Comparison of Aqueous Headspace Air Standard vs SUMMA Canister Air Standard for Volatile Organic Compound Field Screening

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Abstract

This paper describes the application of SUMMA canister and aqueous headspace air standards for ambient air volatile organic compound(VOC) field screening to perform quick on-site analysis using a portable gas chromatograph(GC). Studies were conducted comparing aqueous headspace standards to SUMMA canister standards using a portable gas chromatograph. A comparison of SUMMA canister analytical results from the portable GC versus GC/MS (gas chromatograph/mass spectrometer) was provided. Research on time dependent stability and temperature dependency of SUMMA canister standards was also conducted. A Photovac 10A10 portable gas chromatograph(GC), an HP 5890/5970 gas chromatograph/mass select detector(GC/MSD) and a Tekmar 5000 thermal desorber modified for canister analysis were employed.

Introduction

Toxic volatile organic air pollution is a growing concern because of its widespread presence in the atmosphere, adversely affecting public health. There has been much interest in monitoring ambient air for these toxic compounds. The United States Environmental Protection Agency(U.S. EPA) has developed several methods for measuring toxic organic compounds in ambient air. These include collection on solid adsorbents, such as Tenax GC and spherocarb traps, as well as the collection of whole air in suitable canisters[1,2]. With the increasing interest in air analysis, field screening for ambient air is becoming more important. When performing on-site ambient air analysis for volatile organic compounds (VOCs) using portable gas chromatography, it is important to have a suitable standard to be able to identify and quantitate compounds of interest. The headspace above a

10 μg/L aqueous standard kept at a constant temperature can be used as a VOC field screening standard to perform quick on-site air analysis using a portable gas chromatograph. The headspace standard is a very simple and inexpensive technique for standard preparation. VOCs, with their relatively high vapor pressures, have a natural tendency to migrate from water into air. In a closed VOA(volatile organic analysis) vial filled three-quarters full with an aqueous VOC standard (Figure 1), VOCs will move from the water into the air above the water (headspace) until an equilibrium is reached. This air above the water is a perfect medium for an air VOC standard since it consists of air and the migrating VOCs from the water.

Figure 1. Aqueous Headspace

By the ideal gas equation of state:

$$PV=nRT$$

P: pressure V: volume
R: gas constant n: moles
T: absolute temperature (K)

for a single component i in a gas mixture:

$$p_iV=n_iRT \qquad (1)$$

p_i: Partial pressure of component i
n_i: Moles of component i

the mole fraction or the volume-concentration (ppb/v) of a component i in is:

$$M_i=n_i/\Sigma n_j=p_iRT/\Sigma p_jRT=p_i/P_T \qquad (2)$$

M_i: Mole fraction or volume concentration of component i
P_T: The total pressure of the gas mixture($=\Sigma p_j$)

Because the aqueous solution is very diluted(10 μg/L), it can be treated as a ideal solution. According to Henry's law:

$$p_i=k_i(T)X_i \qquad (3)$$

$k_i(T)$: Henry's law constant;
X_i: Mole fraction of solute i in the water solution.

Therefore, the concentration in the headspace is shown as:

$$M_i=p_i/P=k_i(T)X_i/P_T$$

Henry's law constant k_i varies with temperature(T), therefore, the concentration in the headspace is a function of temperature(T), the total pressure above the solution(P_T) and the mole fraction in the water solution(X_i).

$$M_i=f(X_i,T,P)$$

Whether an aqueous headspace standard can be used for an air analysis standard depends upon the ability to control the concentration of VOCs in the aqueous solution, the pressure of the headspace and the temperature of the standard. The first variable X_i which reflects the concentration of a VOC in the

water solution can be simply controlled by preparing a solution with a known concentration of the VOC. The temperature(T) of the standard can be controlled and kept constant by placing the VOA vial in an ice-water bath, keeping the aqueous standard solution in the vial at approximately 0° - 1℃. The total pressure(P_T) above the solution is equal to atmospheric pressure. Relative changes in atmosphere pressure are negligible. Therefore, for this screening application, the total pressure (P_T) can be considered a constant. With the ability to control the variables above, the aqueous headspace can be used for ambient air field screening analysis as an external standard.

