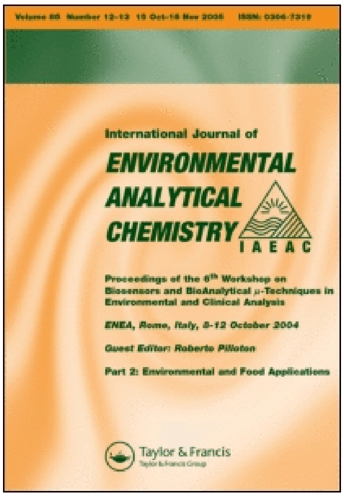

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Evaluation of a Continuous Composite Sampler for Volatile Organic Compounds in Water

O. Mayol[a]; O. Rosario[a]; R. Blanco[a]; I. Colon[a]
[a] Department of Chemistry, University of Puerto Rico, Puerto, Rico

To cite this Article Mayol, O. , Rosario, O. , Blanco, R. and Colon, I.(1995) 'Evaluation of a Continuous Composite Sampler for Volatile Organic Compounds in Water', International Journal of Environmental Analytical Chemistry, 60: 2, 221 — 237

To link to this Article: DOI: 10.1080/03067319508042880

URL: http://dx.doi.org/10.1080/03067319508042880

Intern. J. Environ. Anal. Chem., Vol. 60, pp. 221–237
Reprints available directly from the publisher
Photocopying permitted by license only

EVALUATION OF A CONTINUOUS COMPOSITE SAMPLER FOR VOLATILE ORGANIC COMPOUNDS IN WATER

O. MAYOL, O. ROSARIO, R. BLANCO and I. COLON

Department of Chemistry, P. O. Box 23346, University of Puerto Rico,
Río Piedras Campus, Puerto Rico 00931

(Received, 11 July 1994)

The high volatility and low water solubility of volatile organic compounds (VOCs), make the collection of representative samples difficult. The standard grab sampling method only gives information of that moment in time when the sample is taken. When the composition of VOCs is varying, continuous composite sampling will give a more representative sample. However, no thorough evaluation of its use for VOCs has been reported.

The use of an automatic continuous composite sampler for the analysis of VOCs in water was studied. The causes and magnitude of the VOCs losses during the sampling process were determined.

Adsorbent cartridges were used to trap the VOCs escaping from solution during the sampling process. Sorption phenomena occurring on the containers and/or tubings were also evaluated. Sorption losses were much more significant than volatilization losses.

The results indicate that a modified version of this sampler can be an alternative for the long term sampling of water for VOC analysis.

KEY WORDS: Volatile organic compounds, sampling, composite sampler, water analysis.

INTRODUCTION

Exposure to high levels of VOCs for an extended period of time can cause adverse health effects, including an increased risk of cancer[1-4]. The levels of VOCs permitted in drinking water as well as wastewater are regulated very closely.

To analyze VOCs in water it is critical to be careful in all the following steps: planning of the entire process, sampling, preservation and storage, sample preparation, analysis, and the interpretation of the results. Problems in any of these steps can cause the results of any water monitoring program to be neither useful nor valid. Limitations in the sampling of water for VOCs has hindered their analysis over extended time periods.

In general, water has been sampled by a simple dipping method. But because water is usually dynamic, periodic checks become necessary. Regulation of quality also requires frequent surveillance at multiple points. Because of these needs, sophisticated water sampling equipment has evolved[5-7].

A major sampler evaluation was published by Shelley and Kirkpatrick[8]. This study surveyed about 50 different samplers from 30 manufacturers for suitability in storm or combined sewer sampling applications. They concluded that there is no single sampler that could be universally applicable. However there are some general features that an ideal sampler should have. It should protect the integrity of the sample at the time of collection and should maintain it unchanged until analysis is performed. It must be able to lift an adequate quantity of sample at sufficient height, so that the sampler is not limited to easily accessible areas. Sufficient flow velocity must be maintained in the sample line, to prevent settling of suspended material; however, in meeting this requirement the sampler must not disturb the stream bottom which would give a false representation of the water or wastewater characteristics.

There is a broad range of samplers available. These are based on one of the following possible lift mechanisms: piston, peristaltic, vacuum, and centrifugal pumps, gas pressure, evacuated and mechanical. The selection of any of them should be based on the most labile analytes to be measured.

Standard methods for the sampling of water for VOC analysis are based on grab sampling. Some of the advantages of grab sampling are: low cost, needs no maintenance, is simple and easy to obtain, and gives the opportunity to collect extra samples in a short time when needed. But it has limitations such as inconsistency in collection, probability of increased variability due to sample handling, high cost of labor and, the most critical, it gives information only of that moment in time in which the sample is taken[6,9].

When analytical data is needed over an extended time period a composite sample should be taken. A simple composite sample is one that is made up of a series of aliquots of constant volume collected at regular time intervals and combined in a single container. A flow proportional composite sample is one collected in relation to the flow volume during the period of compositing, thus indicating the "average" condition during the period. Flow proportioning can be achieved by increasing the volume of each aliquot in proportion to the flow, but keeping the time interval between aliquots constant. A sequential composite sample is composed of a series of short-period composites each of which is held in an individual container. Finally, a continuous composite sample is one collected by extracting a small continuously flowing stream from the source and directing it into the sample container.

Some of the advantages of this sampling technique are: collection of consistent samples, decrease in variability caused by sample handling, minimal labor requirements for sampling, reduction in the cost of classifying a large number of samples, and can give fairly representative samples of a water or wastewater flow. Some of its limitations are: maintenance needs (batteries, cleaning,...), sample contamination potential, and, if it is used for VOCs, it may have losses of these compounds into the airspace of the sample collection vessel. Composite sampling is mainly used to sample inorganic compounds and nonvolatile organic compounds. It is not used for VOCs because it is believed that these compounds are lost into the airspace of the sample collection bottle during the sampling process[9].

Several studies have been done with grab and composite techniques. In 1970 Tarazi and colaborators[10] compared automatic grab and composite sampling processes for wastewater discharges. The composite sampler provided the sampling technique most suitable for universally obtaining representative nonvolatile samples of wastewater effluents. The USEPA conducted a study comparing manual (grab) and vacuum type automatic sampling techniques on an individual composite sample basis[11]. It was found that factors such as: configuration of the sampling site, height of the lift, and position of the probe are very important in the final results of the sampling process.

