DRAFT

VOA Compositing Procedures

September 1, 1994

William A. Telliard, Chief
Analytical Methods Staff
Engineering and Analysis Division
Office of Science and Technology
U S. EPA Office of Water

SUMMARY

This paper gives results of a VOA compositing study conducted by the U S Environmental Protection Agency (EPA) in early 1994 In these studies, individual grab samples of real-world effluent were collected over the course of a day These samples were analyzed spiked or unspiked, composited and individually, by isotope dilution GC/MS, using Revision C of EPA Method 1624. Pollutants spiked were the volatile organic GC/MS fraction of the priority pollutants plus additional compounds routinely tested for in EPA's industrial surveys. The objective was to compare the mathematical average of the results from analysis of the individual grab samples with the result of the analysis of the composite sample to determine if bias occurred in the compositing process.

These tests showed that the mathematical average of the results of analysis of the individual grab samples was a few percent higher, on average, than results of the analysis of composite samples. The cause of these slight differences is not known, and these differences are not significant for practical purposes and would not be discernable by non-isotope dilution GC/MS methods.

BACKGROUND

Volatile Organic Compounds (VOCs)

The Federal Water Pollution Control Act of 1972 (PL 92-500) required the Environmental Protection Agency to control the discharge of toxic pollutants to the nation's waters. The toxic pollutants regulated were listed in the act (40 *CFR* 401 15) as 65 compounds and compound classes. This list was refined into an initial list of 129 "priority pollutants" and then a final priority pollutant list of 126 individual compounds (Reference 1).

For determination of the priority pollutants, EPA had to separate the list of 126 into groups based on the analytical technology that could be used to measure the pollutants. Organic pollutants which could be determined by gas chromatography combined with mass spectrometry (GC/MS), pollutants were further categorized into the volatile, acid, and base/neutral fractions

The volatile fraction, also called the "purgeable" fraction, contains those compounds that boil below approximately 130°C and that are capable of being purged from water using a flowing gas stream (Reference 2). Analysis of this fraction is termed a "volatile organic analysis" (VOA) and the compounds in this fraction are termed "volatile organic compounds" (VOCs). Determination of VOCs in the VOA fraction of the list of priority pollutants is the subject of this study.

Pollutant Lists

The list of VOCs in this study is given in Table 1 This table also lists the stable, isotopically labeled analog that was used for isotope dilution quantitation, whether a given analyte is a Priority Pollutant or other pollutant associated with the 1976 Consent Decree (Reference 1); and the Chemical Abstracts Service Registry Number for the pollutant and labeled analog, where available

The list of VOCs in Table 1 is separated into two groups The first group contains VOCs that are determined by calibration of the GC/MS using authentic standards; the second group contains VOCs determined by reverse search for a spectral match during a given retention time window based on mass spectral and retention time data contained in a mass spectral library and given in the method. If a match is found, the compound is quantitated based on a response factor also given in the method. Although results produced by the reverse-search technique are not as precise and accurate as results produced using calibration, the technique is useful for screening and approximation of the concentrations of VOCs in the reverse-search group and is more accurate in identifying compounds than a forward library search in which only the mass spectrum is tested against a large mass spectral file

In addition to the priority pollutant list of VOCs, EPA has established other lists of regulated VOCs under the Safe Drinking Water Act (SWDA) and amendments, the Resource Conservation and Recovery Act (RCRA) and amendments, and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA; Superfund) and amendments. Although these lists are not identical to the list of VOCs in Table 1, most of the compounds on these other lists are included in Table 1, and therefore the results of this study should be applicable to the VOCs on these other lists.

"Gases" and "Water-Soluble" Compounds

Two groups of compounds present unique analytical problems in the determination of VOCs. These groups are the "gases" and "water-soluble compounds " The priority pollutant "gases" consist of chloromethane, bromomethane, chloroethane, and vinyl chloride, but any non-water-soluble compound that boils below approximately 15° C will be lost from aqueous solutions easily. These losses make the analysis somewhat more variable than for compounds that are not lost as readily. Conversely, the water-soluble compounds present analytical problems because they are not readily purged from the water. In this study, the water-soluble priority pollutants tested were acrolein, acrylonitrile, and 2-chloroethylvinyl ether Other non-priority pollutant water-soluble compounds tested were acetone, 2-butanone (MEK), p-dioxane, and diethyl ether. As will be seen from the results presented below, these compounds produce results that are more highly variable than for the non-gas priority pollutant VOCs.

