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NATIONAL WATER QUALITY LABORATORY
TECHNICAL MEMORANDUM 1997.01S

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From: Peter F. Rogerson, Chief
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Subject: Use of Syringes to Add Volatile Organic Compounds to Water Samples for Use as Matrix Spike Samples

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Supplemental: This technical memorandum contains supplementary information for NWQL Tech Memo 97.01

Commencing with this issue, technical memorandums too lengthy for release via electronic mail have more in-depth versions on the Web. Supplemental tech memos are indicated by a reference line in the heading. The Web version will include an "S" after the number. Paper copies will continue to be mailed upon request.

INTRODUCTION

The National Water Quality Laboratory (NWQL) recommends a new procedure for using a syringe to add Volatile Organic Compounds (VOCs) to matrix spike samples. On-site and laboratory studies comparing the use of syringes and micropipets for spiking water samples with VOCs were conducted by the NWQL and the National Water Quality Assessment (NAWQA) Program. Syringes were found to yield significantly improved recoveries and variabilities for fortifying ground- and reagent-water samples in comparison to the micropipets currently in use. No significant disadvantages were reported or observed with the syringe selected for on-site use.

BACKGROUND

On-site matrix spikes are a type of quality control (QC) sample that provides the information necessary to evaluate biases and interferences from sample matrices as well as biases and variations arising from other processes that may occur from the time the sample vial is preserved on-site until it is analyzed at the laboratory. Data from on-site matrix spikes supplement and complement the laboratory QC samples and provide project- and program-specific QC information but are not used to replace the laboratory QC samples. Comparison of on-site and laboratory QC results might be needed to identify the sources of bias.

Micropipets were previously recommended and provided in NWQL spike kits for VOCs because of concerns regarding difficulty in handling, durability, and potential for cross contamination if syringes were used. The fixed-volume micropipet was thought to be more suitable for use on-site than a syringe for accurately measuring a fixed volume. In addition, the syringe was considered to be less durable because of the potential for bending the plunger and needle. Finally, the syringe needed to be rinsed between samples--a potential source of contamination that could be avoided with the disposable bores of the micropipet.

Despite these advantages, the micropipet provided lower recoveries than the syringe. The reasons for this difference are not well understood, although the recoveries using the micropipet decrease as compound volatility increases. This process introduces an additional source of bias for interpreting the effects of matrix or bias from shipping, unless the results are compared to laboratory QC samples prepared using the micropipet. This comparison creates extra work for the laboratory because the laboratory QC samples are routinely prepared with a syringe. While not ideal, the micropipet can provide information regarding bias from matrix or shipping when compared to reagent water samples prepared using the micropipet. Recent experiments were conducted to determine if a robust syringe procedure could be developed for use on-site that could overcome some of the difficulties mentioned previously.

This memorandum describes the results of an on-site and laboratory comparison of syringes and micropipets used to add VOCs to ground- and reagent-water. The performance of the micropipet used with reagent water samples is also summarized. The data provide reference information that can be used to interpret VOC matrix spike samples prepared with the micropipet.

RESULTS

The goals of these laboratory and on-site studies were to evaluate the recovery and variability of both spiking procedures and to gain information concerning the practicality of using syringes on-site. The samples were spiked and analyzed in random order to minimize potential sources of bias caused by volatilization of VOCs from spiking solutions and chronological variations in the response of the laboratory instrument.

Table 1 lists data obtained from the preliminary laboratory study in which the samples were all spiked by one chemist and then analyzed in a single batch by purge-and-trap gas chromatography/mass spectrometry (GS/MS). The relative standard deviation was typically several times higher for samples spiked with the micropipet than those spiked with the syringe. The average recovery for all compounds with the micropipet was 54 percent, and the average recovery for all compounds with the syringe was 84 percent. An older spiking solution was used, making it difficult to compare recoveries with those from other studies, but the differences in recovery and variability between spiking procedures within this study are apparent. Data obtained from on-site studies carried out by eight sampling crews from seven NAWQA study units are listed in Table 2. One pair of samples was excluded from the summary because it appeared that one of the samples was spiked twice. Unlike the samples from the laboratory study, these samples were spiked by several different people into various ground-water matrices, shipped, analyzed in several batches at the

