

Validation of Method EPA 608.3 and EPA 625.1 Using Semi-Automated SPE

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Introduction

Solid Phase Extraction (SPE) has recently gained traction to become a popular technique for sample preparation in environmental analyses. SPE works by first passing an aqueous sample through a sorbent, either in the form of a cartridge or disc, that can retain target analytes while allowing the water to pass through. A solvent is then passed through the sorbent to free the target analytes and make them available for concentration and later chromatographic analysis. Many labs are interested in SPE as a replacement for the cumbersome and solvent-heavy technique of liquid-liquid extraction (LLE). Our lab has fully transitioned from LLE to cartridge-based SPE for both our 608.3 and 625.1 analyses. The analyst Initial Demonstration of Capability (IDOC) and the Method Detection Limits (MDL) are shown in the tables.

Instrumentation

- Agilent 8890 GC-ECD w/ dual columns for EPA 608.3
- Agilent 7890 GC + 5975C MSD for EPA 625.1
- FMS EZ-SPE for sample extraction
- FMS Super-Vap 6 Concentrator for sample concentration
- Genevac Rocket Evaporator for alternate sample concentration

Extraction Consumables

EPA 608.3:

- Thermo Scientific Hypersep C18 2000mg Cartridge (P/N: 60108-780)
- Supelco Supelclean Florisil/Na₂SO₄ Tubes (P/N: 54116-U)

EPA 625.1:

- FMS ABN Exchange Cartridge (P/N: SPE-CAR1-ABN)
- Supelco Supelclean Coconut Charcoal SPE Tube (P/N: 57144-U)

Results for EPA 608.3

Target Analytes	Test Conc. (µg / L)	IDOC 1 (µg / L)	IDOC 2 (µg / L)	IDOC 3 (µg / L)	IDOC 4 (µg / L)	Avg. (%) Recovery	Acceptance Range (%)	MDL (µg / L)
alpha-BHC	0.100	0.083	0.087	0.084	0.083	84%	49-130	0.003
gamma-BHC	0.100	0.085	0.088	0.085	0.081	85%	43-130	0.003
beta-BHC	0.100	0.087	0.093	0.089	0.093	91%	39-130	0.004
delta-BHC	0.100	0.086	0.091	0.085	0.095	89%	51-130	0.003
Heptachlor	0.100	0.085	0.090	0.085	0.091	88%	43-130	0.002
Aldrin	0.100	0.086	0.091	0.084	0.081	86%	54-130	0.001
Heptachlor epoxide	0.100	0.100	0.105	0.098	0.087	98%	57-132	0.004
alpha-Chlordane	0.100	0.102	0.100	0.100	0.102	101%	55-130	0.003
4,4'-DDE	0.100	0.095	0.091	0.097	0.083	92%	54-130	0.003
Endosulfan I	0.100	0.083	0.084	0.080	0.077	81%	57-141	0.003
Dieldrin	0.100	0.090	0.091	0.084	0.083	87%	58-130	0.009
Endrin	0.100	0.101	0.099	0.090	0.096	97%	51-130	0.003
4,4'-DDD	0.100	0.109	0.102	0.092	0.100	101%	48-130	0.003
Endosulfan II	0.100	0.094	0.094	0.085	0.083	89%	22-171	0.003
4,4'-DDT	0.100	0.104	0.094	0.085	0.079	91%	46-137	0.002
Endrin aldehyde	0.100	0.067	0.066	0.065	0.056	64%	23-100	0.002
Methoxychlor	0.100	0.096	0.099	0.092	0.100	97%	27-155	0.002
Endosulfan sulfate	0.100	0.090	0.092	0.086	0.081	87%	38-132	0.003
Endrin ketone	0.100	0.084	0.085	0.077	0.073	80%	47-111	0.004
Aroclor 1016	1.000	0.824	0.760	0.721	0.700	75%	61-103	0.050
Aroclor 1260	1.000	0.642	0.671	0.585	0.531	61%	37-130	0.050