SUMMA canister based sampling systems have gained wide acceptance for the collection of integrated whole ambient air samples containing volatile organic compounds. Utilization of this sample collection method has increased significantly. Some recent research has used SUMMA canisters as VOA standards[4]. As an application, SUMMA canisters are able to be used as field screening standards as well. Canister standards present the true concentration of VOCs within the can and the VOCs stored in a canister exhibit relatively long term stability. In addition, the transportation of a canister standard is easy; therefore, the development of this method can be a very effective approach of SUMMA canister methodology and VOC field screening for ambient air.

The following work is on the method studies of SUMMA canister application and aqueous headspace as ambient air standards for field screening of VOCs. The comparison of aqueous headspace standards to SUMMA canister standards using a portable gas chromatograph and a comparison of SUMMA canister analytical results from the portable GC versus GC/MS were performed. Research on time dependent stability and temperature dependency of SUMMA canister standards was also conducted.

Experimental

(1) Evaluation of aqueous headspace standards:

Experimentation was performed to determine the actual concentration of selected VOCs in the headspace above a 10 μg/L aqueous standard contained in a closed 40ml VOA vial filled with 30ml of aqueous standard kept at a temperature of 0°-1℃. Analysis was performed on a Photovac 10A10 portable gas chromatograph equipped with a 4' 1/8" SE-30 column and a photoionization detector, calibrated with a Research Triangle Institute(RTI) certified mixture of VOCs traceable to NBS primary gas standards. (Table 1.) The

Table 1. RTI Certified Concentration for 18 Component Mixture Containing Volatile Toxic Organic Compound Traceable to NBS Primary Gas Standards

Cylinder No. ALL 21378

Compound	Concentration(ppb/v)
Vinyl Chloride	5.19 ± 0.5
Bromomethane	5.68 ± 0.6
Trichlorofluoromethane (Freon 11)	5.15 ± 0.7
Methylene chloride	4.48 ± 0.5
Chloroform	4.86 ± 0.5
1,2-Dichloroethane	5.02 ± 0.5
1,1,1-Trichloroethane	5.22 ± 0.4
Benzene	5.15 ± 0.3
Carbon tetrachloride	5.02 ± 0.5
1,2-Dichloropropane	5.15 ± 0.3
Trichloroethylene	5.11 ± 0.3
Toluene	5.19 ± 0.3
1,2-Dibromoethane	4.83 ± 0.5
Tetrachloroethylene	5.24 ± 0.3
Chlorobenzene	5.27 ± 0.3
Ethyl benzene	4.85 ± 0.3
o-Xylene	5.12 ± 0.5

Photovac portable GC was calibrated by running a syringe blank and a single point of the RTI certified cylinder standard. Concentrations of VOCs in the cylinder were approximately 5ppb. An aqueous standard (working standard) was prepared using 5.0 μl of commercial (Supelco) and EPA repository standard mix solution (200 μg/ml for each component) diluted to 100 ml with VOC-free water giving a final concentration of 10 μg/L for each component. Table 2 shows the component and concentration of the Supelco and EPA repository stock standards. The working standards were stored in 40ml VOA vials with zero headspace at 0° - 1℃. Before the analysis, 10 ml of water solution was

Table 2. Components and the concentration of the Stock Standard Solution (Supelco Purgeable A and B, and EPA Repository) and of the Canister Standards

Compounds	Concentration Stock Solution (μg/ml)	Canister Standards ($\mu g/m^3$)	(ppb)
Trichlorofluoromethane	200	55.6	9.9
1,1-Dichloroethylene	200	55.6	14.0
Methylene Chloride	200	55.6	16.1
t-1,2-Dichloroethylene	200	55.6	14.0
1,1-Dichloroethane	200	55.6	13.8
Chloroform	200	55.6	11.5
Bromochloromethane	200	55.6	10.6
1,1,1-Trichloroethane	200	55.6	10.2
Carbon Tetrachloride	200	55.6	12.0
Benzene	200	55.6	17.5
1,2-Dichloroethane	200	55.6	13.8
Trichloroethylene	200	55.6	10.4
1,2-Dichloropropane	200	55.6	12.1
Bromodichloromethane	200	55.6	8.3
1,3-Dichloropropene	200	55.6	12.3
Toluene	200	55.6	14.8
1,1,2-Trichloroethane	200	55.6	10.2
Tetrachloroethylene	200	55.6	8.2
Chlorobenzene	200	55.6	12.1
Ethyl Benzene	200	55.6	12.9
Bromoform	200	55.6	5.4
m-Xylene	200	55.6	12.9
o-Xylene	200	55.6	12.9
1,1,2,2-Tetrachloroethane	200	55.6	8.1
1,3-Dichlorobenzene	200	55.6	9.3

withdrawn from the vial, leaving 30 ml of the standard water solution and 10 ml headspace in the vial. The vial was then placed into an ice-water bath to equilibrate for about 30 minutes at 0° - 1℃. After equilibration, the headspace was analyzed on a portable GC. Four trials of analysis were conducted separately. The data in Table 3 presents the analytical results from the portable GC of selected VOC concentrations in the headspace.