Table 1
Volatile Organic Compounds Analyzed

Compounds Calibrated by Internal Standard

Compound	CAS Registry	Labeled Compound Analog	CAS Registry	Priority Pollutant
Acetone	67-64-1	d_6	666-52-4	N
Acrolein	107-02-8	d_4	33984-05-3	Y
Acrylonitrile	107-13-1	d_3	53807-26-4	Y
Benzene	71-43-2	d_6	1076-43-3	Y
Bromodichloromethane	75-27-4	^{13}C	93952-10-4	Y
Bromoform	75-25-2	^{13}C	72802-81-4	Y
Bromomethane	74-83-9	d_3	1111-88-2	Y
Carbon tetrachloride	56-23-5	^{13}C	32488-50-9	Y
Chlorobenzene	108-90-7	d_5	3114-55-4	Y
Chloroethane	75-00-3	d_5	19199-91-8	Y
2-Chloroethylvinyl ether	110-75-8			Y
Chloroform	67-66-3	^{13}C	31717-44-9	Y
Chloromethane	74-87-3	d_3	1111-89-3	Y
Dibromochloromethane	124-48-1	^{13}C	93951-99-6	Y
1,1-Dichloroethane	75-34-3	d_3	56912-77-7	Y
1,2-Dichloroethane	107-06-2	d_4	17070-07-0	Y
1,1-Dichloroethene	75-35-4	d_2	22280-73-5	Y
trans-1,2-Dichloroethene	156-60-5	d_3	42366-47-2	Y
1,2-Dichloropropane	78-87-5	d_6	93952-08-0	Y
trans-1,3-Dichloropropene	10061-02-6	d_4	93951-86-1	Y
Diethyl ether	60-29-7	d_{10}	2679-89-2	N
p-Dioxane	123-91-1	d_8	17647-74-4	N
Ethylbenzene	100-41-4	d_{10}	25837-05-2	Y
Methylene chloride	75-09-2	d_2	1665-00-5	Y
Methyl ethyl ketone (MEK)	78-93-3	d_3	53389-26-7	N
1,1,2,2-Tetrachloroethane	79-34-5	d_2	33685-54-0	Y
Tetrachloroethene	127-18-4	$^{13}C_2$	32488-49-6	Y
Toluene	108-88-3	d_8	2037-26-5	Y
1,1,1-Trichloroethane	71-55-6	d_3	2747-58-2	Y
1,1,2-Trichloroethane	79-00-5	$^{13}C_2$	93952-09-1	Y
Trichloroethene	79-01-6	$^{13}C_2$	93952-00-2	Y
Vinyl chloride	75-01-4	d_3	6745-35-3	Y

Compounds Determined by Reverse Search

Compound	CAS Registry	Priority Pollutant
Carbon disulfide	75-15-0	N
cis-1,3-Dichloropropene	10061-01-5	Y
2-Hexanone	591-78-6	N
4-Methyl-2-pentanone	108-10-1	N
Trichlorofluoromethane	75-69-4	N
Vinyl acetate	108-05-4	N
m-Xylene	108-38-3	N
o- and *p*-Xylene		N

Control of Discharges

The Engineering and Analysis Division (EAD), within the Office of Science and Technology in EPA's Office of Water, is responsible for promulgating regulations controlling the discharge of pollutants to surface waters of the U.S EAD conducts surveys within various categories and sub-categories of the regulated industry to establish the best pollutant control strategies (Reference 3). In these surveys, EAD frequently performs sampling and analyses of wastewaters to determine the presence and concentration of pollutants. Although these studies focus primarily on the 126 priority pollutants (40 *CFR* 423 Appendix A) and the five Conventional Pollutants (40 *CFR* 401.16), other "non-conventional" pollutants may also be surveyed and subsequently regulated.

