DEUTERATED MONITORING COMPOUNDS FOR BETTER ACCURACY AND PRECISION MEASUREMENT OF GC/MS ENVIRONMENTAL DATA

The use of surrogate compounds to measure method performance in Gas Chromatography/Mass Spectroscopy (GC/MS) methods for environmental monitoring is not a new practice. All EPA-approved methods require the use of three to six compounds; however, only a few are deuterated analogs of target analytes. Deuterated analogs are more representative of target analytes, thereby providing more information regarding matrix effects while measuring the accuracy and precision. Since 2001, the EPA's Office of Superfund Remediation and Technology Innovation's Contract Laboratory Program (CLP) has required laboratories to add over a dozen deuterated monitoring compounds (DMCs) to each sample, all analogs of target analytes. Developed to improve data quality used in decision-making processes, this approach ultimately reduced the cost to the Superfund Program. This presentation shows, with thousands of data points, how incorporating more DMCs into EPA-approved GC/MS methods has improved data quality, and provided cost savings to the Agency, and how it may benefit the entire analytical chemistry community.

The USEPA Contract Laboratory Program (CLP)

- Provides high-volume, cost-effective analytical services
- Managed by EPA with experienced contractor support
- Detailed Statements of Work (SOWs) and thorough documentation of data quality
- Scalable operations with automated scheduling and invoicing
- Flexible products from enhanced EXES
- USEPA Headquarters funding
- Laboratories are qualified through the acquisition process
- Comprehensive QA Program

Innovations in the CLP

- Rigid SOWs
- Uniform data and QC reporting forms
- Comprehensive QA Program
- National Functional Guidelines (NFG) for Data Review and Validation
- Staged Electronic Data Deliverables – SEDD
- Environmental Data Management System (SCRIBE)
- On-line sample management tools in CLPSS
- Instituted use of Deuterated Monitoring Compounds

What are Deuterated Monitoring Compounds (DMCs)?

- DMCs are deuterated analogs of native target analytes
- DMC analytical and physical characteristics are nearly identical to their native analogs
- DMCs are spiked into every VOC and SVOC CLP analysis to measure analyte recovery accuracy
- DMC GC elution slightly precedes native target analytes
- DMCs present higher quantitation masses based on the degree of deuteration
- DMCs are not naturally found in environmental samples

DMC Selection Basis

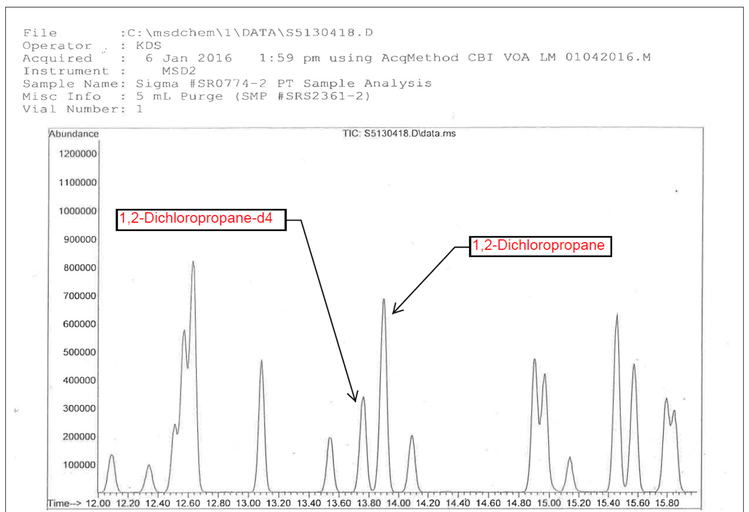
- Cost and availability: including potential suppliers, levels of deuteration, stability and potential for hydrogen exchange, and concentrations of stock solutions
- Representativeness of chemical classes of target analytes
- Toxicity
- Performance based on native target compound accuracy and precision characteristics
- Cost of revising the QC system vs. maintaining existing system; including cost/sample and costs related to altering methods

