VALIDATION OF HOLDING TIMES FOR THE ENCORE™ SAMPLER

David Turriff, PhD.
Chris Reitmeyer

August 7, 1998

EN CHEM, Inc
1795 INDUSTRIAL DRIVE
GREEN BAY, WI 54302
920-469-8827

VALIDATION OF HOLDING TIMES FOR THE ENCORE™ SAMPLER

EXECUTIVE SUMMARY

This report presents the results from a series of experiments designed to evaluate the bias from storage of soil samples collected for volatile organics in the EnCore™ sampler. The study evaluated different soil types against the following storage conditions:

- 48 hours at 4 °C
- 96 hours at 4 °C
- 7 days at 4 °C
- 48 hours at 4 °C and 5 days at -12 °C (7 days total)
- 48 hours at 4 °C and 12 days at -12 °C (14 days total)
- 96 hours at 4 °C and 5 days at -12 °C (7 days total)
- 96 hours at 4 °C and 12 days at -12 °C (14 days total)

The soil types included sterile as well as microbiologically active soils, a variety of soil types, and included controlled spikes into the sampler as well as samples collected from a bulk soil. The results also include split sample results of actual field samples. Finally, the report presents results from multiple laboratories. The report summarizes over 3500 individual data points. The individual results are contained in an appendix.

All of the storage conditions were effective in reducing the loss of volatile organics. However, the following observations can be made:

- Concentrations decrease with time,
- Freezing improves accuracy,
- Bias is much more dependent on the analyte and matrix than the storage conditions and time.

Based on the results in this report, the recommendations below should be followed:

- Samples should be analyzed, or transferred to methanol, as soon as possible after collection.
- Samples not analyzed should be stored in a freezer until the day of a analysis.
- 14 days is an appropriate “holding time,” for soil samples collected in EnCore™ samplers.

1.0 INTRODUCTION

There is a significant body of literature documenting severe losses of volatile organics in soil samples based on the sample collection and handling techniques used[-4] The generally accepted best practice for minimizing these losses is field collection with methanol. [4-5] However, methanol has several significant problems associated with its use as a field preservative, including DOT shipping requirements, hazardous waste concerns, and health and safety issues. [6-7] Alternatives include field preservation with sodium bisulfate and freezing.[8] However these techniques have disadvantages as well. [6-8]

The EnCore™ sampler was developed to collect and store a soil sample with minimal losses while eliminating many of the concerns associated with the use of chemical preservatives in the field. The basic design and validation of the device as a sample collection and storage device has been described. [9-10]

Based on initial validation studies including spike samples, split samples, and other experiments, the EnCore™ sampler has been included as an acceptable sampling approach in various methods, including Method 5035 in SW-846. [11-12]

The EnCore™ was originally developed in a stainless steel version in 1994. Limited validation data from this design was submitted to EPA in 1996, as part of the comments on Update III. Based on this limited data, EPA recommended a storage time of 48 hours for use of the sampler.

This study was performed to collect additional data on the effects of time and storage conditions on the current disposable model of the sampler. The goals of the study were to evaluate two temperatures (4 °C and -12 °C) at different times up to 14 days, on different soil matrices.

Three types of studies were performed. Spike studies were done by adding known amounts of specific volatiles to soil contained in a EnCore™ sampler and immediately capping the device. These types of studies eliminated losses due to sampling. Sampling studies were done by collecting samples from a bulk container spiked with selected volatiles. The true value in the bulk soil was based on replicate measurements a time 0. This approach incorporated sampling error. Finally, split samples from sites with known contamination were analyzed. Although the true concentration is not known, this approach estimates the overall error, and further eliminates potential biases resulting from fortified samples.

2.0 EXPERIMENTAL DESIGN

Replicate measurements were performed on samples stored at various times and conditions. Except where noted, 5 replicate measurements were performed for each variable evaluated using a 5 gram EnCore™ Sampler. Except where noted, all analyses were performed using Method 8260. The following variable storage conditions and times were evaluated:

- 48 hours at 4 °C
- 96 hours at 4 °C
- 7 days at 4 °C
- 48 hours at 4 °C and 5 days at -12 °C (7 days total)
- 48 hours at 4 °C and 12 days at -12 °C (14 days total)
- 96 hours at 4 °C and 5 days at -12 °C (7 days total)
- 96 hours at 4 °C and 12 days at -12 °C (14 days total)

The results from these analyses were compared to identical samples collected at the beginning of the study (time 0.) All samples were transferred into methanol prior to analysis.

