32-Week Holding-Time Study of SUMMA Polished Canisters and Triple Sorbent Traps Used To Sample Organic Constituents in Radioactive Waste Tank Vapor Headspace

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Two sampling methods [SUMMA polished canisters and triple sorbent traps (TSTs)] were compared for long-term storage of trace organic vapor samples collected from the headspaces of high-level radioactive waste tanks at the U.S. Department of Energy's Hanford Site in Washington State. The two methods were found to provide generally equivalent results. Because safety, quality assurance, radiological controls, and somewhat complex sample custody arrangements frequently precluded rapid analysis, the long-term stability of the sampling media during storage needed to be addressed. Samples were analyzed with a gas chromatograph/mass spectrometer (GC/MS) using cryogenic preconcentration or thermal desorption sample introduction techniques. SUMMA canister samples were also analyzed for total non-methane organic compounds (TNMOC) by GC/flame ionization detector (FID) using EPA Compendium Method TO-12 . The 31 target organic analytes studied represented compounds with widely varying polarities and volatilities. To verify the long-term stability of the sampling media, multiple samples were collected in parallel from a typical passively ventilated radioactive waste tank known to contain moderately high concentrations of both polar and nonpolar organic compounds. Two sets of sorbent trap samples were collected to compare the effects of storage under refrigerated (−20 °C) and room temperature conditions. Analyses for organic analytes and TNMOC were conducted at increasing intervals over a 32-week period to determine whether any systematic degradation of sample integrity occurred. Analytes collected in the SUMMA polished canisters generally showed good stability over the full 32 weeks with recoveries at the 80% level or better for all compounds studied. The TST data showed some loss (50–80% recovery) for a few high-volatility compounds even in the refrigerated samples; losses for unrefrigerated samples were far more pronounced with recoveries as low as 20% observed in a few cases. Long-term stability for the other compounds studied was deemed to be generally satisfactory at the 80% recovery level.

Introduction

Plutonium production operations at the U.S. Department of Energy's Hanford Site over the past 5 decades generated large volumes of process waste. Because of safety and environmental protection considerations, the most concentrated forms of the waste were stored in underground tanks. Over the course of the Hanford Project, 149 single-shell tanks with capacities of 210 000–3 800 000 L were constructed to store the high-level waste.

Waste stored in these tanks is a complex mixture of radioactive inorganic and organic constituents in both solid and liquid phases. Organic reagents used for plutonium and uranium separation include alkyl phosphates, methyl isobutyl ketone, methylated decahydronaphthalenes, and mixtures of the straight chain alkanes from decane to pentadecane. The environment in these tanks has in the past been characterized by temperatures of up to 160 °C, high ionic strength, exceptionally high pH, high nitrate levels, and intense radiation fields. While the tanks are now cooler and less radioactive than during plutonium production, the in-tank conditions remain hostile. That environment has caused extensive transformation of the organic materials in the tanks, and a wide variety of organic degradation products have formed, including alcohols, ketones, nitriles, organic nitrates, and branched alkanes and alkenes. In recent years, most of the liquid content of the single-shell tanks has been transferred to 28 newer double-shell tanks.

The single-shell tanks are thus left with a large volume of headspace containing vapors from some of the more volatile components of the primary organic materials and the associated impurities and degradation products. The presence of these gaseous components has raised concerns about the potential flammability, explosivity, and emissions of the tanks. To address these concerns, an extensive tank vapor characterization program was initiated in 1992. Brown (*2*) describes the rationale and objectives of the tank headspace characterization effort. So far, 108 of the 149 single-shell tanks, including all those known to contain large amounts of organics, have been sampled for volatile constituents. Sampling techniques used for organic analytes include the use of both SUMMA polished canisters and triple sorbent traps (TSTs) containing graphitized sorbent media. Because safety concerns, quality assurance, radiological controls, and complex sample custody arrangements present in this work frequently precluded rapid analysis, the long-term stability of the sampling media during storage needed to be addressed. Clearly the stability of vapor analytes under conditions of long-term storage is of broad interest in any such studies in which immediate analysis is not always a practical option. The study described in this paper addresses that concern.

Previous Studies. Applicability of previous studies to this problem is somewhat limited because of differences in sample matrix, analyte list, and duration. Brymer and co-workers recently performed an extensive study (*3*). A literature study performed as part of that work showed that previously published studies (*4–12*) were limited in scope, addressing primarily nonpolar compounds or a small number of polar species over a relatively short time. The Brymer (*3*) study addressed the stability of 194 compounds stored in SUMMA

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TABLE 1. Components of Air Matrix in Tank S-102

component	concentration	units
ammonia	798	ppmv
water	17.6	mg/L
hydrogen	1179	ppmv
nitrous oxide	1041	ppmv
temperature	24.3	°C
humidity	79.5	% relative

polished canisters for 30 days. Compounds addressed by the study included alkanes, alkenes, alkynes, aldehydes, alcohols, ketones, aromatics, halogenates, nitrogenated compounds, and sulfur-containing compounds, which are the majority of the compound types found in Hanford waste tanks. Brymer (3) reported excellent stability for 168 of the 194 compounds studied. Marginal behavior to varying degrees was found for the remainder. The applicability of that study to the Hanford samples was limited, however, because it was performed on standards prepared in pure air at relatively low levels, and it covered a relatively short time period.