NWQL, and varied in holding times before analysis. The mean relative standard deviation (RSD) for the micropipet was 15 percent, similar to the 16 percent in the laboratory study. The mean RSD for the syringe was 8 percent, higher than the 4 percent in the laboratory study. This difference is probably because of the larger number of different sample matrices and variables involved in on-site handling and analysis. It also suggests that the variation associated with the process of spiking with a syringe does not dominate the combined variability measured for all of the relevant processes. The overall mean recovery with the micropipet was 70 percent, and the overall mean recovery with the syringe was 90 percent.

The data presented in Table 2 indicate that the process of spiking VOCs with a micropipet is a significant source of bias, making it difficult to interpret all but the most severe matrix or shipping biases.

Average recovery and variability data for VOCs added to reagent water at the NWQL using a 100-microliter fixed-volume micropipet are listed in Table 3. The procedure is comparable to that recommended for on-site matrix spikes prior to this memo and should be used for evaluation of on-site matrix spike results that were completed using that procedure. The samples were prepared and analyzed during a 3-month period. The average recoveries ranged from 52 to 87 percent.

SUITABILITY FOR ON-SITE USE

A Hamilton 1810RN gas-tight syringe was used in the laboratory and on-site studies. This syringe was selected because it has a replaceable needle, its plunger is sturdy, and the plunger will not completely come out of the barrel by accident.

The data from Table 2 suggest that sampling crews can achieve reliable results for adding VOCs with the syringe without extensive training. However, owing to the potential for cross-contamination, the syringes are not being recommended for on-site use when adding compounds other than VOCs. Micropipets will continue to be used for spiking pesticides and other organic compounds.

Questionnaires were received from four of the participating study units. Two study units commented that the syringe was easy to use, and two commented that the syringe required two hands while the micropipet required one hand. One study unit mentioned that it was easier to get accurate volumes with the syringe and that it was an advantage not to replace glass capillaries between samples. No study unit indicated any disadvantages with the syringe significant enough to outweigh potential improvements in data quality.

SUMMARY

Syringes were found to yield significantly improved recoveries and variabilities for fortifying ground- and reagent-water samples in comparison to the micropipets currently in use. The process of spiking VOCs with a micropipet is a significant source of bias. The average recovery and variability of VOCs spiked with a syringe in the laboratory and on-site were significantly improved in comparison to recovery and variability of VOCs spiked with a micropipet.

Note: The new procedure using a syringe is recommended ONLY for VOCs; micropipets will continue to be used for spiking pesticides and other organic compounds.

Syringes or spike kits with syringes can be obtained from the NWQL by E-mail request to DENSUPPL.

Attachments

Impact on Data Base: None
Supersedes: None
Supplements: NWQL Tech Memo 97.01
Key words: field spike, micropipet, VOC, syringe, QA/QC sample
Distribution: http://wwwnwql.cr.usgs.gov/

Table 1. Recovery and precision data, in percent, from seven determinations of the compounds in reagent water samples fortified at the National Water Quality Laboratory (NWQL) using a micropipet or syringe

[Fortification concentration was 2.5 micrograms/liter (µg/L) (combined concentration of m-xylene and p-xylene was 5.0 µg/L). CAS, Chemical Abstracts Service; RSD, relative standard deviation]