In conducting these surveys, EPA collects aqueous samples from in and around wastewater treatment plants. Unless treatment system characterization dictates otherwise, VOA samples are composited to effect a savings over the costs of analysis of individual grab samples. Normally, four individual grab samples are collected at approximately equal time intervals over the course of a calendar day. These samples are shipped under wet ice to the testing laboratory and composited in the laboratory. Results of these analyses are then used, in part, to develop, propose, and promulgate effluent guidelines and standards under the appropriate industrial category at 40 *CFR* Parts 403 - 499.

THEORETICAL CONSIDERATIONS AND PRIOR WORK

VOA compositing is used extensively in EPA's data-gathering for regulation development and is used for compliance monitoring under EPA rules Technical literature is replete with theoretical discussions of the effects of compositing. Book chapters on the subject by Gilbert (Reference 4) and by Garner et al. (Reference 5) provide comprehensive discussions of the concepts behind composite

sampling and provide extensive bibliographies referencing the technical literature on sample compositing and statistical treatments of the compositing process

Although the technical literature is replete with theoretical discussions of compositing, it is remarkably silent in reports of data gathering to verify the theoretical discussions A search of the online databases revealed only one technical paper that presents actual results of a VOA compositing study (Reference 6)

Variability of Individual and Composite Measurements

Any empirical measurement process has inherent variability, and the measurement of each analyte in each analysis is accompanied by an analytical error. This error is normally characterized by replicate measurements and is expressed as the standard deviation of the concentration of these measurements or is normalized to the concentration as the "relative standard deviation" or "coefficient of variation." For example, the concentration of chloroform may be determined by purge-and-trap GC/MS with a relative standard deviation of 10 percent

The effect of the measurement error on the average result for a composite sample and for the average of individual grab samples can be understood most easily if it is assumed that the concentration of a pollutant is identical in all of the individual grab samples Averaging the results of analyses of four individual samples is equivalent to determining the concentration four separate times. Because the measurement error is inversely proportional to the square root of the number of measurements, the measurement error associated with the four individual grab samples will be one-half of the error associated with any individual measurement. And because the determination of the composite sample is an individual measurement, the error associated with the average of the measurement of the four individual grab samples will be one-half of the error associated with the measurement of the composite sample.

Therefore, if costs are not an important consideration, the most precise and accurate results will be produced if the individual grab samples are analyzed and the results averaged. Of course, similar accuracy could be achieved if the compositing process were replicated four times and the four composites analyzed, assuming that little or no error occurred in the compositing procedure. Pragmatic considerations of cost and time frequently outweigh the ability to measure the grab samples individually, so discussions of error become moot, and the error associated with the composite sample becomes the only measurement error that must be considered.

This study did not attempt to quantify or verify that the measurement error associated with the average of the four individual composite samples was indeed one-half the measurement error associated with the single composite sample. The objective was to compare the mathematical average of the results from analysis of the individual grab samples with the result of the analysis of the composite sample to determine if bias occurred in the compositing process. However, the measurement error plays a role in this comparison. As explained in the section on statistical analyses below, differences in results between mathematically averaged individual grab samples and physically composited samples are dependent on the measurement error. Smaller differences

become statistically significant as the measurement error decreases As will be seen from the results of this study, measurement errors on the order of a few percent allow discernment of differences on the order of a few percent. This high precision is attributable primarily to the isotope dilution quantitation technique, but also to the quality of work performed by the testing laboratory

TYPES OF COMPOSITING

Time Compositing

Time compositing is the most common type of sample compositing. Samples are collected from a fixed sampling point over some fixed period of time, usually one calendar day Samples can be collected as discrete grab samples at intervals throughout the fixed time period or continuously over the period.

Transients

The objective of sampling over time, whether the sampling is grab or continuous, is to attempt to capture transient compounds in the waste stream. Capture of transients in the waste stream requires a knowledge of the flow characteristics of each individual stream. These characteristics are system volumes, flow rates, and the nature of the transient wave. If the objective is to capture the concentration maximum, the ideal scheme is to collect a grab sample at the apex of the wave Unfortunately, this scheme is frequently impractical. The next best scheme is to collect a sample at frequent enough intervals to assure that some fraction of the transient will be captured. Although use of a continuous compositor will assure capture of the transient, the transient may be diluted by the stream before and after the passage of the wave Therefore, if monitoring of transients in a waste stream is necessary to characterize treatment system operation, samples should be collected over the wave to model the wave. After the wave characteristics are known, the intervals for subsequent sampling can be determined.