Using TSTs for air sampling is a relatively recent development and thus has been studied less than air sampling with SUMMA polished canisters. Ma and co-workers (13) recently published the results of a relevant study using TSTs similar to those used in this work. While the Ma (13) study was also intended to address sampling of Hanford radioactive waste tanks, the study was conducted on sorbent traps spiked with standard mixtures rather than on actual tank headspace samples. That approach permitted covering a wider range of analytes than could be obtained from a single tank but may have also eliminated potential matrix effects from the high humidity and ammonia content of the air in the waste tanks. Practical reporting times (PRTs) were calculated for 16 compounds, with the majority of the species studied showing PRTs of 84 days or longer. Refrigeration was generally found to improve stability.

Previous studies of SUMMA and TST methods have not addressed the potential degradation of a typical mixture of organic vapors in high-humidity and high-ammonia matrixes such as exist in the Hanford tanks. This study evaluates the effects on sample integrity of holding times as long as 32 weeks on actual tank headspace SUMMA canister and TST samples. Table 1 presents a summary of some of the more significant matrix components found in the headspace atmosphere of tank 241-S-102 that are potentially capable of contributing to long-term loss of sample integrity. Nine SUMMA canister samples (including two ambient air blanks) and 13 TSTs collected from the headspace of tank 241-S-102 in September 1996 were stored and analyzed periodically to assess the stability of organic vapors.

Experimental Section

Sampling Media. All SUMMA samples were collected in 6-L electropolished canisters (Molectrics Corporation). Prior to collection, the canisters were cleaned by evacuating to a high vacuum with a molecular drag pump and alternately flushed by high-purity air and evacuated through 10 cycles. The canisters were then again evacuated, leak tested, and humidified to at least 80% relative humidity by addition of a small aliquot of high-purity water through the valve.

TSTs used in this study were commercially prepared ground glass tubes (6 mm diameter, 115 mm long, Supelco Carbotrap 300) containing three beds of sorbent media arranged in order of increasing retentivity. Before being shipped to the field, all TSTs were heated to 380 °C for 1 h under reverse helium flow to remove all incidental contamination. Measured quantities of three surrogate com-

pounds (hexafluorobenzene, toluene-d_8, and bromobenzene-d_5) were added to each tube before shipment to form a basis for evaluating the integrity of the sampling process for breakthrough and other potential sources of analyte loss. All three surrogate compounds have routinely shown full recovery during this and all other sampling activities involving TSTs. For example, control charting records maintained for 46 TST runs conducted over a 15-month period show average surrogate recoveries of 98 ± 7%, 99 ± 7%, and 98 ± 5%, respectively, for the three compounds. To minimize loss of tank vapor constituents and incidental contamination during shipment and storage, the TSTs were placed in hard polymer shell storage containers (Supelco TDS[3]). Following receipt in the laboratory, half of the samples were stored at −20 °C, and the rest were stored at room temperature. Traveler blanks included with each sample set were used to assess the effect of incidental contamination.

Sample Collection. All samples were collected on September 24, 1996, from Hanford tank 241-S-102. Detailed collection protocols for tank headspace characterization are described by Buckley (14). Seven SUMMA canisters were filled through a stainless steel transfer line inserted through a tank riser. Two additional samples were collected as ambient air blanks. The transfer line was heated to 50 °C to eliminate water condensation. Fourteen identical TST samples were collected through the same transfer line. A pump and calibrated mass flow controllers were used to draw an accurately measured volume of air through each of the TSTs. One of the samples was lost to breakage and thus was not used in the analysis of unrefrigerated samples.

Organic Speciation of SUMMA Canister Samples. Prior to analysis, all SUMMA canister samples were pressurized with high-purity air to double the initial sampling fill pressure to facilitate transfer during analysis. The SUMMA samples were analyzed for organic analytes according to an internally documented procedure that is a modified version of EPA Compendium Method TO-14 (1). The primary modification from the EPA method was eliminating the Nafion drier for water management. The method instead used a microscale purge-and-trap procedure to minimize water interference while providing high-efficiency throughput for polar compounds. Samples were preconcentrated with an EnTech 7000 cryoconcentration system interfaced to a Hewlett-Packard 5972A gas chromatograph/mass spectrometer (GC/MS). The EnTech concentrator was used to pull a metered volume of sample air from the SUMMA canister, cryogenically concentrate the condensable organic vapors, and then transfer the analytes to the GC/MS for analysis. A fused silica capillary column (J&W Scientific DB-1, 3-μm coating, 60 m by 0.32 mm i.d.) was used for separations. The GC oven was held at 40 °C for 5 min and then ramped at 4 °C/min to a final temperature of 260 °C with a 5-min hold.