Cline and Severin in 1989 evaluated a composite sampler for aqueous solutions containing dilute volatile organic constituents at concentrations typical of an industrial wastewater treatment system influent[12]. This composite sampler was based on the use of a piston pump. The results showed that the sampler used was inadequate for the collection of aqueous streams when the volatile component of these waters is of interest.

All these studies demonstrated that the mode of sampling to be used is dependent on the purpose of the sampling process.

The regulatory protocols established grab sampling as the technique for the sampling of VOCs in water [6,9,13]. The reason being that VOCs can be lost into the airspace of the sample collection container if an automatic composite sampler is used. This is consistent with the observations of Cline and Severin. However, grab sampling only gives information of that moment in time in which the sample was taken and, therefore, it may not be representative of the water or wastewater under study. The low temperature at which the samples are collected in this mode should minimize losses due to biodegradation, and decrease the partial vapor pressure of most VOCs in water, minimizing losses due to volatilization.

In addition to losses by volatilization there is the possibility of some problems of contamination during the sampling process. Contamination during sampling can be due to sampling equipment and/or sorption and leaching of contaminants by sampling tool materials[5,14-22]. When manual grab sampling is used these problems are minimized but when automatic grab or composite sampling are used all these factors become critical. Leaching and sorption of organics from flexible tubing materials and from containers is well documented[5,14,15,18-21].

Barcelona and collaborators[19] published a study comparing the maximum sorption of dilute (400 μg/L) halogenated hydrocarbon mixtures in water by various plastics (Teflon, polyethylene, polypropylene, polyvinyl chloride, and silicone rubber). All these tubes were found to sorb the test compounds in short exposure periods. Virgin tubing materials introduce substantial amounts of leachable organic matter in similar exposures. Tubing made of Teflon showed the least sorption and leaching problems. Polyvinyl chloride (PVC) and silicone are the more flexible and therefore, present more active surfaces for sorption.

Devlin[20] carried out leaching and sorption studies using Teflon and polyethylene to sample VOCs at 50–200 μg/L. In leaching studies neither material was found to substantially contaminate organic-free deionized water. Sorption studies indicated that polyethylene sorbs the organics to a substantially greater degree than Teflon. However, representative samples can be obtained through both tubing materials provided that a flushing procedure is followed prior to sample collection.

Reynolds and colaborators[14] evaluated ten different tubing materials (borosilicate glass, three metals and six synthetic polymers) for their potential to induce sampling bias for low concentrations of halocarbons. Borosilicate glass was the only material that did not diminish the halocarbon concentrations. Stainless steel was the least reactive of the metals. The synthetic polymers absorbed the compounds. The sorption rates were dependent on flexibility of the polymer, water solubility of the compound, solution volume to polymer surface area ratio, and temperature.

The effect of many other sampling variables on the recovery of volatile compounds was studied by James S.-Y. Ho[21]. In this study water from a reservoir was drawn through a line using a peristaltic pump. Fractions were collected as the continuous flow eluted from the pump. The sampling technique was automatic grab sampling. The results showed that

1) PTFE (or Teflon) tubing must be used to reduce the loss of organics;
2) high pumping rates and lifting the sample more than 4.8 m resulted in loss of the VOCs;
3) and with a decrease in concentration, the recovery of these compounds decreased.

The purpose of this study is to evaluate systematically a continuous sampler for VOCs. The range of VOCs will be extended to polar and highly soluble compounds such as methanol and acetone. Parameters such as periodicity of sampling and sample container materials need to be evaluated and optimized. The possible causes and the magnitude of the VOC losses during the sampling processes are critical. Adsorbents will be used to trap the VOCs that are escaping from solution during the sampling process. Sorption phenomena that can occur on the containers and/or the lines must also be evaluated. The use of the polyethylene glycol (PEG) as a cosolvent to minimize losses in the standards solution preparation step will also be tested. Simulated sampling processes will be performed with standard solutions at low (μg/L) and high (mg/L) levels. The analyses of the VOCs under study will be: direct, purge and trap (P&T), and thermal desorption (TD). Two detectors will be used: the flame ionization detector (FID) and the mass spectrometer (MS).

EXPERIMENTAL

Chemicals and solvents

Standards were purchased from Aldrich Chemical Company. Solvents were from OmniSolv Reagent and MCB Reagent.

Cleaning of sampling containers

The polyethylene container (15 L) and the glass container (9.5 L) had a wide mouth to facilitate cleaning. Cleaning was effected only with distilled water. After every sampling process, three rinses of distilled water at room temperature were done, followed by rinses of hot distilled water and, several rinses of distilled water at room temperature. This was performed until acceptable blanks were obtained in the analytical system to be used.

Tubing

The sampler (Figure 1) had two different lines, the suction tubing (vinyl) and the pumping tubing (silicone). The suction tubing extends from the sampler's pump to the source from which a sample was going to be collected. The pump tubing served as a pump tube in the peristaltic pump, and also as a distribution tube, transporting the sample from the pump outlet to the sample container. The pump tubing consists of a single 71 cm long piece of a special silicone rubber tubing. The internal diameter of both lines was 0.95 cm and the length of the suction tube was 304.8 cm.

Both tubes were cleaned following the same procedure as for the sampling containers. The water was pumped through the tubing using the pump controls of the sampler. When hot distilled water was used to rinse the tubing it was left inside the tubing for approximately 20 minutes and then it was pumped out. When acceptable blanks were not obtained, replacement of the sampling tubing was necessary.

For some of the tests the vinyl suction tubing was replaced for a stainless steel tubing of the same length and internal diameter. This tubing was initially cleaned with three rinses of hexane, then three rinses of hot distilled water, and three of distilled water at room temperature, and finally, a nitrogen flow of about 10 mL/min for approximately 10 min.

