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8270D*

Daniel P. Dodson and Robert S. Johnson

GL Sciences B.V.

De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 E-mail: info@glsciences.eu
Internet: www.glsciences.eu

Application of solid-phase extraction and rapid, large-volume injection for routine analysis of environmental samples via U.S. EPA SW-846 Method 8270D

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Eastman Chemical Co.'s Environmental Laboratory in Longview, TX, routinely uses solid-phase extraction (SPE) and rapid, large-volume injection (LVI) to eliminate the postextraction concentration step normally required for the preparation of samples for semivolatiles analyses by U.S. EPA SW846 Method 8270D. Using automated SPE and LVI in place of conventional liquid/liquid extraction eliminates the labour-intensive steps, reduces sample analysis costs, improves accuracy and precision, decreases solvent (methylene chloride) usage, and reduces turnaround time from days to hours.

The SPE-DEX[®] automated extraction system (**Horizon Technology Inc.**, Atkinson, NH) is used to perform the solid-phase extraction on typical environmental matrix water samples such as wastewater, groundwater, and surface water. The samples are delivered to the laboratory in 500-mL bottles. Surrogate compounds used to monitor method performance are added to each sample. Specially designed caps (**Horizon Technology**) are screwed onto the sample containers so that they can be placed directly onto the SPE-DEX extractor. The extraction disk (Speed Disk #8067-06, divinyl benzene [DVB], **J.T. Baker**, Phillipsburg, NJ) is placed in the automated extractor. The analyst selects the appropriate program for the extraction and starts the extraction process. All steps of the extraction process (purge, prewetting, sample delivery, solvent delivery, and rinse) are automated via a programmable SPE-DEX controller. The extracted sample (12-15 mL) is collected in a sample vial placed below the extraction disk. After drying with sodium sulfate, the sample is ready for GC-MS analysis when rapid LVI is used.

In contrast, the standard preparation method used for preparation of water samples for semivolatile analysis, U.S. EPA SW846 Method 3510C (liquid/ liquid extraction), results in 150-200 mL of sample extract. The extract is normally reconcentrated to 1 mL using Kuderna-Danish evaporation in order to achieve the desired detection limits. This labour-intensive and time-consuming step is completely eliminated when LVI is used in combination with automated SPE.

Many advantages are realized by the elimination of the postextraction concentration:

- The amount of analyst time required to process a sample is greatly reduced. A fourfold increase in productivity is attained with the use of automated extraction and LVI. The number of samples processed by the Eastman Chemical Co. Environmental Laboratory increased from 8 to 12 samples per day to greater than 50 with the use of four automated extractors. Automated SPE requires approx. 15 mill of analyst time to prepare. In contrast, liquid/liquid extraction of Method 3510C requires at least 1 analyst hr/sample to process.
- Accuracy and precision are improved by automated extraction and the elimination of an analytical step. The postextraction concentration step is subject to the introduction of significant error. The more volatile compounds in the extract can be lost with the solvent. Percent recovery on the more volatile components is often observed to be significantly lower than less volatile compounds.
- Solvent usage is dramatically reduced. Liquid/liquid extraction requires >200 mL of solvent (methylene chloride) per sample. With solid-phase extraction, this decreases to approx. 30 mL. This not only reduces initial solvent cost, but also lowers solvent disposal cost.
- Turnaround time on sample analysis can be dramatically improved. It is possible to have a sample completely processed and ready for GC-MS analysis within 30 mill using automated SPE. With liquid/liquid extraction, one-day turnaround would likely be the best most laboratories could offer.

The solid-phase extract is processed as follows: 1) The dried extract is diluted to 30 mL with methylene chloride, 2) 1 mL of sample is added to a GC injection vial, 3) internal standards are added, and 4) the vial is sealed with a crimp cap.

Analyses were performed on an HP6890 GC and HP 5973 MSD (**Agilent Technologies**, Wilmington, DE) equipped with an autosampler and the ATAS OPTIC2 programmable temperature vaporization (PTV) injector (**ATAS USA, Inc.**, Whittier, CA).