The GC/MS instrument was calibrated with a gas mixture containing 67 target organic analytes. The calibration mixture was prepared by blending a commercially prepared TO-14 calibration mixture with one created using a Kin-Tek permeation tube standard generation system. Compounds in the permeation tube standard included homologous series of n-alkanes (C4−C14), nitriles (C2−C6), straight chain alcohols (C1−C4), and several other common tank constituents including acetone, 4-methyl-2-pentanone, pyridine, and tetrahydrofuran.

TST Analysis. Prior to analysis, a measured quantity of internal standard (difluorobenzene, chlorobenzene-d_5, and 1,4-bromofluorobenzene) was added to each tube to provide a quantitation reference. Each trap was then mounted on a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 was desorbed by ballistically heating to 350 °C for 7 min to quantitatively transfer the sample to a smaller diameter focusing trap. A 10:1 split was

TABLE 2. SUMMA Data for 32-Week Analytical Study

	analysis date						
analyte	9/25/96 (ppbv)	10/1/96 (ppbv)	10/9/96 (ppbv)	10/24/96 (ppbv)	11/27/96 (ppbv)	1/23/97 (ppbv)	5/8/97 (ppbv)
chloromethane	2.4	2.2	2.7	2.4	2.8	2.1	6.1
methanol	6 825	5 704	6 395	4 287	6 032	5 249	6 648
butane	83.4	88.5	89.8	79.4	104.3	75.0	93.7
ethanol	11 932	8 980	8 282	9 306	9 009	11 141	9 934
acetonitrile	13.0	16.0	14.8	14.9	18.5	16.5	23.5
acetone	373	396	431	450	525	464	465
trichlorofluoromethane	102	107	107	94.2	116	99.5	99.9
pentane	29.2	24.2	30.0	22.9	24.7	23.3	28.8
propanol	79.2	88.8	83.6	88.0	103	107	84.1
propanenitrile	3.8	3.7	4.1	3.6	4.2	5.4	13.1
2-butanone	55.9	58.5	61.3	59.5	71.1	75.6	66.2
hexane	11.5	11.0	11.9	8.7	10.1	12.6	14.9
tetrahydrofuran	62.5	64.6	67.8	45.2	54.1	62.1	48.4
butanenitrile	4.5	7.4	4.6	4.5	4.7	5.6	9.1
1-butanol	747	1063	965	797	1057	795	776
benzene	20.8	23.9	24.5	20.5	23.4	23.8	22.5
heptane	13.4	14.7	15.3	10.8	12.2	16.8	13.7
4-methyl-2-pentanone	14.4	16.2	17.0	6.7	7.7	8.6	11.8
pyridine	6.3	13.0	14.2	6.5	9.3	24.8	13.1
toluene	315	333	365	275	309	335	256
octane	5.6	5.5	6.2	4.4	5.2	7.9	5.6
tetrachloroethylene	5.9	5.8	6.4	4.4	5.2	7.7	6.0
ethylbenzene	2.4	2.4	2.6	1.8	2.3	3.3	3.7
p/m-xylene	7.8	8.0	9.0	6.6	7.7	13.2	9.9
o-xylene	4.1	4.0	4.7	3.1	3.3	5.8	4.9
nonane	4.6	4.0	5.1	2.4	2.6	4.4	4.5
1,2,4-trimethylbenzene	0.6	0.9	1.0	0.4	0.5 U	0.7	2.3
decane	3.4	3.4	3.8	3.1	3.5	4.9	6.6
undecane	1.7	1.4	1.7	1.4	1.6	2.7	2.6
dodecane	1.7	1.3 U	1.5	1.4	1.4	2.7	2.2
tridecane	2.1	1.2	1.3	1.8	2.3	5.9	4.8

[a] U, not detected.

TABLE 3. Target Compounds Not Detected in Tank S-102[a]

1,1,1-trichloroethane	1,3-dichlorobenzene	cyclohexanone
1,1,2,2-tetrachloroethane	1,1,2-trichloro-1,2,2-trifluoroethane	dichlorodifluoromethane
1,1,2-trichloroethane	1,2-dichloro-1,1,2,2-tetrafluoroethane	hexachloro-1,3-butadiene
1,1-dichloroethene	1-ethyl-2-methylbenzene	hexanenitrile
1,2,4-trichlorobenzene	bromomethane	methylene chloride
1,2,4-trimethylbenzene	carbon tetrachloride	pentanenitrile
1,2-dibromoethane	chlorobenzene	styrene
1,2-dichloropropane	chloroethane	tetradecane
1,2-dichloroethane	chloroform	trans-1,3-dichloropropene
1,3,5-trimethylbenzene	cis-1,2-dichloroethene	trichloroethene
1,3-butadiene	cis-1,3-dichloropropene	trichloroethene
1,4-dichlorobenzene	cyclohexane	vinyl chloride