2.1 Spike Studies

The spike studies all involved addition on known amounts of volatile analytes onto a specific soil type contained in an EnCore™ sampler. After spike addition, the sampler was capped until the time of analysis. Spikes were added from an aqueous solution (250 ul) prepared from methanol stocks and/or gasoline saturated water. Seven different soils were evaluated. Two of these (Clay Rich R &D and Sandy R & D) were prepared in the laboratory to represent two extremes in clay/sand content, and were sterilized prior to use. The other 5 soils were all native soils containing varying amounts of silt, sand, and clay. These native soils were all biologically active. The soils contained from 10 to 65 % clay, from 14 to 75 % sand, and from 0 to 5 % organic carbon. A summary of the soil characteristics is presented in Appendix A.

Other studies were performed to evaluate variables associated with analytical methodology and sampler size (5g vs. 25g). Two laboratories were involved in these studies, EnChem in Green Bay, WI, and Western Research Institute (WRI) in Laramie, WY. Thus, as summarized below, 11 different studies were performed in this phase of the validation.

Studies Involving Spiked Soils into EnCore™ Samplers

Study #	Soil Type	Study Variable	Laboratory
1	Clay Rich R&D Soil		EnChem
2	Sandy R&D Soil		EnChem
3	Sandy R&D Soil	Method 8021	EnChem
4	Garden Topsoil		EnChem
5	"C" Horizon Soil		EnChem
6	Mountain Soil		WRI
7	Prairie Soil		WRI
8	River Bank Soil		WRI
9	Mountain Soil	25 gram sampler	WRI
10	Prairie Soil	25 gram sampler	WRI
11	River Bank Soil	25 gram sampler	WRI

2.2 Bulk Soil Study (Study 12)

A large volume (55 lb.) of a homogenized spike soil was prepared in a barrel mixer. The details of this approach have been previously described. [13] The soil used was a mix of commercial play sand, a most garden topsoil and dried garden topsoil. The characteristics of this soil are also described in Appendix A.

The soil was fortified with a mixture of gasoline and selected chlorinated compounds. The gasoline (11 mls) was added directly. The chlorinated compounds were mixed with methanol (1:1) and added in quantities ranging from 50 to 120 ul. After 22 hours of mixing, 56 samples were collected in 5 gram EnCore™ samplers within a period of xx minutes. The samples were numbered to evaluate bias during the collection period. Based on the results from the time 0 samples, concentrations decreased by 28% during the sampling period (See Appendix B).

2.3 Split Samples (Studies 13 and 14)

Two studies were performed on soil samples collected from sites with known contamination. [14-15] Study 1 involved the analysis of soils from various Underground Storage Tanks sites throughout the State of Wisconsin contaminated with volatile aromatic compounds with concentrations ranging from 1 to 150,000 ug/kg. Duplicate samples were collected. One sample was transferred to methanol within 24 hours of sample collection. The other sample was stored at 4 °C for seven days and then transferred to methanol. Analyses were performed using Method 8021.

Study 2 involved the analysis of soils from a site with trichloroethylene contamination.Replicate samples (10-20) were collected at different sampling locations. Half of the replicates (5-10) were immediately transferred into methanol, and the other half were either held for 2 days at 4 °C or for 7 days at 4 °C. Analyses were performed using headspace GC as previously described[6]

3.0 SUMMARY OF RESULTS

Appendix B presents the results from each of the studies described in Section 2. This section summarizes the results. In general, RSDs were less than 15%, in most cases less than 10%. Therefore, only mean recoveries are presented in this section. The primary exception was the bulk soil study, where RSDs were 15-25%, due to the bias associated with time of sampling. However, as this bias was averaged across all samples, the mean recoveries presented below are still good estimates of accuracy.