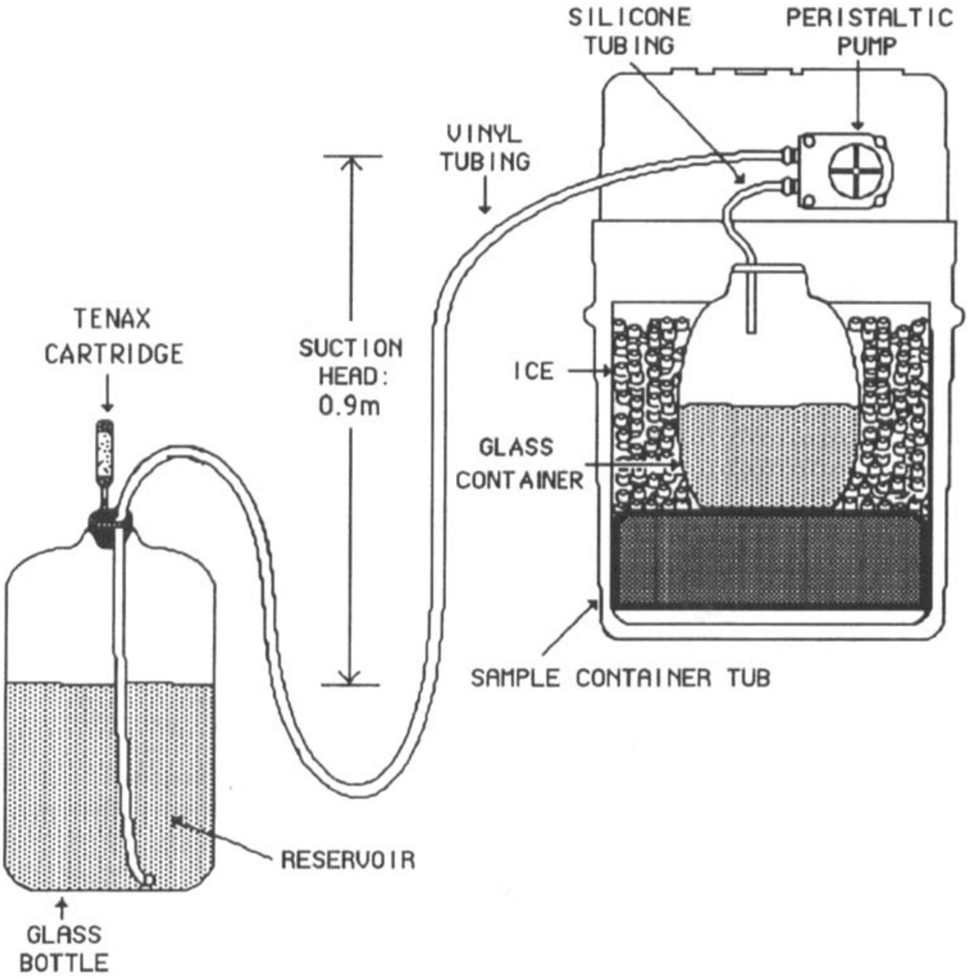

Figure 1 Initial experimental sampling arrangement.

Instruments

Samples were analyzed on a Shimadzu GC (Model GC-14A) equipped with both FID and ECD and on a Hewlett Packard GC-MS (Model 5995A). Purge and Trap was performed with a Tekmar P&T Unit (Model 2710).

For the gas chromatographic systems two different modes of injection could be used: direct injection or P&T. It was equipped to performed analyses using both capillary and packed columns.

To assure the optimum operation of the system various steps were followed: all connections were checked for leaks, septa were changed every 15–20 injections when the GC was used in the direct injection mode, and flows were monitored periodically. Before each analysis a system blank was also analyzed to demonstrate that interferences from the analytical system were under control. At the end of the day, the column temperature was raised to the maximum value in the temperature program ramp and held there until the time for a new analysis.

Continuous composite sampler

The sampler used (Figure 1) was a portable automatic device designed to collect a composite sample from a liquid source by means of a peristaltic pump (ISCO Model 2710). The cover enclosed the mechanical and electrical components of the sampler, giving them additional protection. The center section contained the peristaltic pump, the electronic circuitry, and the programming controls. The sample container tub held the composite sample container and insulated the collected samples from the outside environment. Samples were collected in a 15 L polyethylene container or in a 9.5 L glass container. The sampler was used in the time mode. In this mode samples were collected at equal time increments. The number of samples to be taken, the time interval between samples, and the total sample volume were parameters that could be programmed.

Initial experimental arrangement

All the sampling procedures were effected in an arrangement similar to the one in Figure 1. The reservoir contained the standard solution to be sampled. The purpose of the Tenax cartridge at the outlet of this vessel was to prevent contamination from vapors in the environment. The vinyl tubing was introduced into the reservoir. This tubing was connected to the flexible silicone rubber line that was inserted in the head of the peristaltic pump of the automatic sampler. Before the sampling process, the void space of the tub was filled with ice. This process minimizes sample loss because the temperature of the collected sample most of the time was below 4°C. The vertical distance from the surface of the liquid to the pump inlet is known as the suction head. In this case this distance was 0.9 m. Both the vinyl tubing and the silicone tubing had a 0.95 cm ID. The vinyl tubing was of 3.5 m and the silicone tubing was of 0.71 m in length.

General sampling procedure

The sampler was programmed according to the needs of the experiments to be performed. Sampling simulations were for a 15 h period. Thirty samples of 250 mL each were taken at 30 min intervals. The sampler was calibrated for the volume to be sampled. This was done every time the lines were changed. After calibration the sampler was ready to perform the tests. The suction line was introduced into the reservoir (standard solution). The process was as follows:

1) the peristaltic pump had a prepurge period in which the rotation of the pump was inverted to remove any water residue in the tubing,
2) after this the pump rotated in such a way that it took the sample from the reservoir and transferred it to the collector,
3) and immediately after this, the pump inverted the direction of rotation one more time in a postpurge cycle in order to remove any residue of the sample previously taken. Before and after the sampling process (after the 15 h period), aliquots from both containers were taken in 22 mL or 40 mL Teflon faced silicone vials.

Volatilization tests

The following experiment was designed in order to get a better insight of the magnitude of the possible losses due to volatilization during the sampling process. The set up for the sampling test is shown in Figure 2. Both bottles were sealed. The reservoir stopper had two holes, one for the vinyl tubing connection and the other for an arrangement in series of three packed cartridges. An analogous arrangement is observed for the collector.

All cartridges were initially packed with Tenax-GC (2,6-diphenyl-p-phenylene oxide). Cartridge #l trapped the VOCs that could escape from solution during the sampling process. Cartridge #3 trapped any VOCs from the atmosphere of the laboratory that could interfere with the analysis. And, cartridge #2 (a type of buffer zone), indicated if breakthrough had occurred in one or the other direction.