[a] Typical detection limits were 0.5−1 ppbv.

used during the transfer with the smaller split sent to the focusing trap for prompt analysis and the larger split routed to an identical Carbotrap 300 archive trap for re-analysis if needed. At least one sample per batch was routinely re-analyzed for quality control purposes. The focusing trap was ballistically heated to 350 °C to thermally desorb analytes and purged with helium at a flow rate compatible with the column and mass spectrometer interface (1.2 mL/min). Determinant analyses were then performed on a Hewlett-Packard 5972A GC/MS system with a fused silica capillary column. GC conditions were similar to those described above for the SUMMA system except that subambient cooling to −10 °C was used at the start of the cycle to provide better front-end separations. The same instrument calibration mixture was used for both the TST and SUMMA analysis systems. Data analysis procedures were also identical.

TNMOC Analysis. Analyses for TNMOC in the headspace vapor samples were performed by the EPA Compendium Method TO-12 (1). Samples were pumped from the SUMMA canisters through an EnTech 7000 cryoconcentration system interfaced to a Hewlett-Packard 5890 GC equipped with an FID. A multiple concentration calibration curve generated using dilutions of a certified propane standard of known concentration was used for quantitation.

Results and Discussion

SUMMA Canister Results. A complete list of all analytical measurements for organic speciation of SUMMA canister samples is shown in Table 2, which includes all target analytes found at sufficient levels to obtain quantitation. Table 3 lists the target compounds included in the study but not found in vapor samples from tank S-102. Table 4 is a summary of averages and relative standard deviations (RSDs) computed for all seven measurement periods. Only compounds above their estimated quantitation limits (EQLs) are included in Table 4. Figure 1 plots selected individual data

TABLE 4. Summary of 32-Week Averages and Trends

target analyte	SUMMA av (ppbv)	% RSD	trend[a]	TST refrig av (ppbv)	% RSD	trend[a]	TST refrig av (ppbv)	% RSD	trend[a]
methanol	5,877	15	0	NA	NA	NA	NA	NA	NA
butane	87.7	11	0	95.7	11	0	80.8	17	0
acetonitrile	17	21	0	112	37	0	86.0	17	0
ethanol	9,934	14	0	NA	NA	NA	NA	NA	NA
acetone	443	11	0	392	31	−	268	59	- -
trichlorofluoromethane	104	7	0	107	17	−	53.0	77	- -
pentane	26.1	12	0	18.7	12	0	17.7	18	0
propanol	90.5	12	+	99.0	18	0	51.8	64	- -
propanenitrile	5.4	63	0	6.8	24	0	5.7	8	0
2-butanone	64.0	11	+	55.2	31	−	38.9	65	- -
hexane	11.5	17	0	13.5	14	0	13.9	15	0
tetrahydrofuran	57.8	15	0	63.0	9	0	46.5	41	- -
butanenitrile	5.8	31	0	5.8	25	+	5.2	26	- -
1-butanol	886	16	0	871	9	0	692	28	0
benzene	22.8	7	0	23.1	5	0	23.5	7	0
heptane	13.8	14	0	14.8	6	0	14.7	8	0
4-methyl-2-pentanone	11.8	36	0	13.6	40	0	13.8	42	0
toluene	313	12	0	287	8	0	287	11	0
octane	5.8	19	0	6.0	10	0	6.5	20	0
p/m-xylene	8.9	25	0	9.0	15	0	9.8	14	0
o-xylene	4.3	22	0	4.2	15	0	4.6	20	0
nonane	4.0	26	0	3.9	20	0	4.2	21	0
tetrachloroethylene	5.9	17	0	6.2	13	0	6.53	5	0