Treatment System Detention Times

For treated effluents, a common mistake made by personnel unfamiliar with treatment system operation is to require grab samples at intervals more frequent than the detention time of the treatment system. For example, if the treatment system has a detention time of 6 hours, sampling the effluent from the system more frequently than every few hours is unnecessary, particularly if the samples are analyzed individually.

Spatial Compositing

Samples from different sampling points can be composited in an effort to save analysis costs. If an analyte is present in a composited sample, each sampling point can then be sampled individually to determine the point or points contributing to the level of the analyte in the sample. Spatial compositing of up to five streams is allowed at the discretion of the States under the EPA

drinking water regulations to reduce the total number of samples that small drinking water treatment system operators must analyze (40 *CFR* 141 24[f][14]). However, the analytical system must be capable of detecting one-fifth of the maximum contaminant level (MCL) required for an individual sample This requirement can usually be met by compositing five 5-mL samples and purging a 25-mL composite, as suggested in the *CFR*.

Flow or Volume Compositing

As the name implies, flow or volume compositing involves proportioning the sample according to the flow rate or volume of the stream being sampled. The most common use of flow compositing is in EPA's stormwater rules (40 *CFR* 122.21[g][7]; Reference 7). These rules require that the composited sample proportionately represent the runoff that occurs in a stormwater event. However, because it is impossible to know beforehand the total volume that will be discharged during the event, individual grab samples must be collected at various time intervals throughout the event, and varying volumes from these individual grab samples must be composited to reflect the flow during the entire stormwater event. The details of stormwater sampling and analysis, along with an example of the compositing associated with a stormwater discharge event, have been explained by Stanko (Reference 8).

Problems Unique to VOA Compositing

The nature of volatiles, and particularly of the volatile gases, makes these analytes particularly susceptible to loss during any manipulation, including collection and compositing.

Headspace During Sampling

Losses of analytes, particularly the gases, to the headspace of a container have been documented by Cline and Severin (Reference 6). Therefore, it is imperative that headspace be eliminated during sampling and sample shipment. In this study, the loss of volatiles was not critical because the objective was to compare the results of analyses of individual grab samples with the results of analysis of a composited sample. So long as the loss of VOCs from the individual grabs and from the grabs that feed the composite are the same, there is no consequence to this loss.

Losses During Compositing

None of the compositing procedures requires that compositing of grab samples be performed with zero headspace, and such a system is difficult to envision. Because such a system does not exist, exposure of the sample to the atmosphere can result in analyte losses. The amount of loss can be minimized by keeping the sample cold and minimizing the exposure time. In this study, all compositing was performed rapidly with the VOA vials chilled to 0 - 4° C.

COMPOSITING PROCEDURES

Definitions

Sample The water collected in a sample jug from a specific location at a specific time

Individual grab sample An aliquot poured from the sample jug

Duplicate grab sample. A second aliquot poured from the sample jug.

Replicate grab sample. Any aliquot poured from the sample jug.

Composite sample. The combination of four grab samples collected at different times on the same calendar day.

Mathematical composite: The mathematical average of the results of four individual grab samples.

Manual Compositing

Two types of manual compositing procedures were tested in this study· flask compositing and purge device compositing. Each of these procedures is described below. A third procedure, syringe compositing, is also described below but was not tested because of resource limitations.

Flask Compositing (44 *FR* 69555)

In the flask compositing procedure, a 300- to 500-mL round-bottom flask is immersed in an ice bath. The individual VOA grab samples are maintained at 0 - 4°C and are slowly poured into the round-bottom flask. The flask is swirled slowly to mix the individual grab samples. After mixing, multiple aliquots of the composited sample are poured into VOA vials and sealed for subsequent analysis, or an aliquot can be poured into a syringe for immediate analysis.

Purge Device Compositing (40 *CFR* 141.24[f][14][v])

Equal volumes of individual grab samples are added to a purge device to a total volume of 5 or 25 mL The sample is then analyzed.