(2). Preparation and GC/MS Calibration of SUMMA canister standards:

Duplicate standards were prepared in 6L pre-vacuumed Anderson made SUMMA passivated canisters. The canisters were cleaned by vacuum and heating. Canisters were vacuumed to <5 mmHg at about 100℃ for 4 hours. 5.0 μl of the stock standard solution (Supelco purgeable A and B, and EPA VOC repository) was injected into the each canister. The canisters were then pressurized to 30

Table 3. Concentration of Selected VOCs in Aqueous Headspace(*)

Compound	Concentration (ppb/v) Trial 1	Trial 2	Trial 3	Trial 4	Average	RSD%
Benzene	146	161	161	135	151	7.3
Trichloroethylene	163	129	141	134	142	9.2
Toluene	166	153	191	127	159	14.5
Tetrachloroethylene	212	229	177	187	201	10.2
Ethyl benzene	128	154	134	115	133	10.6
o-Xylene	98	122	95	47	91	30.1

(*): Above a 10 μg/L water solution at 0°-1°C.

psi with 25% relative humidity. The concentrations of each VOC in the canister was 55.6 ng/l. Table 2 shows the VOC concentration of the canister standards. Following a 24 hours equilibration period at room temperature, the canisters were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with a 60 m megabore capillary column and 5970 Mass Selective Detector. A Tekmar 5000 thermal desorber modified for canister analysis was used for desorbing. The calibration results are shown in Table 4. The canister cleaning and analysis were performed according to EPA Method TO-14 and EPA Region I draft SOP for ambient air VOC analysis.

Table 4. GC/MS Certified Concentration of Standard Canisters

Compound	Calc.(*)	Concentration (ppb/v) GC/MS Can A	GC/MS Can B
Trichlorofluoromethane (Freon 11)	9.9	10.7 ± 1.3	11.4 ± 2.6
Methylene chloride	16.0	12.2 ± 2.0	13.6 ± 2.9
Chloroform	11.4	9.7 ± 0.6	10.9 ± 1.3
1,2-Dichloroethane	13.7	12.0 ± 0.9	13.0 ± 1.7
1,1,1-Trichloroethane	10.2	9.3 ± 1.1	10.7 ± 1.7
Benzene	17.4	15.7 ± 2.6	17.4 ± 2.6
Carbon tetrachloride	11.9	10.0 ± 1.0	11.2 ± 2.9
1,2-Dichloropropane	12.0	11.3 ± 1.2	12.2 ± 1.9
Trichloroethylene	10.3	9.1 ± 0.9	10.4 ± 1.3
Toluene	14.8	13.6 ± 0.7	14.8 ± 1.6
Tetrachloroethylene	8.2	7.3 ± 0.6	8.1 ± 1.0
Chlorobenzene	12.1	10.7 ± 0.7	11.5 ± 1.6
Ethyl benzene	12.8	12.5 ± 1.6	13.2 ± 1.5
o-Xylene	12.8	11.4 ± 0.9	11.7 ± 1.5

(*): Calculated according to dilution.

(3). Portable GC analytical results of canister standards:

The GC/MS certified canister standards were analyzed on a Photovac 10A10 portable GC which was calibrated with the aqueous headspace working standard of VOCs. Table 5 shows the analytical results of benzene, trichloroethylene, toluene, tetrachloroethylene, ethyl benzene and o-xylene.