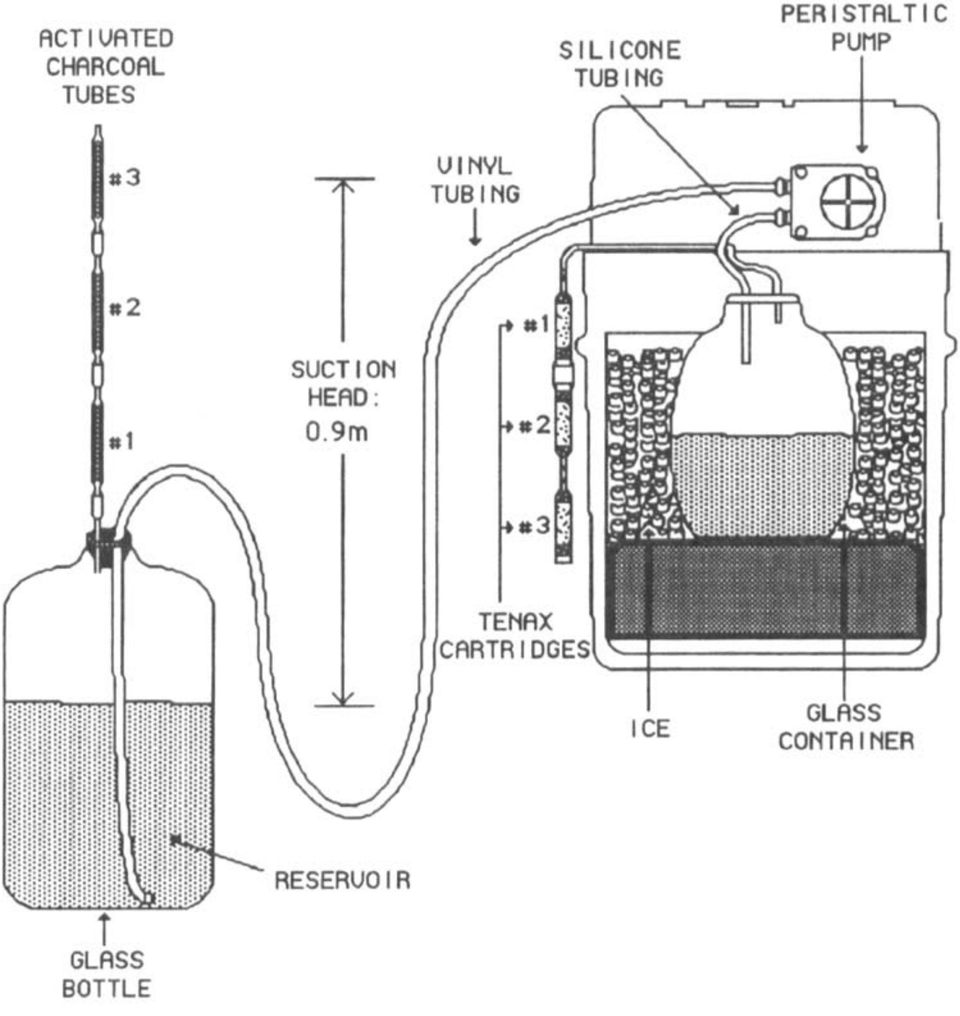

Figure 2 Sampling arrangement for the volatilization tests.

Two different concentrations of the standard solution were evaluated: 20 mg/L and 10 µg/L. Aliquots in the mg/L levels were taken and analyzed by direct injection. Low concentration samples were analyzed by P&T-GC-FID.

Calibration curves were generated in order to quantitate the results obtained from the analyses performed in the GC-FID, GC-MS, and P&T-GC-FID. When in the GC-FID, standards were prepared in carbon disulfide (CS_2).

Real samples

The system was tested by sampling drinking water. Samples were taken at one of the Puerto Rico Aqueducts and Sewer Authority (PRASA) drinking water purification plants on September 29, 1993.

RESULTS AND DISCUSSION

Frequency of sampling

The sampler used in this study was configured to collect composite samples (Figure 1) instead of individual discrete samples. This sampler was programmed to collect samples at equal increments of time. Time intervals of 15, 30, and 60 min were evaluated. The reservoir contained 10 L of the standard solution and aliquots were taken before and after the sampling processes from the reservoir and the collector. Aliquots in 22 mL vials were taken from both containers before and after the sampling process and analyses were performed by GC-FID. The 15 min time interval showed 25 to 30% higher losses for dichloromethane and toluene relative to the other time intervals. The greater losses for dichloromethane and toluene are probably due to the more frequent purging action for this time interval. Hexene was not detected. The mechanical action generated within the reservoir in each sampling episode induces losses of VOCs. For a changing flow of water a high frequency of sampling gives a more accurate picture but because of the larger losses, 15 min intervals were not chosen. The losses for the 60 min time interval were similar to those for the 30 min. The 30 min periods were chosen because the higher sampling frequency which is more desirable for a real sampling process.

Container material

Synthetic materials are usually not used for the sampling of organic compounds due to sorption and or leaching interferences[5,14,15,18–21]. A comparison of possible sorption problems of the plastic (polyethylene) and glass (borosilicate) collectors available with the sampler was carried out. A solution of approximately 20 mg/L from the same stock was evaluated before and after a 15 h period. Chlorobenzene was added as one of the standards in this test to follow the behavior of chlorinated aromatic compounds. Aliquots before and after the 15 h period in both containers were taken and analyzed by GC-FID. No losses were observed for methanol in either container. This is not surprising since methanol is miscible with water. The same results were expected for acetone but, due to contamination from ambient vapors, an increase in the area was observed. This was common in other studies and is indicative that in work of this type permeation of ambient levels of volatile compounds will contaminate the water. In the plastic container 5% losses were observed for dichloromethane and hexene, and 23% and 31% losses were observed for toluene and chlorobenzene, respectively. On the other hand, for the glass container any losses observed were within the standard deviation observed. These results indicate that the main effect in the sampling of these compounds was in the plastic container for chlorobenzene and toluene.

This test was also performed for low concentration samples (μg/L) since losses could be dependent on initial concentration levels. It could not be performed for the plastic container because acceptable blanks could not be achieved at these concentrations. For this reason the test was only carried out in the glass container. This is especially necessary when sampling at the μg/L level. The only losses observed were for toluene and chlorobenzene but these were minimal (only 5%). The results for acetone were too variable due to interferences with ambient acetone; therefore, it was not included. Dichloromethane and hexene gave negative percentages probably due to contamination with ambient levels of these compounds.