[a] Trends were estimated from visual examination of graphs. NA, analytical data not available; 0, no significant trend; +, small increasing trend; −, small decreasing trend; - -, large decreasing trend.
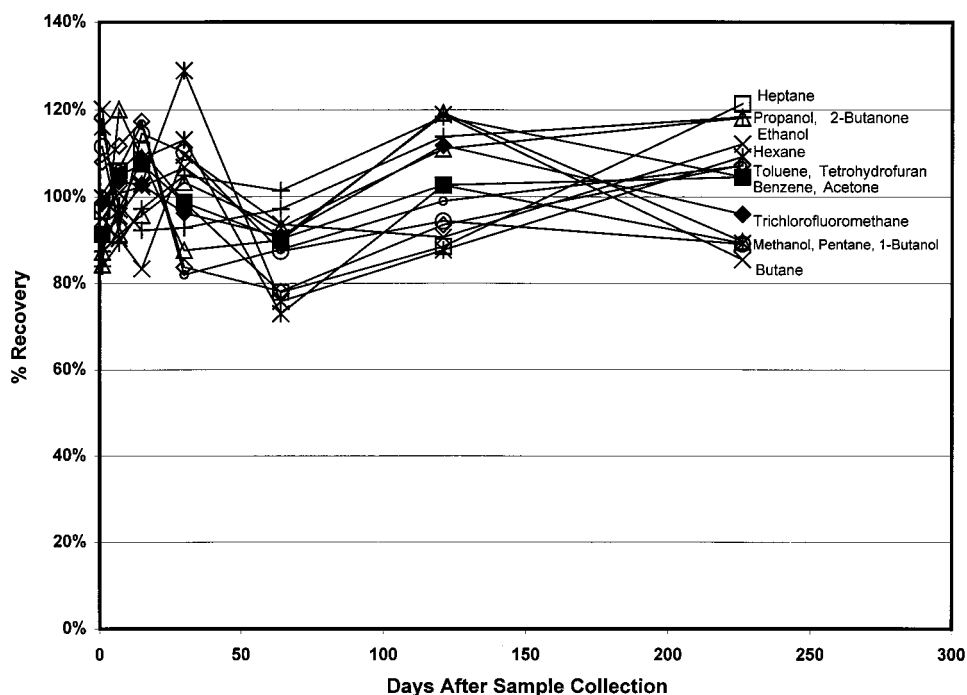

FIGURE 1. SUMMA selected organic speciation results normalized to average of all points for each constituent.

points normalized to the average computed for each data set. Plotted in that manner, data spanning a wide range of concentrations may be visually evaluated on an equivalent basis. Only species detected at levels significantly above the detection limits were plotted to minimize the effect of threshold-related analytical scatter. All species plotted showed excellent stability over the 32 weeks. The scatter of data in Figure 1 is probably associated with reproducibility of calibration and other analytical uncertainties. Analytical precision for this method has generally been found to be at the ±20% level. Any trends indicated through visual examination of the data plots are noted in Table 4.

Results of the TNMOC analyses are plotted in Figure 2. The TNMOC data showed a very high degree of stability over the duration of the study. The RSD of the seven data points was 3.9% for the full 32-week period with no trend evident. It thus appears that samples collected in SUMMA canisters for total organic content or organic speciation spanning the diverse range of compound types addressed in this study can be stored for a long time without compromising analytical integrity at least with respect to total organic content, However, since TNMOC is by nature an integral-type measurement, transformations within the canister between organic species with similar FID response are not ruled out.
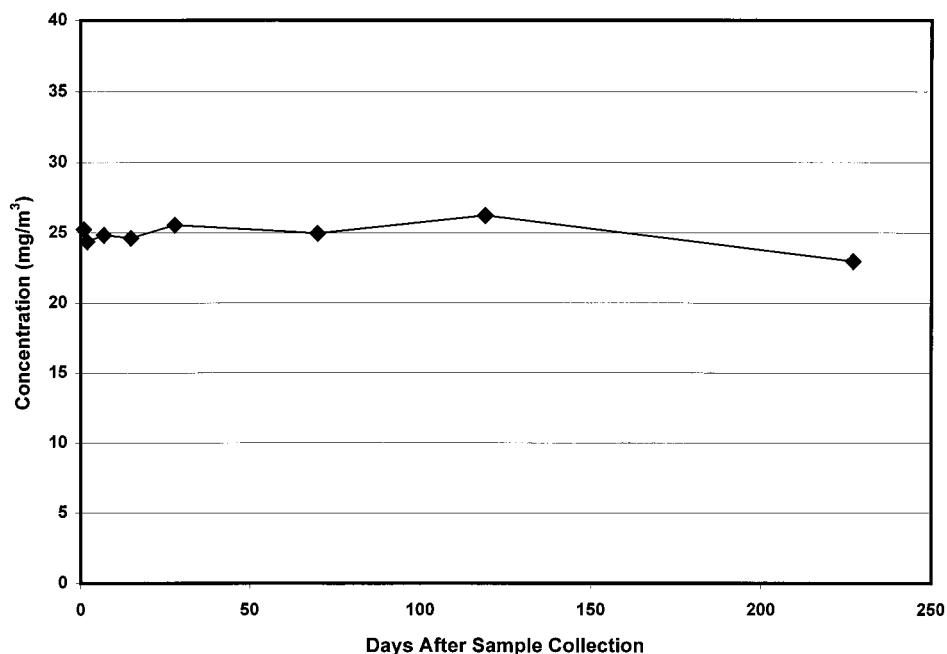
FIGURE 2. Total non-methane organic compound (TNMOC) analysis over 32-week holding-time study.