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Table 1

Comparison of liquid/liquid and SPE for characteristic Method 8270 semivolatile compounds

	Laboratory control sample spiked @ 20 ppb		Automated SPE*	
	Liquid/Liquid* % Recov.**	Std. dev. (ppb)	% Recov.**	Std. dev. (ppb)
1,4-Dichlorobenzene	68	0.8	65	1.5
N-nitroso-di- <i>n</i> -propylamine	93	0.4	90	0.4
1,2,4-Trichlorobenzene	75	0.6	76	1.2
Naphthalene	88	0.1	78	1.2
2-Methylnaphthalene	85	0.7	76	0.8
Acenaphthylene	90	0.7	89	0.5
Acenaphthene	90	0.7	87	0.5
2,4-Dinitrotoluene	78	0.6	93	0.5
Dimethylphthalate	84	1.0	97	0.7
Diethylphthalate	90	0.4	100	0.7
Fluorene	92	0.5	94	1.0
Phenanthrene	101	0.7	100	0.7
Anthracene	102	0.7	96	0.8
Di- <i>n</i> -butylphthalate	96	0.7	91	0.8
Fluoranthene	103	0.6	96	1.0
Pyrene	90	1.4	96	1.1
Butylbenzylphthalate	82	0.8	86	1.1
Benzo[<i>a</i>]anthracene	91	1.0	88	0.9
Chrysene	91	1.2	97	1.1
bis(2-Ethylhexyl)phthalate	81	0.8	76	0.7
Di- <i>n</i> -octylphthalate	82	2.3	70	0.7
Benzo[<i>b</i>]fluoranthene	93	1.1	74	1.5
Benzo[<i>k</i>]fluoranthene	87	1.1	100	1.2
Benzo[<i>a</i>]pyrene	87	0.7	87	0.8
Ideno[1,2,3- <i>cd</i>] pyrene	92	0.9	102	1.0

*Analysis was performed using the PTV injection technique.

**Average of four replicates.

This injection allows the introduction of large sample volumes into the injection port. Nominal injection volume with standard injection techniques is 1 μL . With the PTV injection technique, as much as 100 μL can be introduced into the injection port. A sample volume of 30 μL has been found sufficient to meet detection limits required for **Eastman Chemical Co.'s** regulatory projects. The injection port liner is a packed liner (part # IL020202, **SGE**, Austin, TX) containing a proprietary packing material. The PTV injector is operated in the cold splitless injection mode with solvent elimination. Liquid carbon dioxide is used to maintain the injection port at 10°C during injection and solvent elimination. On completion of solvent elimination, the injector is quickly ramped to 300°C and the split valve is closed, ensuring transfer of analytes into the GC column. Analyses are performed on a 30-m Rtx-5 capillary column (**Restek**, Bellefonte, PA) with 0.25- mm i.d. and 0.50- μm film. The Environmental Laboratory established performance of the procedures by evaluation of percent recovery of characteristic compounds analysed by Method 8270D.

Table 2

Comparison of liquid/liquid and automated SPE extraction techniques on wastewater effluent

	Spiked at 100 ppb			
	Wastewater*		Groundwater*	
	LLE % Recovery	SPE % Recovery	LLE % Recovery	SPE % Recovery
Nitrobenzene-d5 Surr**	43.2	79	62.8	73.6
2-Fluorobiphenyl Surr	40.4	84	54.7	72.2
Terphenyl d-14 Surr	21.7	58	34.3	27.2
1-4 Dichlorobenzene	30.5	67	54.9	47.5
N-Nitroso-di- <i>n</i> -propylamine	39.1	70	63.8	73.4
1,2,4-Trichlorobenzene	36.4	74	58.4	63.9
Acenaphthene	37.5	83	58.7	75.4
2,4-Dinitrotoluene	40.4	90	72.3	88.7
Pyrene	35.1	73	53.5	57.2

*Eastman Chemical Co. Environmental Laboratory historical average data for matrix spikes.

**Surr = surrogate.

Solid-phase extraction and liquid/liquid extraction methods were compared using a clean matrix (laboratory control standards), a wastewater matrix, and a groundwater matrix. These matrixes are representative of the majority of water matrixes received in the environmental laboratory. The data in *Table 1* compare extraction methods in reagent water (clean matrix). The two techniques give comparable extraction efficiencies in a clean matrix.

Table 2 presents average historical data from Environmental Laboratory matrix spike samples for wastewater and groundwater matrixes. The liquid/ liquid data were generated using conventional methods, i.e., postextraction concentration to 1 mL and 1 μL injection volume. Automated solid-phase extraction in combination with the PTV injection technique give significantly better performance than conventional techniques for actual environmental sample matrixes.