The tables in this section are summaries of all the data in Appendix B except for a few outliers. Most of the outliers were in the WRI data set, and are attributed to less experience in the use of the sampler. The Grubbs outlier test was used on all of the WRI data, and on selected data (2 samples) from the EnChem data which appeared to be inconsistent with other results. The rejected data are primarily attributed to a poor seal on the sampler, as evidenced by deformed o-rings. Less than 2% of the data were excluded due to outlier tests.

To enhance review of the tables, the following compound identifiers are used:

Code	Compound
MTBE	Methy tertiary butyl ether
TCE	Trichloroethylene
BZ	Benzene
DCA	1,2-Dichloroethane
TOL	Toluene
PCE	Tetrachloroethylene
EB	Ethyl Benzene
mpX	m/p-Xylene (sum)
oX	o-Xylene
135TMB	1,3,5-Trimethylbenzene
124TMB	1,2,4-Trimethylbenzene
MEK	2-Butanone
DCE	cis-1,2-Dichloroethene
DCB	1,4-Dichlorobenzene

Each of the tables presents the mean recovery (as compared to time 0), at one of the combinations of storage and time. As discussed in Section 2, samples were stored at either 4 or -12 °C, for varying periods of time. As all samples were stored initially at 4 °C for at least 48 hours, the freezer storage only occurred after a 48 or 96 hour storage at 4 °C. The tables below indicate the storage conditions using the convention of days at 4 °C plus days at -12 °C. for example, a 48 hour storage at 4 °C is shown as “2”, while 48 hours at 4 °C with 5 additional days in the freezer is shown as “2 + 5.”

Table 3-1. Summary of Results for Study 1 (Clay R & D Soil)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	DCB	Ave
2	97	101	103	100	103	103	107	105	108	109	104
4	93	91	92	89	93	88	93	93	96	95	92
7	138	75	78	71	82	82	88	82	93	100	87
2 + 5	107	96	92	94	99	84	95	98	97	95	96
4 + 3	116	85	88	84	94	87	98	100	101	108	95

Table 3-2. Summary of Results for Study 2 (Sandy R & D Soil)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	DCB	Ave
2	80	84	86	81	86	88	88	90	90	92	86
4	81	81	81	77	82	80	83	84	85	86	82
7	108	75	73	71	80	70	80	82	83	85	80
2 + 5	113	83	87	79	85	81	86	86	87	88	86
4 + 3	110	73	82	68	77	75	79	79	82	86	79

Table 3-3. Summary of Results for Study 3 (Sandy R & D Soil Analyzed by Method 8021)*

Time	BZ	TOL	EB	mpX	oX	135TMB	124TMB	Ave
2	75	77	83	84	86	89	98	85
4	67	70	77	76	79	101	96	81
7	56	66	78	79	83	100	105	81
2 + 2	81	86	96	96	98	102	110	96
4 + 3	71	77	87	88	91	105	109	90

* Results are mean recovery from four replicates

Table 3-4. Summary of Results for Study 4 (Garden Topsoil)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	DCB	Ave
2	92	85	90	81	87	93	89.9	89.7	91	98	90
4	90	68	75	65	74	82	79	78	81	90.5	79
7	90	75	82	68	76	89	85	84	86	103	84
2 + 5	105	90	97	86	98	104	103	103	104	109	101
4 + 3	110	81	90	76	87	99	94	94	96	106	93
2 + 12	109	77	74	70	84	84	88	87	91	100	87
4 + 10	114	71	70	65	79	82	85	83	87	98	84

Table 3-5. Summary of Results for Study 5 (C Horizon)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	DCB	Ave
2	96	73	65	64	57	65	60	57	60	77	68
4	83	48	41	40	38	44	41	38	42	60	48
7	88	42	36	31	34	42	42	40	42	76	47
2 + 5	113	68	72	61	68	81	75	71	76	96	78
4 + 3	111	58	56	48	51	63	58	54	59	82	64
2 + 12	95	35	42	30	44	54	54	51	55	79	54
4 + 10	88	34	35	27	38	38	49	46	52	74	48

Table 3-6. Summary of Results for Study 6 (Mountain Soil)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	Ave
2	84	87	92	87	90	96	92	90	96	91
4	77	78	83	74	84	88	90	87	91	83
2 + 5	72	84	92	84	97	99	96	101	96	91

