|
| SS:2-Fluorobiphenyl | 60.6 | 4.7 |
| SS:Terphenyl-d14 | 68.7 | 8.8 |
| SS:2,4,6-Tribromophenol | 99.2 | 4.7 |
| Acenaphthylene | 49.4 | 2.6 |
| Acenaphthene | 45.4 | 2.9 |
| Anthracene | 51.9 | 14.3 |
| Benzo[a]anthracene | 67.2 | 5.8 |
| Benzo[b]fluoranthene | 66.2 | 6.7 |
| Benzo[k]fluoranthene | 68.2 | 5.9 |
| Benzo[g,h,i]perylene | 65.4 | 6.8 |
| Benzo[a]pyrene | 67.7 | 6.0 |
| Chrysene | 79.0 | 5.6 |
| Dibenza[a,h]anthracene | 78.5 | 6.3 |
| Fluoranthene | 52.9 | 5.0 |
| Fluorene | 48.2 | 3.4 |
| Indeno[1,2,3-cd]pyrene | 68.7 | 5.8 |
| Naphthalene | 44.5 | 2.8 |
| Phenanthrene | 55.0 | 3.9 |
| Pyrene | 65.3 | 5.1 |
| Diethylphthalate | 84.5 | 2.5 |
| Dimethylphthalate | 81.1 | 1.5 |
| Di-n-butylphthalate | 74.7 | 2.1 |
| Di-n-octylphthalate | 89.1 | 6.9 |

### Analysis of Example Spike Recoveries

Analyze extracts on a gas chromatograph equipped with mass selective detectors. The following results were obtained using a gas chromatograph with a MSD on a 30 M long, 0.25 mm ID capillary column with a 0.5 µm film coating.

500 mL of sample was spiked with 50 µL of 1000 ng/µL base/neutral surrogate solution and 100 µL of 2000 ng/µL acid surrogate solution. Extracts at 1000 µL were fortified with 10 µL of 4000 ng/µL internal standard solution. Analytes were fortified into the samples by adding 25 µL of 2000 ng/µL spiking solution.

## Conclusion

The Application Brief has shown that Dionex AutoTrace 280 SPE instrument provides an automated solution to EPA Method 625.

## Acknowledgements

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