Effect of the cosolvent

Preparation of standard solutions of VOCs is a difficult process due to the high volatility and low solubility in water of these compounds. Initially all standard solutions were prepared in distilled water without the use of a cosolvent.

Because of the significant losses of VOCs even during the preparation of the solutions, alternate procedures were explored. Cosolvents such as methanol, and acetone have been widely used in order to minimize the losses due to volatilization, however in this study they were two of the standards therefore, they could not be used as cosolvents. In addition, when a non selective detector is used in the determination, these would obscure some of the volatile components. Other possible volatile cosolvents were not considered for this reason.

Polyethylene glycol (PEG) of an average molecular weight of 400 was reported by Ligon and Grade as an efficient cosolvent for the preparation of standard solutions of VOCs[23]. For this reason it was tested for the preparation of the solutions in this study. The solutions were again prepared but now using PEG. The hexene was now detected, lower losses of VOCs were reflected, and the results were more reproducible.

Effect of stirring

Because of the high viscosity of the PEG a homogeneous solution was not instantly obtained upon addition. Homogeneity is necessary for reproducible results. However, the mechanical action of stirring induces losses of VOCs. The first approach to overcome this problem was to allow homogenization of the solution by letting it stand for 1 h. No stirring was involved in this test. This was adopted from the study of Ho[21] in which some sampling variables were evaluated for the recovery of VOCs in water. When this was tried under the conditions of this study the results demonstrated that it was not an efficient process. Peak areas were irreproducible and it was evident that the solution was not homogeneous. Stirring was then attempted. A Teflon coated magnetic stirring bar was introduced into the reservoir after the components were added. Then the reservoir was placed on a mechanical stirrer at low velocity. Stirring times of 0.5, 1.5, and 2.5 min were evaluated. The results showed that the different losses due to the stirring processes for the different periods of time were not statistically significant for the time scales tested. But it is logical that the lower the stirring time the lower the losses. The results indicated that 0.5 min of stirring was enough to obtain a homogeneous solution with a minimum of losses.

Temperature stabilization studies

Temperature is one of the variables that affects the loss of compounds since the higher the temperature the greater the tendency of the compounds to volatilize.

A study sponsored by the EPA[11] demonstrated that the initial sample collected needs about 6 h to cool from 21°C to approximately 4°C. But if the bottles and sampler were cooled prior to sampling (i.e., overnight) samples required 3 h to cool to 4°C.

A test was designed in order to determine the time it took the collector and sample to reach thermal equilibrium. These results indicate that the drop in temperature for both containers had an exponential behavior from room temperature (approximately 22°C) to about 0°C. It took the glass container approximately 5 h to reach 4°C and approximately 9 h to reach 0°C. For the plastic container, results showed no significant statistical difference in the time it took to reach the 4°C but it reached 0°C in a shorter time (about 6 h). For this reason it was decided to cool the collector for about 5 h before the sampling starts, thus when the initial sample comes into the container the losses due to volatilization would be minimized. However, as will be presented in other tests, the volatilization studies showed that these losses were not significant. Therefore, cooling the collector for 5 h was not found to be practical and the container was cooled approximately 1 h before the sampling began.

Losses of the compounds during the sampling process

To determine losses one needs an initial value against which subsequent measurements are compared. Unfortunately this study has shown that generally the levels of standards in the reservoir at the start of a sampling cycle are higher than at the end of the cycle due to losses. If the variation in concentration in the reservoir was linear one could use the average of the initial and final measurement, but if losses were much greater at the beginning or at the end, an average would not reflect the actual losses. Therefore, it became necessary to undertake a study to determine the rate of change in concentration.

The results in Table 1 show that the change in amount in the reservoir is dependent on the compound and the range of concentration, mg/L or µg/L, being studied. In general, the concentration drops with the progression of sampling events. In the case of methanol there is no statistically significant difference at both mg/L and µg/L levels during the cycle. This is logical since methanol is miscible in water. In the case of acetone interferences due to its ambient concentration impeded reaching any conclusion. For dichloromethane, toluene, and chlorobenzene at mg/L levels there is a clear trend showing a decrease with the progression of the sampling event. At µg/L levels the dichloromethane did not show a significant difference but toluene and chlorobenzene did. Hexene showed a large decrease after the first event at mg/L levels. This is understandable considering the volatility of hexene. However, at µg/L levels the difference after the first event was not significant.

It was decided to use as a reference value the average between sampling event 0 and 5. This was equivalent to taking the average between the sample taken before the sampling began (RBS) and after the sampling ended (RAS) in the reservoir.

Table 1 Losses of the VOCs tested during the sampling period in the reservoir.

Concentration	*Sampling event*	*Methanol*	*Acetone*	*Dichloromethane*	*Hexene*	*Toluene*	*Chlorobenzene*
mg/L[1]	0	27 ± 4	80 ± 30	86 ± 4	130 ± 20	97 ± 4	220 ± 20
	1	22 ± 3	90 ± 20	82 ± 3	106 ± 1	91 ± 30	240 ± 10
	2	22 ± 4	105 ± 5	79 ± 2	70 ± 20	70 ± 10	210 ± 20
	3	28 ± 7	110 ± 10	81 ± 1	63 ± 6	82 ± 6	203 ± 6
	4	19 ± 5	100 ± 30	78 ± 6	60 ± 10	70 ± 10	180 ± 20
	5	27 ± 5	120 ± 10	73 ± 5	40 ± 20	50 ± 10	150 ± 30
mg/L[2]	0	11 ± 8	*	100 ± 60	140 ± 20	240 ± 20	323 ± 9
	1	11 ± 5	*	90 ± 40	140 ± 30	250 ± 10	310 ± 1
	2	11 ± 7	*	90 ± 30	100 ± 20	200 ± 10	270 ± 10
	3	8 ± 3	*	98 ± 40	70 ± 10	180 ± 10	250 ± 20
	4	8 ± 3	*	90 ± 30	79 ± 4	170 ± 10	236 ± 6
	5	8 ± 3	*	90 ± 30	90 ± 20	156 ± 6	220 ± 40

Sampling Event—refers to the sequence of samples taken approximately every 4 h during the cycle.
* Acetone was not analyzed due to interferences at ppb.
[1] Area values determined by direct injection GC-FID (X 10^3).
[2] Area values determined by P&T-GC-FID (X 10^3).