TABLE 5. TST Data (Refrigerated) for 32-Week Analytical Study

	analysis date						
analyte	9/24/96 (ppbv)	10/1/96 (ppbv)	10/8/96 (ppbv)	10/24/96 (ppbv)	11/19/96 (ppbv)	4/9/97 (ppbv)	5/6/97 (ppbv)
methanol	11 670 E[a]	7 791 E	5 045 E	7 766 E	14 190 E	8 226 E	7 913 E
butane	100	94.4	80.1	102	84.9	111	97.2
ethanol	16 024 E	10 995 E	10 504 E	18 842 E	6 986 E	13 550 E	9 347 E
acetonitrile	98.5	125	65.7	100	80.2	194	120
acetone	536	459	425	506	332	260	225
trichlorofluoromethane	123	116	110	132	98.4	90.5	80.8
pentane	19.7	18.8	16.0	19.0	16.3	22.8	18.4
propanenitrile	6.3	6.2	5.5	6.3	5.4	10.0	7.7
propanol	106	104	88.1	107	71.4	126	89.5
2-butanone	74.8	61.1	61.5	70.3	54.3	35.3	29.3
hexane	15.4	15.1	12.7	10.3	12.4	15.4	13.4
tetrahydrofuran	71.0	70.2	61.8	61.2	58.7	61.0	57.1
butanenitrile	5.9	4.6	4.9	4.9	5.3	8.8	6.6
1-butanol	926	871	796	953	776	956	818
benzene	24.0	23.5	21.9	24.7	21.5	23.8	22.6
heptane	15.4	15.6	13.5	16.1	14.3	14.8	14.3
4-methyl-2-pentanone	18.5	18.3	15.5	6.4	5.8	17.3	13.7
pyridine	14.8	22.5	16.6	22.0	29.0	26.7	27.2
toluene	309	303	285	318	262	268	263
octane	6.0	6.4	5.1	6.4	5.2	6.7	7.8
tetrachloroethylene	6.5	6.7	5.9	7.4	5.8	4.9	6.2
ethylbenzene	2.3	2.6	2.0	2.8	2.0	2.0	2.5
p/m-xylene	9.3	10.2	8.3	10.5	7.9	6.8	9.7
o-xylene	4.4	4.6	3.8	5.1	3.5	3.5	4.7
nonane	4.4	4.8	3.6	4.2	2.5	3.4	4.3
decane	3.0	3.3	2.4	4.3	2.0	3.3	4.3
undecane	1.5	2.0	1.3	2.1	1.3	1.3	3.8
tridecane	6.6 U	4.2	6.6 U[b]	4.4	3.2 U	4.1	4.1
tetradecane	4.5	6.7	2.6	10.6	8.5	9.4	7.5

[a] E, concentration exceeds upper calibration standard. [b] U, not detected.

The high-humidity, high-ammonia atmosphere of the tank does not appear to have caused any significant overall sample degradation.

TST Results. Complete results for the TST analyses are presented in Tables 5 (refrigerated) and 6 (unrefrigerated). Selected results from Table 5 are plotted in Figure 3 using the approach described for the SUMMA canister samples. Table 4 lists average concentrations and RSDs for the quantitated compounds. Trends evident from examination of Figure 3 indicate significant losses with time for 2-butanone, acetone, and trichlorofluoromethane in both the refrigerated and unrefrigerated TSTs. All other compounds in the refrigerated TSTs showed excellent long-term stability within the constraints of analytical reproducibility at the ±20% level.

The effect of refrigeration on TST storage is illustrated in Figure 4, where the ratio of each unrefrigerated TST result to its corresponding refrigerated TST result has been plotted