Syringe Compositing (40 *CFR* 141.24[f][14][iv])

In the syringe compositing procedure, equal volumes of individual grab samples at a temperature of 0 - 4° C are added to a 25-mL syringe while maintaining zero headspace in the syringe. Either the total volume in the syringe or an aliquot is subsequently analyzed. The disadvantage of this technique is that the individual samples must be poured carefully to attempt to achieve equal volumes of each. An alternative procedure uses multiple 5-mL syringes that are filled with the individual grab samples and then injected sequentially into the 25-mL syringe.

Automated Collection and Compositing

Two types of automated equipment are available for sample collection and/or compositing These are (1) automated grab collection and (2) automated continuous collection/compositing. These devices are described below Neither of these devices were tested in this study.

Automated Grab Collection

Automated grab collection can be accomplished using devices such as the ISCO Corp Model 6000 automatic VOC sampler. With this system, a small bladder pump forces sample into a 40-mL VOA vial after rinsing the vial with three vial volumes to eliminate headspace. Up to 25 samples can be collected at a minimum of 5-minute and a maximum of 10-hour intervals Samples are maintained at 0 - 4° C during collection.

Automated Continuous Collection/compositing

An automated system such as the Associated Design and Manufacturing Corp (ADM) automated continuous compositing system can be used to collect samples over a given sampling period Samples are maintained at 0 - 4° C during collection.

SITE SELECTION AND SAMPLE COLLECTION

Sampling Sites

Samples were collected from seven "real-world" sites, which are described in Table 2. Information about each site was recorded in an on-site log and included the EPA sample number, collection date and time, descriptions of sample and sampling location, sample pH and temperature, and preservatives used, if any.

Sample sites were selected specifically in an attempt to find effluents that contained volatile organics. However, volatile organics were seldom found.

Table 2
Description of Sites and Samples

Episode	Industrial Category	Sampling Point	pH
4559	Organic Chemicals	Primary Effluent	8 8
4561	Organic Chemicals	Primary Effluent	7 3
4563	Drum Reconditioning	Scrubber Water	8 6
4573	Shore Reception	Oily Wastewater	5.6
4575	Transportation	Separator Effluent	6.0
4593	Transportation	Separator Effluent	6.8
4595	MSW Landfill	Leachate	6.8

Sample Collection, Shipment, and Storage

All samples collected at industrial or municipal sites were preserved to pH <2, refrigerated, and shipped to the laboratory under wet ice via overnight courier. If free chlorine was present in the sample, the sample was additionally preserved with sodium thiosulfate. Samples were stored in the laboratory at 0 - 4° C from the time of collection until analysis. All analyses were performed within the 14-day holding time.

Samples were collected by passage of a portion of the flowing sample stream through a coil of pre-cleaned polytetrafluoro-ethylene (PTFE) tubing that was immersed in a commercial picnic cooler filled with ice This practice reduced the temperature of the effluent to 0 - 4° C, thus reducing the volatility of the VOCs. The stream from the PTFE tubing was collected in a refrigerated one-liter glass jug.

Samples were preserved to pH <2 in this jug and free chlorine was removed as required using sodium thiosulfate After preservation, samples were allocated from the 1-L jug into 40-mL VOA vials. Eight vials were filled from the common jug, thus assuring that each replicate VOA vial in the set contained the same pollutants and concentrations as the others. The vials were filled to overflowing, then capped with a PTFE-faced silicone rubber septum. After capping, each VOA vial was inverted and inspected for an air bubble. If a bubble was present, the vial was uncapped and refilled to overflowing and re-capped until completely filled without an air bubble Each vial was

assigned a unique sample number. Sampling times were at approximately 9 a.m., noon, 3 p.m., and 6 p.m.

LABORATORY TESTING

Sample Spiking

All spiking solutions were prepared in the laboratory and all spiking was performed in the laboratory.