Volatilization tests

The main reason for composite sampling not being used to sample VOCs in water is because it is believed that during the sampling process significant losses of the compounds occur due to their volatilization. It was decided to actually determine how significant these losses are. A specific procedure was effected to determine these losses This was done by the use of adsorbent cartridges at the opening of the reservoir and the collector to trap the VOCs that volatilize from solution during the sampling process (Figure 2). The amount trapped in these adsorbents can be quantitated and these values can be used to determine the percentage of losses due to volatilization in the sampling process.

Escaping organic vapors from the reservoir were trapped on Tenax adsorbent cartridges and analyzed by thermally desorbing into the analytical system. However, the amount of compounds trapped saturated the analytical system with the mg/L solution. For this reason, these cartridges were substituted for activated charcoal cartridges in the reservoir, and removal of the VOCs trapped in these cartridges was achieved with CS_2. This solvent is effective for the elution of compounds on activated charcoal and is also amenable for GC-FID analyses because it is not seen by this type of detector. The recovery of 2 mL of the eluent has been shown to be enough to remove the VOCs trapped in a cartridge[24]. Analyses of 1 μL of the eluent was performed by GC-FID. Tenax cartridges were still used for the collector and the μg/L reservoir level study, then these were analyzed by TD-GC-MS.

Analysis of the middle cartridge (#2) from the reservoir did not show the presence of compounds breaking thru from cartridge #1 or cartridge #3. Analysis of the #1 cartridges showed the losses from the respective containers. When extracted from the charcoal cartridges, analysis for dichloromethane and hexene could not be effected due to a persistent interference in the CS_2. Different sources of CS_2 showed the same interference and attempts to purify the CS_2 also failed to eliminate it. The results for the activated charcoal cartridges connected to the reservoir showed greater losses for toluene (10%)

and chlorobenzene (5%), and minimal losses were observed for methanol (< 1%) and acetone (< 1%). Percentages were determined by substracting the amount of the compound in the cartridge from the average of the values in the reservoir before and after sampling, dividing by the average values and multiplying by 100. Dichloromethane and hexene could not be analyzed because of interferences. But the losses would have been expected to be even higher.

For the µg/L level for the reservoir, now with Tenax cartridges, all losses were less than 1%.

Analysis of the Tenax cartridges connected to the glass collector for the mg/L and µg/L solutions and comparing with the levels in the collector after sampling, showed volatilization losses to be less than 1% in both cases. Significant losses due to volatilization are not occurring.

A comparison was effected between the average amounts in the reservoir with the amounts in the glass collector to determine the total level of losses. These values were generated from the aliquots taken from each container. These results appear in Tables 2 and 3.

Table 2 represents the peak areas of the different standards lost from the glass collector with the mg/L solution. These results show no losses for acetone and methanol (probably because they are completely soluble in water), 15% for dichloromethane, 20% for toluene, 35% for chlorobenzene and, 56% for hexene. Hexene is the one with the highest Henry's constant and lowest solubility in water.

When the plastic container was used as the collector for high level samples (mg/L) the aliquots taken showed relatively greater losses for chlorobenzene (42%), hexene (34%), toluene (31%), and dichloromethane (16%) and no losses for methanol and acetone. In comparing these losses in the glass and plastic collectors similar values are obtained except for hexene. Overall though one would tend to use glass because of the nature of the compounds.

Total losses were also determined for the µg/L level solution (Table 3). These results represent a relative percentage of loss of 28% for chlorobenzene, 27% for hexene and 21% for toluene. Acetone and dichloromethane seemed to be increasing during the sampling process probably due to diffusion of ambient concentrations of these compounds into the vessels resulting in negative percentages. Acetone vapors are so

Table 2 Response for the aliquots taken from the glass collector to evaluate total sample losses at mg/L levels.

Sample	*Peak area (X 10^3)*					
	Methanol	*Acetone*	*Dichloromethane*	*Hexene*	*Toluene*	*Chlorobenzene*
RBS	35 ± 3	93 ± 9	79 ± 2	110 ± 40	99 ± 20	171 ± 20
RAS	37 ± 3	95 ± 10	71 ± 6	45 ± 10	67 ± 5	158 ± 10
CAS	36 ± 3	95 ± 20	64 ± 7	34 ± 7	66 ± 7	106 ± 20
$\frac{(RBS + RAS)}{2}$	36	94	75	77	83	164
Losses (%)	0	–1	15	56	20	35

RBS–reservoir before sampling
RAS–reservoir after sampling
CAS–collector after sampling

Table 3 Response for the aliquots taken from the glass collector to evaluate total sample losses at µg/L levels.

Sample	*Peak area (X 10^3)*					
	Methanol	*Acetone*	*Dichloromethane*	*Hexene*	*Toluene*	*Chlorobenzene*
RBS	ND	28 ± 8	92 ± 1	146 ± 10	233 ± 9	331 ± 10
RAS	ND	34 ± 4	101 ± 10	219 ± 20	154 ± 9	207 ± 3
CAS	ND	41 ± 1	101 ± 30	132 ± 4	153 ± 4	195 ± 10
$\frac{(RBS + RAS)}{2}$	–	31	96	182	193	269
Losses (%)	–	-32**	-5**	27	21	28

ND–Not detected.
– Can not be calculated.
**Negative percentages probably resulting from the entry of ambient vapors.

prevalent that it was not possible to avoid this interference. We have no explanation for the apparent increase in the area of RAS vs RBS for hexene and is not consistent with what had been observed.

A similar determination could not be done with the µg/L level in the plastic collector because it was not possible to obtain acceptable blanks for the plastic collector due to carryover problems (sorption in the plastic).

These results indicate that another phenomena is responsible for the losses besides volatilization.

Sorption tests

Losses due to volatilization of the compounds during the sampling process do not account for the total losses of the compounds. It was thought that sorption phenomena (adsorption and/or absorption) were also taking place in the containers used and/or in the tubing that transported the samples.

Containers It is well documented in the literature that glass is the best material to store or sample organic samples[6,25] because by its chemical nature sorption and leaching interferences are minimized. This does not mean that these phenomena are totally absent in these processes; in fact they are occurring. Evidence of this was observed in this study because after every sampling process the containers needed to be cleaned in order to start a new test. The odor of organic compounds and their detection in blanks were additional proof. This indicates that sorption processes were occurring during the sampling. Acceptable blanks and, therefore, clean containers were difficult to obtain even after exhaustive cleaning. Background interferences are more critical when working at the µg/L level.