TABLE 6. TST Data (Unrefrigerated) for 32-Week Analytical Study

|	analysis date					
analyte	9/24/96 (ppbv)	10/1/96 (ppbv)	10/8/96 (ppbv)	11/19/96 (ppbv)	4/9/97 (ppbv)	5/6/97 (ppbv)
methanol	11 760 E[a]	5 125 E	4 066 E	13 293 E	2 264 E	1 865 E
butane	93.6	93.3	77.9	80.1	82.7	57.1
ethanol	15 214 E	8 731 E	6 595 E	6 510 E	2 217 E	2 619 E
acetonitrile	92.2	117	83.9	84.1	84.5	71.0
acetone	534	343	278	226	116	114
trichlorofluoromethane	117	83.0	55.8	24.7	21.0	16.0
pentane	18.3	18.5	17.0	16.6	22.7	13.0
propanenitrile	5.5	5.8	6.0	5.3	6.3	5.1
propanol	108	76.1	68.5	30.1	27.2	15.7
2-butanone	70.4	49.8	58.1	34.5	11.4	9.0
hexane	14.6	15.1	13.4	12.4	16.8	10.9
tetrahydrofuran	68.4	66.7	54.5	34.8	24.0	30.4
butanenitrile	4.5	7.4	5.2	5.2	3.8	0.5
1-butanol	901	853	796	615	865	398
benzene	23.6	23.7	22.6	21.6	26.6	22.7
trichloroethene	4.9	2.8	8.3	10.4	4.3	17.0
heptane	15.0	15.5	14.1	14.0	16.4	13.4
4-methyl-2-pentanone	17.6	17.5	15.6	5.3	19.1	8
pyridine	12.9	18.3	14.2	14.1	16.0	14.4
toluene	297	304	286	250	332	257
octane	6.0	6.2	6.1	4.8	8.5	7.5
tetrachloroethylene	6.5	6.7	6.4	5.8	6.7	6.6
ethylbenzene	2.5	2.5	2.4	2.3	3.2	3.2
p/m-xylene	9.6	9.9	9.7	7.6	11.7	10.7
o-xylene	4.4	4.6	4.3	3.3	6.2	5.0
nonane	4.3	4.7	4.4	2.2	5.8	3.7
decane	2.8	3.1	2.6	1.8	7.9	4.0
undecane	1.7	1.9	2.0	1.0	4.0	4.0
tetradecane	3.6	6.1	4.3	14.0	14.4	8.4

[a] E, concentration exceeds upper calibration standard.
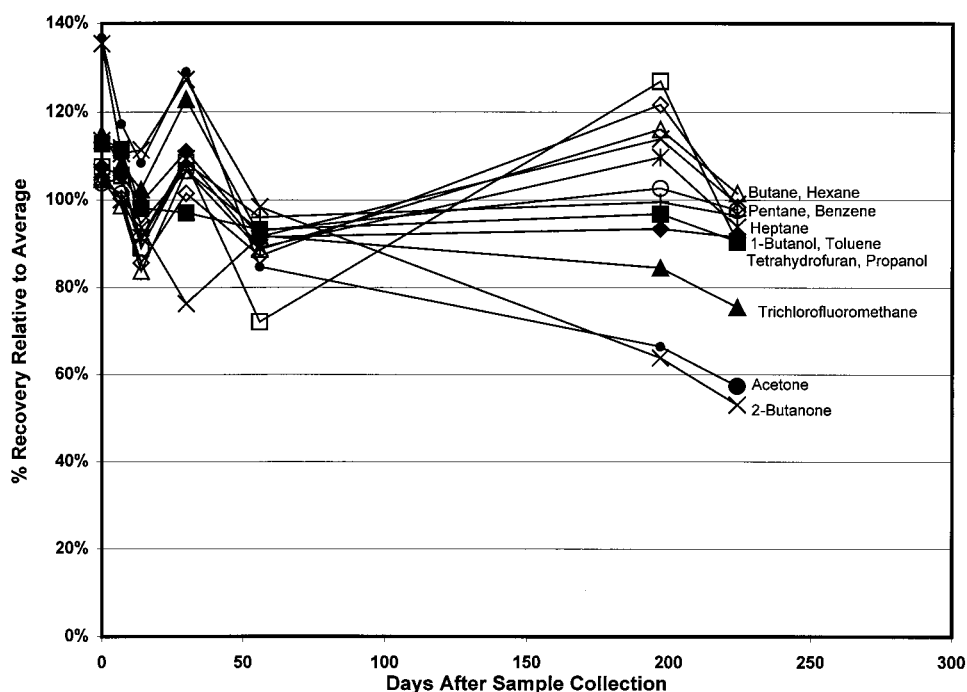
FIGURE 3. TST (refrigerated) selected organic speciation results normalized to average of all points for each constituent.