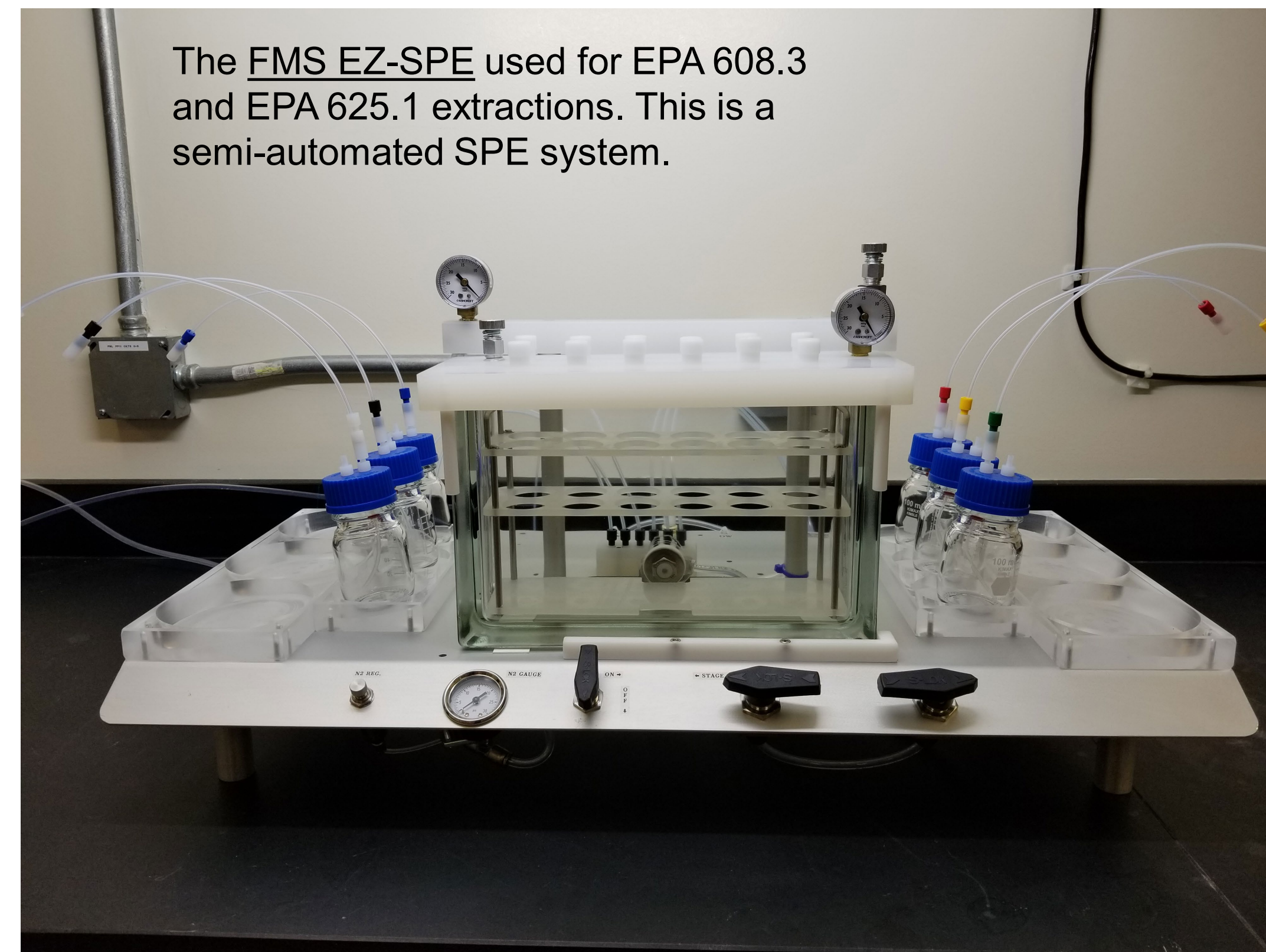
Extraction Procedures

- Sample Prep:** Samples are pre-weighed and tested for oxidizers and pH. Sample pH is then adjusted to less than 2.0 using 50% HCl. Surrogate and spike solution are added.
- Extraction:** Samples are loaded on to the pre-conditioned SPE cartridges (C18 for EPA 608.3 or an ABN Exchange/charcoal cartridge stack for EPA 625.1). The sample loading is done at an approximate rate of 15mL/min. The cartridges are then dried for 10 minutes with nitrogen gas.
- Elution:** After drying, the 608.3 cartridges are eluted with 50mL of a 10% acetone/90% hexane mix passing through Florisil/Sodium Sulfate clean-up cartridges into collection vials. For 625.1, the cartridges are each eluted with 30-40mL of methylene chloride into a collection vial.
- Base Adjustment (EPA 625.1):** The ABN Exchange cartridges are next treated with 30mL of 1% NaOH. After this base treatment, the ABN cartridges are eluted a second time with 30-40mL of methylene chloride to collect the base fraction.