Table 5. Comparison of GC/MS results versus portable GC on Canister Standards

Compound	Concentration (ppb/v)				
		Can A		Can B	
	CALC.	GC/MS	PGC	GC/MS	PGC
Benzene	17.4	15.7	12.0	17.4	11.6
Trichloroethylene	10.3	9.1	8.7	10.4	8.7
Toluene	14.8	13.6	14.0	14.8	14.1
Tetrachloroethylene	8.2	7.3	9.9	8.1	10.1
Chlorobenzene	12.1	10.7	10.5	11.5	9.0
Ethyl benzene	12.8	12.5	12.0	13.2	12.0
o-Xylene	12.8	11.4	10.0	11.7	13.0

(4).Comparison of aqueous headspace standards versus canister standards:

The certified canister standards and aqueous headspace standards were used for calibrating the portable GC to analyze prepared air samples. Four air samples of different concentrations were prepared in SUMMA canisters and were certified on GC/MS. The samples were then analyzed on the portable GC. Table 6 shows the analytical results. Based on different calibration standards, two groups

Table 6. Comparison of Aqueous Headspace Standards vs Canister Standards on Portable GC Analysis

Compound	Sample:	Concentration (ppb/v)											
		#1			#2			#3			#4		
		(MS)*	AH	Can	(MS)	AH	CAN	(MS)	AH	CAN	(MS)	AH	CAN
Benzene		(27)	22	32	(14)	12	18	(6.8)	6.1	8.8	(2.7)	3.3	5.0
Trichloroethylene		(16)	24	29	(8.1)	8.1	9.7	(4.1)	3.5	4.2	(1.6)	1.6	2.1
Toluene		(23)	32	34	(12)	13	14	(5.8)	6.5	6.5	(2.3)	2.4	2.4
Tetrachloroethylene		(13)	17	14	(6.4)	7.6	6.0	(3.2)	5.0	4.2	(1.3)	1.3	1.6
Ethyl benzene		(20)	18	16	(10)	9.0	8.0	(5.0)	6.5	5.5	(2.0)	ND**	ND
o-Xylene		(20)	22	20	(10)	13	12	(5.0)	4.5	4.2	(2.0)	ND	ND

(*): Results of GC/MS analysis
(**): Non-detected

of data were obtained. The data in the columns under "AH"(Aqueous Headspace) are the results from the portable GC calibrated by the aqueous headspace standard and those in the columns under "CAN"(CANister) are the results from the portable GC using the canister calibration. Comparisons between the two data groups on benzene, toluene, trichloroethylene, tetra-chloroethylene, ethyl benzene and o-xylene were performed.

(5).Stability of canister standards and temperature dependency:

The study of time dependent stability of different manufactures' SUMMA canisters has been reported[3]. The study in this paper focused on the time dependent stability of benzene, toluene, trichloroethylene, tetrachloroethylene, ethyl benzene and xylenes. Two canister standards were analyzed on a periodic basis using HP 5890/5970 GC/MSD. With seven months of analytical results, there were no significant variation of VOC concentrations in the canisters. Figure 2 shows the time dependent

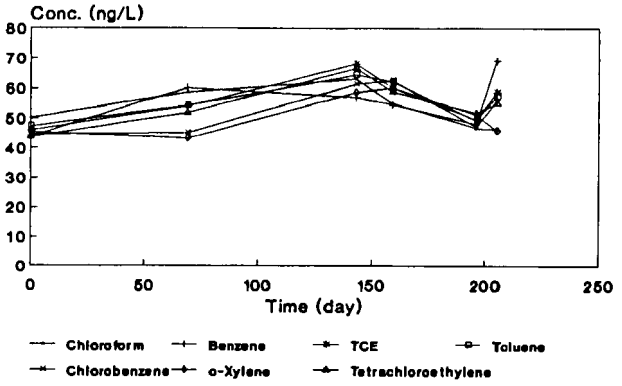
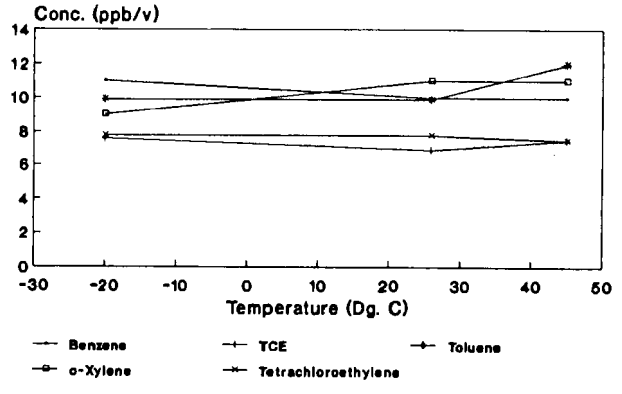