DMCs in CLP Use

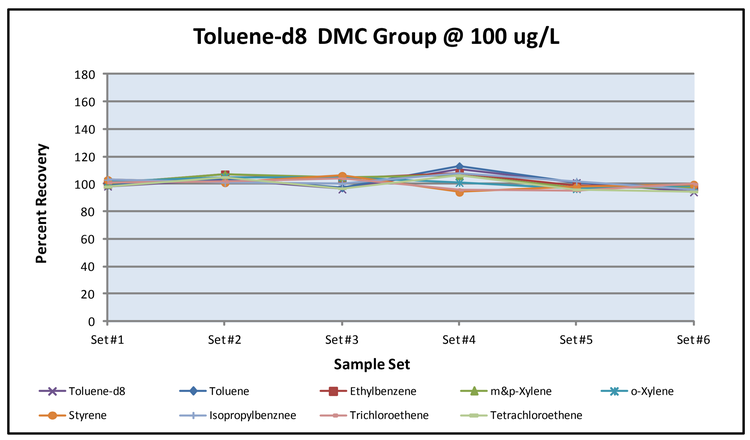
- 13 VOC DMCs representing all 5 VOC chemical classes, compared to the previous 3 surrogates representing 2 chemical classes
- 16 SVOC DMCs representing 13 of 16 chemical classes compared to the previous 6 surrogates representing 4 chemical classes
- All target compounds are assigned to a specific DMC by chemical class

DMC Development Studies

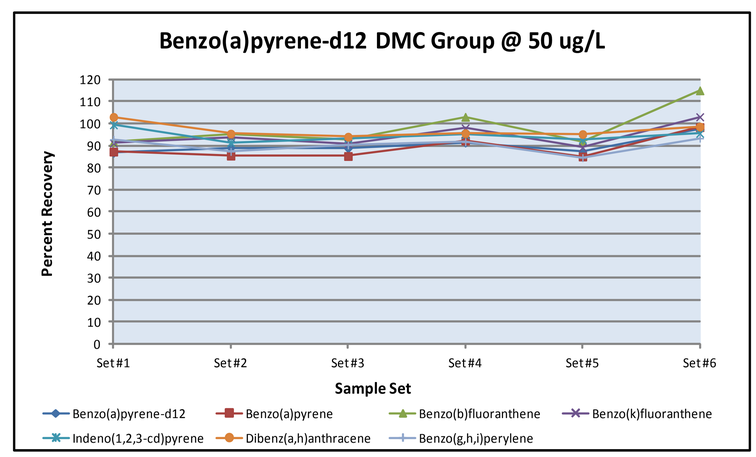
- Initial single- and multi-lab development studies analyzed multiple DMC-spiked calibration sets using all target analytes, and water samples with targets at various levels to assess DMC and target analyte recovery and precision correlation, as well as DMC ruggedness
- VOC study involved analyzing samples under normal and stressed purge & trap and GC/MS conditions
- SVOC study involved analyzing and extracting samples under normal and stressed extraction and GC/MS conditions



Example of DMC GC elution: 1,2-Dichloropropane and deuterated analog 1,2-Dichloropropane-d4



Sample Set #1 = Normal Purge/Normal Analysis
Sample Set #2 = Low Purge Flow/Normal Analysis
Sample Set #3 = High Purge Flow/Normal Analysis
Sample Set #4 = Purge Tube Leak/Normal Analysis
Sample Set #5 = Spent Purge Trap/Normal Analysis
Sample Set #6 = Normal Purge/Spent GC Column



Sample Set #1 = Normal Extraction/Normal Analysis
Sample Set #2 = 6 Hour Extraction/Normal Analysis
Sample Set #3 = Boiled Dry Extraction/Normal Analysis
Sample Set #4 = Evaporated Extraction/Normal Analysis
Sample Set #5 = Normal Extraction/Dirty Injection Liner
Sample Set #6 = Normal Extraction/Spent GC Column

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Subsequent to the initial DMC evaluation projects, several studies were conducted to assess DMC recovery and precision within Sample Delivery Groups (SDGs) using both aqueous and soil samples for the volatile and semivolatile analytical fractions. All data were generated by CLP laboratories using CLP methods. The objective of one particular study was to determine if the DMC statistical information within an SDG can be used to replace the current recovery and precision data provided by matrix spike (MS) and matrix spike duplicate (MSD) analyses, thus eliminating the need for 2 analyses per SDG and lowering costs.