Seven field samples were spiked in the laboratory and analyzed in Phase II. Of these seven samples, three were flask composited and four were purge device composited. Schematic diagrams of the flask and purge device compositing procedures are shown in Figures 1 and 2, respectively. For the samples that were flask composited, the grab sample from the first sample time was analyzed unspiked to determine the background concentrations of VOCs present. For the samples that were purge device composited, the grab samples from all four sample times were analyzed unspiked to determine the background concentrations present. The reason for this testing was to determine the constancy of the background throughout the sampling period.

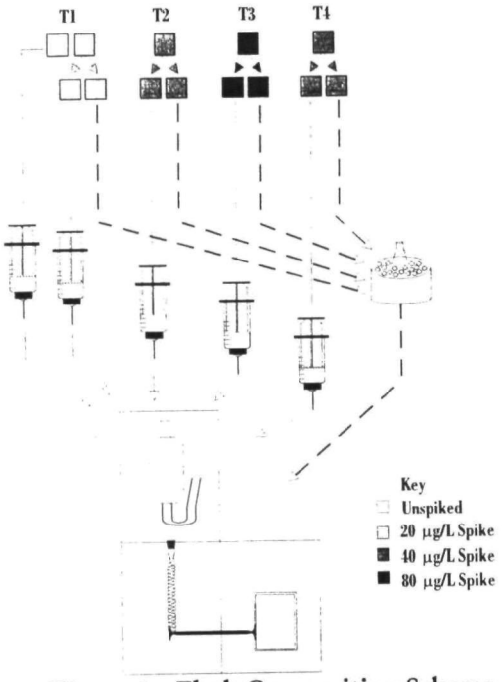

Figure 1. Flask Compositing Scheme

Individual grab sample VOA vials from the four sample times were spiked at concentrations of 20, 40, 80, and 40 μg/L, respectively, to produce an average concentration of 45 μg/L. An aliquot from these spiked VOA vials was analyzed and another aliquot was used for compositing, thus assuring that the spike levels were identical for analyses of the individual and composited samples.

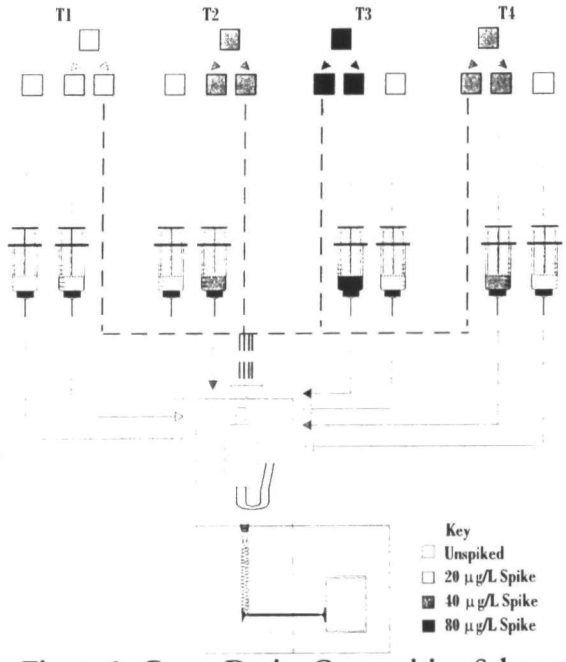

Figure 2. Purge Device Compositing Scheme

Analyses

All laboratory analyses were performed at the laboratories of Pacific Analytical, Inc., in Carlsbad, California. A single laboratory was chosen for this work because EPA desired that analytical variability be minimized in order to increase the probability of detecting differences between grab and among compositing procedures.

Calibration

All analyses were performed by isotope dilution GC/MS using Revision C of EPA Method 1624. Revision C is an updated version of the method promulgated for use in water programs (40 *CFR* 136, Appendix A). Revision C includes a "reverse-search" technique for identification and quantitation of pollutants in addition to the priority pollutants. In the promulgated version and in Revision C of Method 1624, the Priority Pollutants and certain

additional compounds are determined using a 5-point calibration for quantitation Nominal calibration points are 10, 20, 50, 100, and 200 μg/L In addition, the list of "reverse search" compounds is determined from relative retention time data and response factors given in the method. Although the reverse-search quantitation procedure is not as accurate as the 5-point calibration, it serves screening purposes to provide an estimate of the presence and concentration of pollutants over and above the priority pollutants that may be present in environmental samples.