Compound	CAS	Micropipet		Syringe	
	number	Recovery	RSD	Recovery	RSD
Summary, all analytes:		54	16	84	4
1,1,1,2-Tetrachloroethane	630-20-6	57	12	87	1
1,1,1-Trichoroethane	71-55-6	59	20	94	2
1,1,2,2-Tetrachloroethane	79-34-5	66	11	89	3
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	53	17	94	5
1,1,2-Trichoroethane	79-00-5	54	15	77	2
1,1-Dichloroethane	75-34-3	62	18	99	2
1,1-Dichloroethylene	75-35-4	53	20	86	3
1,1-Dichloropropene	563-58-6	51	20	86	3
1,2,3-Trichlorobenzene	87-61-6	52	14	77	3
1,2,3-Trichloropropane	96-18-4	71	13	97	2
1,2,4-Trichlorobenzene	120-82-1	48	15	74	3
1,2,4-Trimethylbenzene	95-63-6	52	16	82	2
1,2-Dibromo-3-chloropropane	96-12-8	51	33	73	17
1,2-Dibromoethane	106-93-4	53	13	75	1
1,2-Dichlorobenzene	95-50-1	64	14	94	2
1,2-Dichloroethane	107-06-2	69	15	99	4
1,2-Dichloropropane	78-87-5	58	17	89	3
1,3,5-Trimethylbenzene	108-67-8	50	15	81	3
1,3-Dichlorobenzene	541-73-1	60	15	94	2
1,3-Dichloropropane	142-28-9	47	12	67	3
1,4-Dichlorobenzene	106-46-7	61	14	94	2
2,2-Dichloropropane	594-20-7	28	18	44	9
2-Chlorotoluene	95-49-8	47	14	75	3
4-Chlorotoluene	106-43-4	56	16	90	3
Benzene	71-43-2	56	18	88	3
Bromobenzene	108-86-1	60	14	90	2
Bromochloromethane	74-97-4	71	18	103	3
Bromodichloromethane	75-27-4	61	16	91	3
Bromoform	75-25-2	61	13	90	4
Bromomethane	74-83-9	48	17	79	9
Butylbenzene	104-51-8	38	16	68	4
Chlorobenzene	108-90-7	48	13	75	2
Chloroethane	75-00-3	48	19	80	7
Chloroform	67-66-3	61	17	95	2
Chloromethane	74-87-3	41	17	67	14
cis-1,2-Dichloroethylene	156-59-2	63	16	97	3
cis-1,3-Dichloropropene	10061-01-5	47	15	72	3
Dibromochloromethane	124-48-1	55	14	80	2
Dibromomethane	74-95-3	70	14	100	3

Dichlorodifluoromethane	75-71-8	37	22	67	28
Dichloromethane	75-09-2	77	21	106	7
Ethylbenzene	100-41-4	41	14	67	2
Hexachlorobutadiene	87-68-3	41	16	73	3
Isopropylbenzene	98-82-8	47	15	78	2
m- and p-Xylene	108-38-3; 106-42-3	42	14	68	2
Naphthalene	91-20-3	57	13	77	4
o-Xylene	95-47-6	48	13	76	2
p-Isopropyltoluene	99-87-6	43	16	73	3
Propylbenzene	103-65-1	48	15	82	3
sec-Butylbenzene	135-98-8	53	16	87	3
Styrene	100-42-5	52	13	82	3
tert-Butylbenzene	98-06-6	54	17	86	2
tert-Butylmethyl ether	1634-04-4	78	15	110	1
Tetrachloroethylene	127-18-4	51	16	87	3
Tetrachloromethane	56-23-5	60	22	100	3
Toluene	108-88-3	57	19	90	4
trans-1,2-Dichloroethylene	156-60-5	57	17	96	4
trans-1,3-Dichloropropene	10061-02-6	52	16	76	4
Trichloroethylene	79-01-6	56	18	92	3
Trichlorofluoromethane	75-69-4	52	18	87	7
Vinylchloride	75-01-4	40	18	71	12

Table 2. Recovery and precision data, in percent, from seven determinations of the compounds in environmental samples fortified on-site by seven different National Water-Quality Assessment Program (NAWQA) sampling teams in 1995 using a micropipet and syringe

[Fortification concentration was 2.5 micrograms per liter (µg/L) (combined concentration of m-xylene and p-xylene was 5.0 µg/L). CAS, Chemical Abstracts Service; RSD, relative standard deviation]