Table 3-7. Summary of Results for Study 7 (Prairie Soil)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	Ave
2	95	81	79	75	83	92	91	91	92	87
4	95	64	62	54	75	82	85	87	91	77
2 + 5	83	51	62	44	77	88	93	96	99	78

Table 3-8. Summary of Results for Study 8 (River Bank Soil)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	Ave
2	100	91	98	94	99	100	101	102	99	98
4	100	97	100	94	97	100	100	100	99	98
2 + 5	91	97	100	93	99	99	101	98	101	98

Table 3-9. Summary of Results for Study 9 (Mountain Soil, 25 gram sampler)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	Ave
2	87	88	94	89	94	98	96	93	98	93
4	84	82	87	79	88	93	95	91	96	88
2 + 5	73	73	81	71	90	93	98	98	97	86

Table 3-10. Summary of Results for Study 10 (Prairie Soil, 25 gram sampler)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	Ave
2	96	75	73	69	80	86	90	89	94	84
4	93	59	56	50	65	73	80	81	87	71
2 + 5	92	58	63	54	76	85	92	94	97	79

Table 3-11. Summary of Results for Study 11 (River Bank Soil, 25 gram sampler)

Time	MEK	DCE	TCE	BZ	TOL	PCE	EB	mpX	oX	Ave
2	95	91	93	90	94	95	97	98	98	95
4	96	95	95	95	95	100	100	98	100	97
2 + 5	92	90	98	88	98	102	102	101	102	97

Table 3-12. Summary of Results for Study 12 (Bulk Soil)

Time	MTBE	TCE	BZ	DCA	TOL	PCE	EB	mpX	oX	135TMB	124TMB	Ave
2	104	79	70	91	80	89	86	84	86	90	90	86
4	100	78	69	90	78	88	84	83	85	88	88	85
7	86	60	47	75	63	79	75	74	77	83	83	73
2 + 5	81	70	59	78	73	85	84	83	85	90	90	80
4 + 3	87	72	61	78	72	87	81	80	82	87	87	79
2 + 12	88	72	57	83	76	88	84	84	85	93	93	82
4 + 10	90	72	60	82	74	87	81	80	82	90	90	81

Table 3-13. Summary of Results from Study 13 (UST Split Samples)

Sample	BZ	TOL	EB	mpX	135TMB	124TMB	Average
1	129	129	133	142	125	118	129
2	120	120	125	103	-	98	113
3	112	112	86	83	78	85	93
4	80	93	68	64	59	62	71
5	71	35	45	44	36	38	45
6	102	-	111	125	170	124	126
7	-	32	20	18	13	15	20
8	-	-	57	78	85	86	76
9*	-	-	100	140	128	140	127
10	81	80	78	114	108	114	96
11	78	43	51	47	37	59	53
12	74	84	68	70	65	69	72
13	75	154	95	98	96	104	104
14	95	-	87	96	58	104	88
15	45	37	58	59	30	94	54
16	60	64	65	65	64	64	64
17	-	88	88	97	-	88	90
18	96	-	83	83	84	82	85
19	74	23	93	98	107	114	85
20	90	-	55	15	32	5	39
21	85	88	104	117	122	132	108
					Overall Average		83

Table 3-14. Summary of Results from Study 14 (TCE Split Samples)

Sample	2 Days	7 Days
1	92	
2		88
3	89	
4		86
5	97	
6		94
7	85	
8		86
9	94	
10	98	
11		96
	Overall Average	91