Rinsing of the reservoir and collector with 20 mL of methanol showed dichlorometane, acetone and low levels of chlorobenzene in the reservoir. Hexene and toluene were not detected. A similar tendency was observed for the collector but qualitatively much lower levels.

Tubing The literature gives evidence that, due to its organic nature, vinyl tubing sorb organic compounds[5,14,19,20], Sorption by the tubing was clearly evident from the fact that blank runs after an experimental sampling always showed presence of the standards. In the events when acceptable blanks could not be obtained, the tubing was replaced. It was also observed that the pump tubing (silicone) adsorbed significant amounts of the compounds. This too was replaced when acceptable blanks were not obtained.

It was necessary to evaluate the levels of sorption by the tubing of the compounds under study. For this, vinyl tubing was substituted by stainless steel tubing. Stainless steel is an alloy relatively inert to reactions with organic compounds. Sampling processes were effected for high and low level solutions and the results were compared relative to those for vinyl tubing. The experimental arrangement used is shown in Figure 1 where the suction tubing was either vinyl or stainless steel depending on the test. The silicone tubing could not be substituted for stainless steel or any other material because its flexibility was needed in order for a proper rotation of the peristaltic pump.

The results for the sampling tests with the stainless steel tubing for the high level solutions (mg/L) are shown in Table 4. These results show 57% in relative losses for hexene, 23% for toluene, 19% for dichloromethane, 18% for chlorobenzene and, 3% for methanol. No losses were observed for acetone.

The results for low level solutions (μg/L) are shown in Table 5. These results show 35% in relative losses for hexene, 26% for toluene, 21% for chlorobenzene and, 1% for dichloromethane.

When the percentages in Table 4 (determined with stainless steel tubing) were compared with the ones in Table 2 (determined with vinyl tubing) the results were similar for methanol (3% vs 0%), acetone (0% vs -1%), dichloromethane (19% vs 15%), hexene (57% vs 56%), and toluene (23% vs 20%). Chlorobenzene showed the largest difference (18% vs 35%). This shows greater sorption for chlorobenzene on the vinyl tubings. It is important to mention that significant differences were observed in the time required to clean the two different tubings. It took much greater effort to obtain acceptable blanks from the vinyl tubing.

The comparison of the low level concentrations for both types of tubing reflected greater differences than in the previous case. The stainless steel tubing showed higher losses for hexene (35% vs 27%) and toluene (26% vs 21%). Chlorobenzene gave higher losses with the vinyl tubing (28% vs 21%), while the results for dichloromethane, and acetone were interfered by ambient concentrations of these compounds. We would have

Table 4 Response of the compounds for the aliquots taken for the sampling processes at mg/L levels using the stainless steel tubing.

Sample	*Peak area (X 10^3)*					
	Methanol	*Acetone*	*Dichloro-methane*	*Hexene*	*Toluene*	*Chloro-benzene*
RBS	32 ± 1	103 ± 1	89 ± 2	129 ± 20	110 ± 10	210 ± 20
RAS	31 ± 2	101 ± 3	72 ± 3	40 ± 9	82 ± 2	180 ± 20
CAS	30 ± 4	102 ± 5	65 ± 2	36 ± 6	74 ± 3	160 ± 30
$\frac{(RBS + RAS)}{2}$	31	102	80	84	96	195
Losses (%)	3	0	19	57	23	18

Table 5 Response of the compounds for the aliquots taken for the sampling processes at μg/L level using the stainless steel tubing.

Sample	*Peak area (X 10^4)*					
	Methanol	*Acetone*	*Dichloro-methane*	*Hexene*	*Toluene*	*Chloro-benzene*
RBS	26 ± 1	290 ± 100	140 ± 20	167 ± 2	242 ± 3	315 ± 4
RAS	20 ± 4	510 ± 200	123 ± 10	129 ± 5	175 ± 5	230 ± (σ < 1)
CAS	34 ± (σ < 1)	460 ± 100	130 ± 10	96 ± 20	154 ± 6	216 ± 3
$\frac{(\mathrm{RBS} + \mathrm{RAS})}{2}$	23	400	131	148	208	272
Losses (%)	-11	-15	1	35	26	21

Negative percentages probably are from the entry of ambient vapors.
σ–standard deviation.

expected dichloromethane's losses to be higher in the vinyl tubing since it is a chlorinated polymer.

Real samples

The continuous composite sampler was tested by sampling drinking water. After the sampling period aliquots were taken in 40 mL vials and analyzed by P&T-GC-MS. The chromatogram obtained appears in Figure 3.

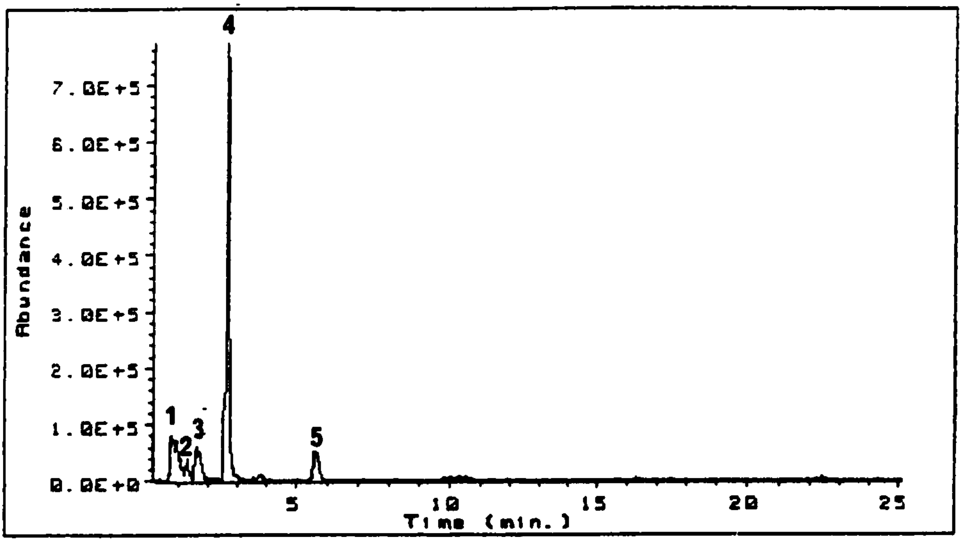

Figure 3 GC-MS chromatogram of the drinking water sample, (1) not identified, (2) acetone, (3) dichloromethane, (4) chloroform and (5) bromodichloromethane.