In this study, the method of quantitation was examined in relation to recovery of the VOCs for which the instrument was calibrated. The calibration procedures in Method 1624 require use of an average relative response or a calibration curve for isotope dilution calibration based on the five calibration points. However, because the analytes were spiked at known concentrations, it is also possible to use the calibration point closest to each known concentration for calibration. This technique of using the closest calibration point was used for calculation of all concentrations in this study and reduced the analytical error to less than that obtained using the average of the five calibration points or a calibration curve. It must be emphasized that this practice of using the closest calibration point should be employed only when the concentration of a pollutant in a sample is known to be close to the calibration point. For samples containing unknown concentrations, the most accurate concentration will be found using the entire 5-point calibration curve

Data Processing and Reporting

Data were received by the EPA Sample Control Center in the form of quantitation reports on diskette. These data included quality control (QC) data for each analysis. The QC data included recoveries for each labeled compound spiked. The QC data were tested against the QC acceptance criteria in the method using a modified version of QA Formaster™ supplied by Thermo-Finnigan Corp. Non-compliant data were resolved with the laboratory

STATISTICAL ANALYSES AND RESULTS

Analytes Tested

As mentioned above, data were evaluated with respect to QC requirements Three analytes were dropped from further analysis due to poor quantitation. 1,1,1-trichloroethane, 2-chloroethylvinyl ether, and trans-1-2-dichloroethene All other analytes met QC requirements

Background Subtraction

The background level determined from the single, unspiked sample in each of the Flask-composited episodes was subtracted from the result of all grab and composite samples for that episode. For each grab sample in the purge device composited episode, the background levels from the sample collected at the same point and time was subtracted from the analytical result. For each

composite sample, the results of the four individual backgrounds were averaged, and the resulting value was subtracted from the composite results

Outlier Screening

For each analyte in each sample, the percent recovery relative to the spike amount was determined A robust outlier screen was developed according to the following formulae

$$LL = Q1 - 1.5 \times Qrange$$
$$UL = Q3 + 1.5 \times Qrange$$

where
LL = *Lower limit*
UL = *Upper limit*
$Q1$ = *25th percentile, value below which fall 25% of data*
$Q3$ = *75th percentile, value below which fall 75% of data*
$Qrange = Q3 - Q1$

Any result where the percent recovery was below the lower limit, or above the upper limit, was removed from further statistical analyses.

Statistical Analyses

For each analyte in each episode, the percent recoveries in the four grab samples were averaged, as were those of the two physical composites. The median recovery across all analytes and episodes was calculated. In addition, the ratio of mathematical composite recovery to physical composite recovery was calculated for each analyte in each episode, according to the formula

$$Ratio = \frac{\text{Mean mathematical composite recovery}}{\text{Mean physical composite recovery}}$$

A two-tailed t-test was performed to determine if this ratio was significantly different from 1.0, at the 5% level. In addition, a two-tailed t-test using Satterthwaite's correction for unequal variances was performed to determine if there were any differences between recoveries in samples composited in a flask and recoveries in samples composited in the purge device

Results

The pollutants detected in the real-world samples were mainly the water-soluble compounds, resulting in high analytical error and precluding discernment of differences between the mathematically averaged results from analysis of the individual grab samples and the result from analysis of the physically composited sample

Comparison of Grab and Composite Results

Results for these tests showed that, for the analytes for which background subtraction was not required and from which the gases and water-soluble compounds were excluded, the mathematical average of the individual grab samples was 10 percent higher than the average of the two composite samples for the flask compositing procedure, and 5 percent higher for the purge device compositing procedure. The median recovery for the non-gas/non-water-soluble, non-indigenous analytes was 105.6 for the mathematical average of the grab samples and 100 3 for the composite samples using the flask compositing procedure and 96.9 and 87 percent, respectively, for the purge device compositing procedure.

The results of the t-test for all combinations of analytes is shown in Table 3.