4.0 REFERENCES

1. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., "Comparison of Analytical Methods for Determination of Volatile Organic Compounds", Envir Sci Tech, 1992; 26; 1932-8.
2. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., "Soil Sampling and Analysis for Volatile Organic Compounds", Envir Monitoring & Assessment, 1994; 30; 213-46.
3. Parr, J.L.; Walters, G.; Hoffman, M, Sampling and Analysis of Soils for Gasoline-Range Organics. Proceedings from West Coast Conference on Hydrocarbon Contaminated Soil and Ground Water, Newport Beach, CA, February 21, 1990.
4. Siegrist, R. L., Jenssen, P. D., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Envir Sci Technol, 1990; 24; 1387-92.
5. Urban, M,; Smith, J.; Schultz, E.; Dickinson, R. Volatile Organic Analysis for a Soil, Sediment or Waste Sample. Proceeding from Fifth Annual Waste Testing and Ouality Assurance Symposium, July 24-28, 1989 Washington, DC.
6. Nebelsik, J.; "Sample Collection and Preparation Strategies for VOCs in Solids (Draft)", March, 1998, US Army Corps of Engineers
7. Parr, J. and Burrows, R., "Issues in Sampling and Analysis of Volatile Organics in Soils", Environmental Testing & Analysis, January, 1998
8. Maskarinec, M.P.; Johnson, L. H.; Holladay, S. K.; "Recommendations for Holding Times of Environmental Samples", Proceeding from Fourth Annual Waste Testing and Quality Assurance Symposium, July 11-15, 1988 Washington, DC.
9. Reitmeyer, C; Turriff, D."Performance Validation of the Disposable EnCore Sampler" in Proceedings from the XXXXX
10. Turriff, D.; Reitmeyer, C.; Jacobs, L.; Melberg, N. "Performance of a New Disposable Sampling and Storage Device for Soil VOCs", Proceeding from Twelfth Annual Waste Testing and Quality Assurance Symposium, July 23-26, 1996 Washington, DC
11. Schultz, D.; "New VOC Sediment Sampling Method 5035", March 31, 1998, Michigan DEQ
12. Niedergang, N. R.; "Determination of Volatiles in Soil - Directive for Change", EPA Region 5, December 22, 1997.
13. Turriff, D.; Klopp, C.; "Studies of Sampling, Storage and Analysis of Soils Contaminated with Gasoline and Diesel", Wisconsin DNR, August, 1994
14. ACIL, Guidance Document for Implementation of Update III, March, 1998
15. Hewitt, A. D.; "A Tool for the Collection and Storage of Soil Samples for Volatile Organic Compound Analysis", Ame Environ Lab, November, 1997
16. Hewitt, A. D., Lukash, N. J. E., "Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil", Am Environ Lab, 1996; Aug; 15-9.

APPENDIX A

Physical and Biological Characteristics of Soils

1. Clay Rich R&D Soil -- Mixed at En Chem, Inc., Green Bay, WI

Microbial Degrader Population -- Soil Was Sterilized
Soil Makeup:
64% Clay Soil
22% Farm Topsoil
14% Coarse Sand
Soil Moisture after addition of Aqueous Spike was 10%

2. Sandy R&D Soil -- Mixed at En Chem, Inc., Green Bay, WI

Microbial Degrader Population -- Soil Was Sterilized
Soil Makeup:
10% Clay Soil
45% Farm Topsoil
45% Coarse Sand
Soil Moisture after addition of Aqueous Spike was 10%

Soils were sterilized by soaking in Methanol and burning.

3. Garden Topsoil -- Obtained From The Reitmeyer Residence, Green Bay, WI

Microbial Degrader Population -- 1E+07

Gravel	1%
Sand	58%
Silt	30%
Clay	11%

4. "C" Horizon Soil -- Obtained From The Reitmeyer Residence, Green Bay, WI

Microbial Degrader Population -- 9E+06

Gravel	4%
Sand	66%
Silt	20%
Clay	10%

5. Validation Soil Used in Mixing Drum Study -- Mixed at En Chem, Inc.

Microbial Degrader Population -- 4E+06

Gravel	0%
Sand	71%
Silt	18%

Clay	11%

6. River Bank Soil -- Obtained from Western Research Institute, Laramie, WY

Microbial Activity	22 mg TPF/g/24 hr
Sand	49%
Silt	26%
Clay	24%
Organic Material	50%
Moisture	14 %

7. Mountain Soil -- Obtained from Western Research Institute, Laramie, WY

Microbial Activity	11 mg TPF/g/24 hr
Sand	75%
Silt	13%
Clay	12%
Organic Material	4%
Moisture	12%

8. Prairie Soil -- Obtained from Western Research Institute, Laramie, WY

Microbial Activity	17 mg TPF/g/24 hr
Sand	67%
Silt	17%
Clay	16%
Organic Material	2%
Moisture	8%