DMC Recovery and Precision Study Approach

- 105 SDGs evaluated to determine DMC recovery & precision within each SDG
- DMC recovery compared against established acceptance limits
- DMC precision compared to pre-determined acceptable baseline
- DMCs in each SDG assessed by:
  - ✓ Average percent recovery
  - ✓ Standard deviation
  - ✓ RSD value
  - ✓ Low & high DMC recovery in data set
  - ✓ Number of DMCs exceeding QC limits
  - ✓ Number of data points
- MS/MSD results evaluated in a similar manner
- Five different fractions were evaluated
- DMCs recovery and precision statistics demonstrate that DMCs outperform MSCs

VOC DMC/MSC Pair	*VOC DMC*	*Associated VOC MSC*	*Average % Recovery*		*RSD*	
			DMC	*MSC*	*DMC*	*MSC*
#1	1,1-Dichloroethene-d_2	1,1-Dichloroethene	101	96	15.7	23.2
#2	Benzene-d_6	Benzene	100	101	13.6	15.0
#3	Toluene-d_8	Trichloroethene	98	102	12.8	18.7
#4	Toluene-d_8	Toluene	98	101	12.8	14.6
#5	1,2-Dichlorobenzene-d_4	Chlorobenzene	106	103	11.1	13.2

Evaluating 5,889 VOC DMC data points and pairing VOC DMCs with associated VOC matrix spike compounds (MSCs), data and statistics demonstrate equivalent recovery and overall greater precision for the VOC DMCs over the VOC MSCs.

SVOC DMC/MSC Pair	*SVOC DMC*	*Associated SVOC MSC*	*Average % Recovery*		*RSD*	
			DMC	*MSC*	*DMC*	*MSC*
#1	Phenol-d_5	Phenol	69	64	25.3	32.5
#2	2-Chlorophenol-d_4	2-Chlorophenol	71	63	23.6	33.2
#3	Nitrobenzene-d_5	N-Nitroso-di-n-propylamine	76	76	24.4	27.9
#4	Nitrobenzene-d_5	2,4-Dinitrotoluene	76	81	24.4	23.3
#5	2,4-Dichlorophenol-d_3	4-Chloro-3-methylphenol	70	70	26.0	31.6
#6	2,4-Dichlorophenol-d_3	Pentachlorophenol	70	90	26.0	34.8
#7	Pyrene-d_{10}	Pyrene	84	84	21.3	27.7
#8	Acenaphthylene-d_8	Acenaphthene	74	79	18.1	29.6
#9	4-Nitrophenol-d_4	4-Nitrophenol	82	77	19.4	33.2

Evaluating 3,232 SVOC DMC data points and pairing SVOC DMCs with associated SVOC matrix spike compounds (MSCs), data and statistics demonstrate equivalent recovery and overall greater precision for the SVOC DMCs over the SVOC MSCs.

DMC Precision Study Analytical Fraction Summary

Fraction	No. of DMC Data Points	No. of DMCs Exceeding Limits	% of DMC Results Exceeding Limits	% of MS/MSD Results Exceeding Limits	% of MS/MSD RPD Results Exceeding Limits
Trace Aqueous VOCs	5,889	83	1.4	11	2.0
L/M Aqueous VOCs	4,634	88	1.9	5.5	3.6
L/M VOCs in Soil	4,550	472	10.4	7.3	18.2
Aqueous SVOCs	3,232	108	3.3	9.3	0.0
SVOCs in Soil	4,224	114	2.7	3.4	0.9

Conclusions and Benefits of Using DMCs in Environmental Analysis

- DMCs mimic the chemistry and analytical behavior of native compounds
- DMC recoveries correlate well with MSC recoveries
- DMCs are not naturally present in environmental samples, unlike some surrogates
- DMCs can be used to indicate matrix effect in every sample
- Current DMCs provide a greater representation of chemical classes
- High number of DMCs per sample results in greater statistical significance
- DMC statistics allow for precision assessment across an entire SDG
- Quantitation bias is not observed for DMCs
- DMC statistics provide for greater verification and validation of environmental data
- Eliminating MS/MSDs conserves resources and reduces waste
- Additional DMC evaluation studies are planned
- Overall, DMCs provide cost savings for the CLP, and can do likewise for other EPA Programs