Compound	CAS	Micropipet		Syringe	
	number	Recovery	RSD	Recovery	RSD
Summary, all analytes:		70	15	90	8
1,1,1,2-Tetrachloroethane	630-20-6	75	11	93	6
1,1,1-Trichoroethane	71-55-6	65	18	92	5
1,1,2,2-Tetrachloroethane	79-34-5	79	11	89	11
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	61	28	92	6
1,1,2-Trichoroethane	79-00-5	80	10	93	6
1,1-Dichloroethane	75-34-3	66	16	93	5
1,1-Dichloroethylene	75-35-4	63	22	93	7
1,1-Dichloropropene	563-58-6	66	19	92	5
1,2,3-Trichlorobenzene	87-61-6	84	16	99	9
1,2,3-Trichloropropane	96-18-4	86	13	97	6
1,2,4-Trichlorobenzene	120-82-1	77	16	93	6
1,2,4-Trimethylbenzene	95-63-6	74	10	94	5
1,2-Dibromo-3-chloropropane	96-12-8	71	23	77	16
1,2-Dibromoethane	106-93-4	79	9	92	4
1,2-Dichlorobenzene	95-50-1	82	8	97	4
1,2-Dichloroethane	107-06-2	76	10	93	5
1,2-Dichloropropane	78-87-5	74	11	95	4
1,3,5-Trimethylbenzene	108-67-8	73	11	93	5
1,3-Dichlorobenzene	541-73-1	77	10	95	6
1,3-Dichloropropane	142-28-9	78	8	92	7
1,4-Dichlorobenzene	106-46-7	76	10	95	6

2,2-Dichloropropane	594-20-7	47	21	65	12
2-Chlorotoluene	95-49-8	68	12	88	13
4-Chlorotoluene	106-43-4	76	10	97	8
Benzene	71-43-2	67	14	90	4
Bromobenzene	108-86-1	79	9	95	5
Bromochloromethane	74-97-5	78	11	94	5
Bromodichloromethane	75-27-4	74	10	91	6
Bromoform	75-25-2	68	13	76	11
Bromomethane	74-83-9	53	25	74	13
Butylbenzene	104-51-8	68	15	89	8
Chlorobenzene	108-90-7	74	10	93	7
Chloroethane	75-00-3	54	30	74	27
Chloroform	67-66-3	72	12	96	11
Chloromethane	74-87-3	55	27	83	18
cis-1,2-Dichloroethylene	156-59-2	71	13	93	4
cis-1,3-Dichloropropene	10061-01-5	65	17	82	8
Dibromochloromethane	124-48-1	81	13	88	8
Dibromomethane	74-95-3	81	9	95	6
Dichlorodifluoromethane	75-71-8	49	42	75	29
Dichloromethane	75-09-2	72	12	95	8
Ethylbenzene	100-41-4	72	12	92	10
Hexachlorobutadiene	87-68-3	68	16	89	4
Isopropylbenzene	98-82-8	72	13	94	9
Naphthalene	91-20-3	86	13	97	7
p-Isopropyltoluene	99-87-6	72	13	95	7
Propylbenzene	103-65-1	70	13	93	8
sec-Butylbenzene	135-98-8	72	13	95	8
Styrene	100-42-5	74	10	91	4
tert-Butylbenzene	98-06-6	66	12	86	7
tert-Butylmethyl ether	1634-04-4	78	9	93	5
Tetrachloroethylene	127-18-4	59	17	81	6
Tetrachloromethane	56-23-5	67	19	94	5
Toluene	108-88-3	66	13	86	3
trans-1,2-Dichloroethylene	156-60-5	64	18	90	5
trans-1,3-Dichloropropene	10061-02-6	67	13	82	6
Trichloroethylene	79-01-6	69	12	95	4
Trichlorofluoromethane	75-69-4	46	35	72	32
Vinylchloride	75-01-4	56	29	87	15
Xylenes	133-02-07	73	11	93	8

Table 3. Recovery and precision data, in percent, from eight determinations of the compounds in reagent water samples fortified at the National Water Quality Laboratory (NWQL) using a micropipet

[Fortification concentration was 2.5 micrograms per liter (µg/L) (combined concentration of m-xylene and p-xylene was 5.0 µg/L). CAS, Chemical Abstracts Service; RSD, relative standard deviation