The list of compounds in *Table 2* represents the limited number of compounds with which matrix samples are spiked to evaluate method performance during routine laboratory analyses. Additional data were obtained by the Environmental Laboratory on a more extensive list of semivolatiles compounds that are routinely analyzed using Method 8270D. Wastewater, river water, and a clean matrix (reagent water) were spiked to 100 ppb for all compounds except phenols, which were spiked to 200 ppb. The samples were extracted using SPE and analyzed using PTV injection techniques. The data in *Table 3* are the average of four replicates. The recoveries of the semivolatiles compounds are well within the acceptance criteria for Method 8270D.

Table 3

Recovery of characteristic semivolatile compounds with automated SPE and LVI

Compound	Wastewater		Matrix samples spiked @ 100 ppb River water		Laboratory control sample	
	Recovery**	%RSD	Recovery**	%RSD	Recovery**	%RSD
Phenol*	17.9	23.9	34	8.0	23	36
2-Chlorophenol*	66.5	17.0	58	13.3	62	26
1,4-Dichlorobenzene	66.5	18.1	46	10.6	56	20
Benzyl alcohol	12.0	43.8	26	10.5	32	35
<i>o</i> -Cresol*	60.6	24.1	73	10.4	62	29
<i>m,p</i> -Cresol*	54.9	22.6	82	10.6	63	27
N-nitroso-di- <i>n</i> -propylamine	69.7	21.5	78	7.7	72	22
1,2,4-Trichlorobenzene	73.7	15.5	54	9.9	62	20
Naphthalene	75.8	15.4	61	9.6	63	20
2-Methylnaphthalene	79.0	15.1	62	8.6	68	18
1,4-Naaphthoquinone	51.8	11.2	70	4.1	76	17
Acenaphthylene	87.6	11.6	62	5.5	68	18
Acenaphthene	83.3	10.7	63	6.0	71	17
2,4-Dinitrophenol*	83.5	11.0	57	10.6	62	27
2,4-Dinitrotoluene	90.5	15.0	76	6.9	83	18
4-Nitrophenol*	N.D.	N.D.	65	16.0	61	28
Dimethylphthalate	80.8	12.5	74	5.7	78	18
Diethylphthalate	84.4	14.8	76	6.9	82	18
Fluorene	79.6	10.3	67	5.5	75	15
Phenanthrene	76.8	9.3	72	5.4	76	12
Anthracene	76.5	10.2	68	6.0	75	11
Di- <i>n</i> -butylphthalate	81.7	11.7	73	5.0	81	14
Fluoranthene	81.8	12.5	66	6.4	82	15
Pyrene	72.7	10.4	63	7.1	76	10
Butylbenzylphthalate	83.3	7.0	79	5.2	76	10
Benzo[<i>a</i>]anthracene	79.7	9.2	72	5.5	77	10
Chrysene	77.6	9.6	73	5.9	75	10
bis(2-Ethylhexyl)phthalate	91.6	8.8	79	4.1	77	11
Di- <i>n</i> -octylphthalate	78.2	15.4	75	5.1	79	10
Benzo[<i>b</i>]fluoranthene	75.0	16.7	71	5.4	78	9
Benzo[<i>k</i>]fluoranthene	72.2	16.0	68	5.2	78	8
Benzo[<i>a</i>]pyrene	72.7	15.7	70	5.6	74	10
Indeno[1,2,3- <i>cd</i>]pyrene	66.8	12.3	70	4.0	65	14

*Phenol concentration was 200 ppb.

**Average of four replicates.

Some of the highly water-soluble compounds such as phenol had low recovery. Liquid/liquid extraction also yields low recovery for these types of compounds. Recovery for polar water-soluble compounds can be improved by using a sorbent with greater affinity for these compounds than the DVB sorbent (Speed Disk # 8067-06) used in these analyses.

Conclusion

Automated solid-phase extraction in combination with large-volume injection techniques provide environmental laboratories with methods that completely eliminate the

postextraction reconcentration step normally required for the analysis of semivolatile compounds. Elimination of this step and automating the SPE sample preparation procedure reduce analyst labour, solvent usage, and turnaround time, and improve accuracy and precision.

Mr. Dodson is Lab Supervisor, Eastman Chemical Co., Longview, TX, U.S.A., and Mr. Johnson is CEO, Horizon Technology, 8 Commerce Dr., Atkinson, NH 03811, U.S.A.; tel.: 603-893-3663; fax: 603-893-4994; e-mail: rj@horizontechinc.com.

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De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
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