The compounds identified were acetone, dichloromethane, chloroform, and bromodichloromethane. Acetone probably originated from ambient concentrations in the laboratory. The other three compounds are common to the chlorination of the water in the disinfection step in the purification plant.

Quantitation was achieved by comparison with calibration curves. The levels obtained were 16 μg/L for dichloromethane, 34 μg/L for chloroform and 6 μg/L for bromodichloromethane. Since it has been shown that some losses do occur, mainly due to sorption, the actual levels should be higher.

CONCLUSIONS

An automatic continuous composite sampler was evaluated for the long term sampling of VOCs in water. No thorough and systematic evaluation had been carried out for its use with VOCs before this study.

For the study standard solutions of VOCs were prepared. Compounds with higher volatilities and lower water solubilities were readily lost in the preparation. PEG was used as a cosolvent. It helped in the retention of the highly volatile compounds such as hexene. Despite its use, high losses were observed in the preparation and handling processes. Standard solutions were sampled in order to determine the causes and magnitude of the losses during the sampling process. Volatilization losses during sampling were not significant. This differs from the study of Cline and Severin where volatilization losses were high. This difference may be due to the difference in the pumping system and the fact that Cline and Severin did not cool their receiving vessel. In our study a significant sorption problem by the containers and tubings used was the main cause of the losses. This was confirmed by the difficulty in obtaining acceptable blanks in sequential analyses. Our observation of sorption problems with vinyl tubing coincide with Ho's results in which silicone tubing also gave high levels of sorption for VOCs. Stainless steel tubing proved to be less susceptible to this type of contamination. Compounds with high solubility in water had minimal losses due to volatilization and/or sorption processes.

A critical problem in the analysis of VOC samples is the tendency of contamination from ambient levels of the compounds under study. This will adversely affect the results of the analysis, therefore, an environment free of the VOCs of interest is necessary when this kind of analysis is to be done. In addition, all sources of possible contamination, especially memory effects, were more critical when working at lower concentrations.

A real sample of drinking water was taken with the composite sampler. Significant levels of dichloromethane, chloroform, and bromodichloromethane were found. The results indicate that a modified version of this sampler could be an alternative for the long term sampling of VOCs.

Although several questions were answered in this study new questions arose. The evaluation of new materials for the sampling could be effected to minimize the losses of VOCs due to sorption processes. Various treatments of the surfaces in contact with water can be done to try to minimize sorption.

Acknowledgement

The authors acknowledge the financial support provided by the NIH-MBRS program and the support for instrumentation facilities provided by NIH-RCMI Grant Number RR03641.

References

1. R. A. Neal, in: *Safe Drinking Water* (R. G. Rice, ed. Lewis Publishers, Michigan, 1985), Chapter 1.
2. J. R. Hickman, in: *Safe Drinking Water,* (R. G. Rice, ed., Lewis Publishers, Michigan, 1985), Chapter 2.
3. N. M. Ram, in: *Organic Carcinogens in Drinking Water* (N. M. Ram, E. J. Calabrese and R. F. Christman, eds. John Wiley and Sons, New York, 1986) Chapter 1.
4. C. Gron, *Intern. J. Environ. Anal. Chem.*, **41**, 47–55 (1990).
5. U. M. Cowgill, in: *Principles of Environmental Sampling,* (L. H. Keith, ed. American Chemical Society, Washington, D. C., 1988) Chapter 11.
6. *Handbook for Sampling and Sample Preservation of Water and Wastewater* (U.S. EPA U.S. Government Printing Office, Washington, D.C., 1982), EPA–600/4–82–029.
7. J. J. Barkley, K. M. Peil and J. W. Highfill, *Water Pollution Sampler Evaluation* (Army Medical Bioengineering Research and Development Laboratory, Fort Detrich, MD, 1975), AD/A–009–079.
8. P. E. Shelley and G. A. Kirkpatrick, *An Assessment of Automatic Sewer Flow Sampler* (U.S. EPA U.S. Government Printing Office, Washington, DC, 1973), EPA–122–73–261.
9. J. E. Norris, in: *Principles of Environmental Sampling* (L. H. Keith, ed. American Chemical Society, Washington, D. C., 1988) Chapter 16.
10. D. S. Tarazi, L. L. Hiser, R. E. Childers and C. A. Boldt, *J. Water Pollut. Contr. Fed.*, **42**, 708–732 (1970).
11. *Comparison of Manual (grab) and Vacuum Type Automatic Sampling Techniques on an Individual and Composite Sample Basis* (U.S. EPA Office of Enforcement, National Field Investigations Center, Denver, Colorado, 1974).
12. S. M. Cline and B. F. Severin, *Wat. Res.*, **23**, 407–412, (1989).
13. Q. V. Thomas, J. R. Stork and S. L. Lammert, *J. Chromatogr. Sci.*, **18**, 583–593 (1980).
14. G. W. Reynolds, *Environ. Sci. Technol.*, **24**, 135–142 (1990).
15. J. F. Barker, G. C. Patrick, L. Lemon and G. M. Travin, *Ground Water Monit. Rev.*, **7**, 48–54 (1987).
16. S. P. Levine, *Environ. Sci. Technol.*, **17**, 125–127 (1983).
17. R. E. Gossett and R. O. Hegg, *Trans. ASAE*, **30**, 387–390 (1987).
18. G. A. Junk, H. J. Svec, R. D. Vick and M. J. Avery, *Environ. Sci. Technol.*, **8**, 1100–1106 (1974).
19. M. J. Barcelona, J. A. Helfrich and E. E. Garske, *Anal. Chem.*, **57**, 460–464(1985).
20. J. F. Devlin, *Water Pollut. Res. J. Canada*, **22**, 65–72 (1987).
21. J. S.-Y. Ho, *J. Am. Water Works Assoc.*, **75**, 583–586 (1983).
22. A. R. Berens, *J. Am. Water Works Assoc.*, **77**, 57–64 (1985).
23. W. V. Ligon and H. Grade, *Anal. Chem.*, **53**, 920–921 (1981).
24. *Methods of Air Sampling and Analysis,* (M. Katz, ed. American Public Health Association, Washington, D.C., 1977) Method **834**, 894–902.
25. J. Parr, M. Bollinger, O. Callaway and K. Carlberg, in: *Principles of Environmental Sampling* (L. H. Keith, ed. American Chemical Society, Washington, D. C., 1988) Chapter 14.