Compound	CAS number	Average recovery	Standard deviation	RSD
1,1,1,2-Tetrachloroethane	630-20-6	75	7.6	10
1,1,1-Trichoroethane	71-55-6	67	8.1	12
1,1,2,2-Tetrachloroethane	79-34-5	87	7.9	9
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	62	11.6	19
1,1,2-Trichoroethane	79-00-5	80	6.1	8
1,1-Dichloroethane	75-34-3	70	7.5	11
1,1-Dichloroethylene	75-35-4	61	8.9	15
1,1-Dichloropropene	563-58-6	65	8.9	14

1,2,3,4-Tetramethylbenzene	488-23-3	80	8.8	11
1,2,3,5-Tetramethylbenzene	527-53-7	79	6.8	9
1,2,3-Trichlorobenzene	87-61-6	81	5.9	7
1,2,3-Trichloropropane	96-18-4	87	7.2	8
1,2,3-Trimethylbenzene	526-73-8	77	7.1	9
1,2,4-Trichlorobenzene	120-82-1	80	6.4	8
1,2,4-Trimethylbenzene	95-63-6	74	6.4	9
1,2-Dibromo-3-chloropropane	96-12-8	80	11.9	15
1,2-Dibromoethane	106-93-4	81	9.6	12
1,2-Dichlorobenzene	95-50-1	77	6.6	9
1,2-Dichloroethane	107-06-2	79	9.3	12
1,2-Dichloropropane	78-87-5	74	8.1	11
1,3,5-Trimethylbenzene	108-67-8	74	6.5	9
1,3-Dichlorobenzene	541-73-1	76	7.6	10
1,3-Dichloropropane	142-28-9	81	7.3	9
1,4-Dichlorobenzene	106-46-7	76	8	11
2,2-Dichloropropane	594-20-7	68	8.9	13
2-Chloroethylvinyl ether	110-75-8	14	23.7	173
2-Chlorotoluene	95-49-8	72	6	8
2-Ethyltoluene	611-14-3	74	7.3	10
4-Chlorotoluene	106-43-4	73	6.2	9
Benzene	71-43-2	70	7.8	11
Bromobenzene	108-86-1	77	7.9	10
Bromochloromethane	74-97-4	75	5.6	7
Bromodichloromethane	75-27-4	73	10	14
Bromoform	75-25-2	78	10.1	13
Bromomethane	74-83-9	61	10.8	18
Butylbenzene	104-51-8	72	6.6	9
Chlorobenzene	108-90-7	73	7.1	10
Chloroethane	75-00-3	62	10	16
Chloroform	67-66-3	73	6.7	9
Chloromethane	74-87-3	52	11.9	23
cis-1,2-Dichloroethylene	156-59-2	70	6.2	9
cis-1,3-Dichloropropene	10061-01-5	70	8.2	12
Dibromochloromethane	124-48-1	73	9.5	13
Dibromomethane	74-95-3	80	11.7	15
Dichlorodifluoromethane	75-71-8	52	7	13
Dichloromethane	75-09-2	73	7.1	10
Dichloromethane	75-09-2	70	8.4	12
Hexachlorobutadiene	87-68-3	70	9.5	14
Isopropylbenzene	98-82-8	70	7	10
m- and p-Xylene	108-38-3; 106-42-3	72	7.1	10
Naphthalene	91-20-3	87	5	6
o-Xylene	95-47-6	74	6	8
p-Isopropyltoluene	99-87-6	73	6.7	9
Propylbenzene	103-65-1	70	7.3	10
sec-Butylbenzene	135-98-8	70	7.1	10
Styrene	100-42-5	76	6.7	9
tert-Butylbenzene	98-06-6	71	6.9	10
tert-Butylmethyl ether	1634-04-4	88	5.2	6
Tetrachloroethylene	127-18-4	66	7.3	11
Tetrachloromethane	56-23-5	65	9.7	15
Toluene	108-88-3	72	8	11
trans-1,2-Dichloroethylene	156-60-5	64	8.1	13
trans-1,3-Dichloropropene	10061-02-6	82	10	12
Trichloroethylene	79-01-6	68	9.1	13
Trichlorofluoromethane	75-69-4	58	12.1	21
Vinylchloride	75-01-4	56	8.6	15