Table 3
Results of Paired-T Tests

Composite Location	Background	Gas/H_2O Soluble	N	Mean Ratio	RSD (%)	T	Prob
Flask	Exclude	No	49	1.08	5.5	8 8	0 001
		Yes	19	1.07	10.3	2.7	0.015
	Subtract	No	58	1.08	5.5	10.2	0.001
		Yes	23	1.10	10.7	3.9	0.001
Purge Device	Exclude	No	63	1.12	8.0	10.4	0.001
		Yes	28	1.10	9.1	5.2	0.001
	Subtract	No	79	1 14	9 6	11.3	0.001
		Yes	36	1 09	9.2	5.4	0.001

"Background" indicates whether analytes present prior to spiking were background-subtracted or excluded from the analysis, "Mean Ratio" is the average grab-recovery-to-composite recovery ratio, "T" is the value of the paired T-statistic; and "Prob" is the probability that the ratio is statistically different from 1.00

Flask vs Purge Device Compositing

Results comparing flask and purge device compositing techniques are summarized in Table 4 As with comparisons of grab and compositing results, a paired t-statistic was used to determine the significance of differences between the two techniques. As shown in Table 4, statistically significant differences exist between the flask and purge device compositing techniques, with the purge device technique producing recoveries approximately 5 percent higher than the flask technique As with comparisons of grab and compositing results, these differences are so small that they are likely undiscernible by other than isotope dilution quantitation and, although significant statistically, should not be considered significant from an analytical chemistry perspective

Table 4
Comparison of Flask and Purge Device Compositing Recoveries

Composite Location	N	Mean Ratio	RSD (%)	T	Prob
Flask	72	1 08	7.0	-3.52	0.0005
Purge Device	114	1.13	9.6		

OVERALL CONCLUSIONS

Mathematical averages of the results from analyses of grab samples were found to be larger than the result from the analysis of either Flask or Purge Device composited samples, although these differences are on the order of a few percent and would not be discernable except by isotope dilution quantitation procedures. In addition, the number of samples tested in this study (7) was relatively small, even though the number of analytes per sample (40) was large. Because the behavior of one analyte can be expected to be correlated with that of other analytes in the sample, it is possible that the small number of samples results in differences that would be negated or lost in a larger study Further, in tests of reagent water preliminary to this study of actual field samples, composited samples yielded results that were a few percent larger than mathematically averaged results of analyses of grab samples; i.e., the results in reagent water tests were the opposite of the results with field samples. The reasons for these differences are not known but are likely to measuring or compositing errors, even though calibrated syringes and volumetric glassware were used

DISCUSSION

Compositing can be useful in some situations and will result in a cost savings over the analysis of individual grab samples

EPA plans to continue the use of VOA compositing in its effluent guidelines program and, after further studies, may promulgate compositing procedures for wastewaters

REFERENCES

1. Larry H Keith and William A. Telliard, Env. Sci. & Tech. 1979, 13(4) 416 - 423.
2. T.A. Bellar, J.J. Lichtenberg, and R.C Kroner, J. Am. Water Works Assoc. 1974, 66, 703 - 706.
3. William A. Telliard, Marvin B. Rubin, and D.R. Rushneck, J. Chromatog. Sci 1987, 25, 322 - 327.
4. "Compositing and Three-Stage Sampling", from Statistical Methods for Environmental Monitoring, R.O. Gilbert Editor, D Van Nostrand, New York, 1987
5. Forest C Garner, Marin A. Stapanian, and Llewellyn R. Williams, "Composite Sampling for Environmental Monitoring", from Principles of Environmental Sampling, Lawrence H. Keith Editor, American Chemical Society, Washington DC, 1988.
6. Sharon M. Cline and Blaine F. Severin, Water Res. 1989, 23(4) 407 - 412
7. EPA 833-B-92-001, 1992
8. G.H. Stanko, Environmental Lab 1994, 6(2) 10 - 15

ACKNOWLEDGEMENTS

The author wishes to thank Roger Litow of DynCorp Viar for assistance in collection and tracking of the samples and statistical analysis of the results, the laboratories of Pacific Analytical, Inc. for the isotope dilution GC/MS analyses, and Dale Rushneck of Interface, Inc. for technical support.

This chapter has been reviewed by the Analytical Methods Staff of the EPA Office of Water Mention of company names, trade names, or commercial products does not constitute endorsement or recommendation for use.