Results for EPA 625.1*

Target Analytes	Test Conc. (µg / L)	IDOC 1 (µg / L)	IDOC 2 (µg / L)	IDOC 3 (µg / L)	IDOC 4 (µg / L)	Avg. (%) Recovery	Acceptance Range (%)	MDL (µg / L)
N-Nitrosodimethylamine	20.00	11.77	13.86	13.59	14.66	67%	2-150	1.08
Phenol	20.00	13.26	15.83	14.90	15.86	75%	17-120	0.16
bis(2-chloroisopropyl)ether	20.00	15.89	19.04	18.23	19.12	90%	63-139	0.16
n-Nitroso-di-n-propylamine	20.00	17.40	20.57	19.60	19.41	96%	14-198	0.24
p-Cresol	20.00	14.04	16.67	15.82	16.18	78%	10-125	0.15
Hexachloroethane	20.00	11.65	13.99	13.55	14.49	67%	55-120	0.13
bis(2-Chloroethoxy)methane	20.00	13.84	16.51	15.89	15.90	78%	49-165	0.11
Naphthalene	20.00	13.54	16.04	15.45	15.55	76%	36-120	0.12
Hexachlorocyclopentadiene	20.00	7.40	9.87	10.95	9.48	47%	2-125	0.68
2,4,5-Trichlorophenol	20.00	13.71	16.50	15.60	15.06	76%	37-144	0.27
2-Chloronaphthalene	20.00	13.47	16.23	15.96	14.93	76%	65-120	0.18
2,4-Dinitrophenol	20.00	12.43	13.82	13.56	14.24	68%	D-173	1.78
4-Nitrophenol	20.00	12.08	13.39	13.60	14.10	66%	13-129	0.77
Diethylphthalate	20.00	16.78	17.74	18.43	18.10	89%	D-120	0.16
Fluorene	20.00	14.46	16.59	16.36	15.48	79%	70-120	0.16
4,6-Dinitro-2-methylphenol	20.00	16.02	17.43	17.64	18.16	87%	53-130	0.39
Azobenzene	20.00	14.06	16.13	15.75	15.40	77%	10-150	0.22
Pentachlorophenol	20.00	14.79	15.78	16.12	16.89	79%	38-152	0.28
Benzidine	20.00	5.88	10.11	9.35	11.68	46%	2-150	0.68
3,3'-Dichlorobenzidine	20.00	6.23	6.35	6.42	7.20	33%	8-213	0.61
Chrysene	20.00	17.29	18.36	19.06	18.73	92%	44-140	0.27
Benzo(b)fluoranthene	20.00	18.21	20.40	21.14	20.07	100%	42-140	0.24
Indeno(1,2,3-cd)pyrene	20.00	16.38	17.53	18.45	18.72	89%	D-151	0.28
Benzo(g,h,i)perylene	20.00	16.39	17.57	18.43	18.64	89%	D-195	0.29

* This is just a partial list of compounds analyzed, please reach out to presenter for more info.



Conclusions

The City of San Jose (CSJ) laboratory was able to fully validate EPA methods 608.3 and 625.1 using a cartridge-based SPE. Following SPE method validation, we have analyzed industrial compliance samples, plant effluent/influent, and Performance Testing (PT) samples with great success. By extracting with SPE instead of LLE we have greatly reduced both time and solvent used by our extractions.

References

EPA Method 608.3 Organochlorine Pesticides and PCBs by GC/HSD, United States Environmental Protection Agency, December 2016, www.epa.gov/sites/default/files/2017-08/documents/method_608-3_2016.pdf

EPA Method 625.1 Base/Neutrals and Acids by GC/MS, United States Environmental Protection Agency, December 2016, https://www.epa.gov/sites/default/files/2017-08/documents/method_625-1_2016.pdf

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