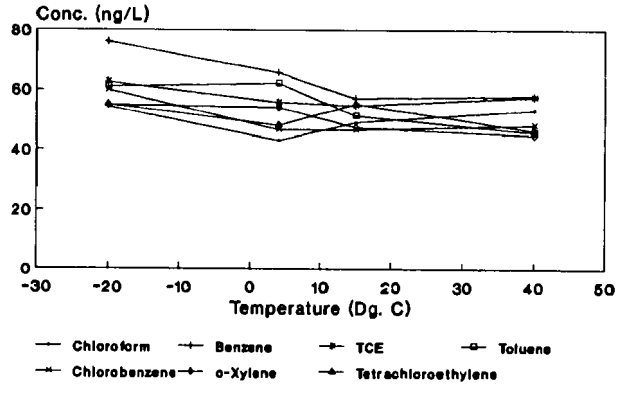
Figure 2. Time dependent Stability of Canister Standards

stability for several selected compounds.

As a standard for field screening, the temperature variation is an important factor for the canisters. The temperature dependency study was performed at various temperatures ranging from -20℃ to 45℃. A canister standard and a duplicate were stored at each temperature environment for at least three hours, then analyzed on GC/MSD and on the portable GC. Figure 3 shows the temperature dependency result of canisters. The data shows those standards were very stable over the temperature range of -20℃ to 40℃.



(a). Portable GC Analysis



(b). GC/MS Analysis

Figure 3. Temperature Dependency of Canister Standards

Conclusions

According to both the theoretical and experimental results, the aqueous headspace standard is a suitable VOC standard for ambient air field screening analysis. The field screening headspace standard is easy to prepare with materials that are readily available in any environmental laboratory. It takes very little time to prepare and the cost to prepare this type standard is minimal.

Canister standards possess high accuracy for most of the VOCs and reflect real concentrations of the VOCs inside. Canisters are easy to store and transport, and are reusable. The temperature dependency study on canister standards showed that VOC concentration in canisters remain stable over the normal field condition ambient temperature range of -20℃ to 40℃. The time dependent canister stability tests showed that canister VOC standards have long term stability. Over a seven month time period, VOC concentrations in canister standards remained stable.

Compared with aqueous headspace standards, canister standards are relatively expensive. Because of all the necessary accessary equipment needed for standard preparation, this method is only recommended to those laboratories which have a canister analysis set up.

Acknowledgment

The authors wish to thank the Regional Laboratory of the U. S. EPA Region I, in which all of the experiments were conducted.

Reference

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DISCUSSION

THOMAS SPITTLER: I have to say that I saw this data just about two or three days before I left for this meeting, and I was literally astounded at how well that the simple, inexpensive, standard preparation correlated with the incredibly expensive, complicated GC/MS canister technology in our lab. We didn't show you half the slides he had of all the equipment required to prepare and analyze the canister standard.

RALPH SULLIVAN: When you remove about ten cc's of liquid, did you back fill with air, or make any provision to clean up that air as it went in, if you did that?

HUI WANG: No, that's just the same procedure as we prepared the headspace standard for soil and water screening. We just pull the air out and just use it. We have a mobile lab that's relatively clean. Is your question about the cross-contamination from the air getting into the headspace?

RALPH SULLIVAN: Yes.

HUI WANG: The mobile lab is relatively clean. It has probably very, very low levels of those target compounds. It's never going to affect our standard.

THOMAS SPITTLER: We've actually looked at the lab air in our building and it's as clean as the outside air. And that means about 1 ppb of benzene and toluene and nothing else. We've never seen much need to put a big charcoal scrubber in for that make-up air.

RALPH SULLIVAN: But you do put another hypodermic syringe in there to dissolve the air?

THOMAS SPITTLER: Yes, the needle is just stuck in there. Room air just goes in to replace the drawn water.

RALPH SULLIVAN: The next question has to do with the canisters. I saw nothing in the diagram that indicated that you put any water into the canister. Did you put water into the canister with a syringe?

HUI WANG: Yes, in many canisters there's about 25% relative humidity. I calculated the amount of water we need and injected more water to the canister directly.

RALPH SULLIVAN: Do you have mixtures of standards or single component standards in the vials and in the canisters?

HUI WANG: Yes, composed of multi-components not only single components.

RALPH SULLIVAN: So, you added various quantities of say, neat compounds into the vials and also into the canisters?

HUI WANG: Yes. Actually, I used the same stock solution. We use the same stock solution for canister and headspace standards.

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