for selected compounds. Data were normalized in that fashion to minimize the effect of long-term calibration uncertainties. Although several compounds (e.g., benzene, toluene, and heptane) were apparently unaffected by the lack of refrigeration during the 32-week study, the lack of refrigeration significantly reduced the recovery of many others. As shown in Figure 4, the larger and less polar molecules had similar recoveries from both refrigerated and unrefrigerated TSTs; smaller, more polar molecules tended to exhibit higher losses in the unrefrigerated TSTs. These results are consistent with the assumption that TST analyte losses are due to migration of analytes deeper into the pores of the sorbent media and are not to consumption by chemical reaction. Storage of the TSTs at room temperature appears
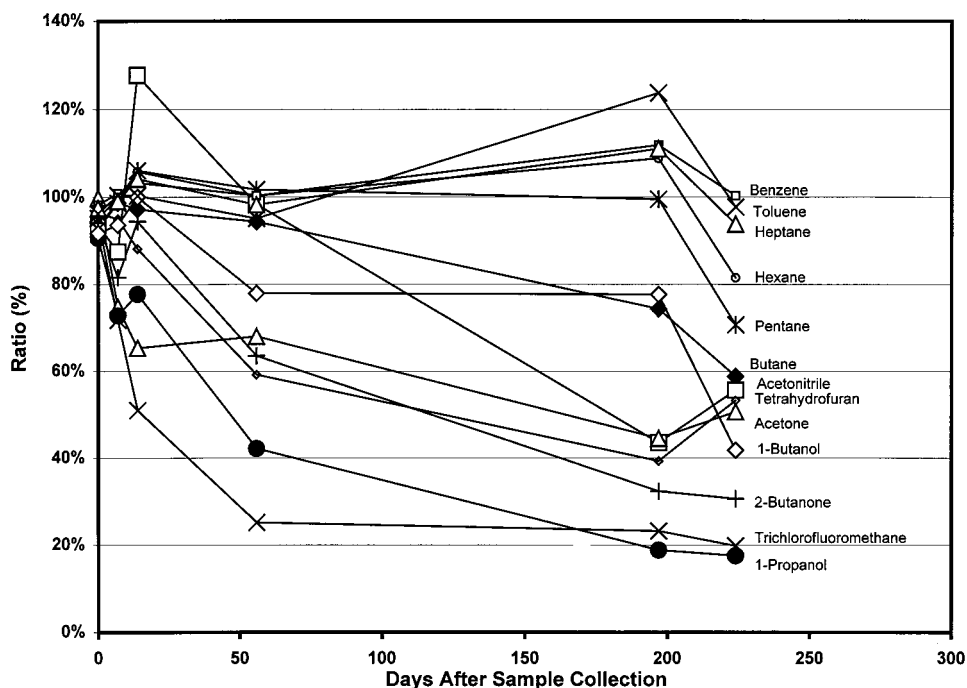
FIGURE 4. Comparison of TST analyses performed at the same time on refrigerated and unrefrigerated samples during 32-week holding-time study.
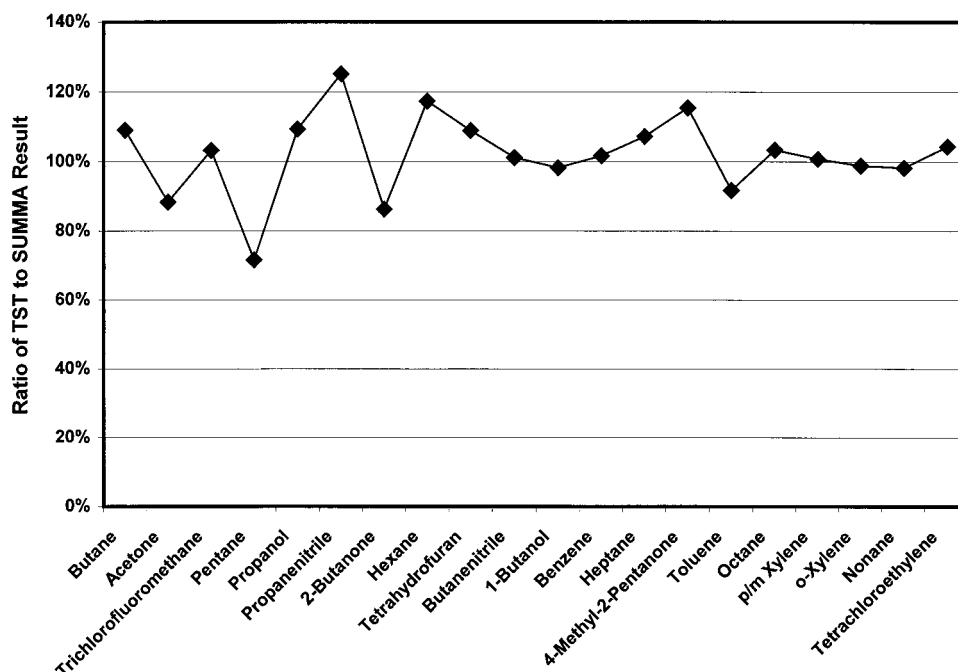

FIGURE 5. Comparison of SUMMA and TST selected organic speciation results. Average of seven measurements each over the 32-week holding-time study.

to have deleteriously affected the recovery of the smaller molecules (which have higher diffusion rates and higher mobility within pores) and more polar molecules (which are more strongly adsorbed by the media). Refrigeration definitely improved long-term stability in TSTs for these compounds.

Method Comparison. Figure 5 shows the ratio of the TST average results (refrigerated) taken from Table 4 to the corresponding average SUMMA results. The figure clearly shows that both methods give essentially equivalent results. One exception, acetonitrile, was not plotted. The TSTs gave a much higher acetonitrile content throughout the entire series than did the SUMMA analyses. The reason for the

difference is not known. In general, the TST method was easier to implement and showed much higher analytical sensitivity, particularly for low-volatility compounds. The SUMMA method as implemented was capable of a wider dynamic range and was less prone to problems associated with blank contamination during sampling and transport. Using the two significantly different methods in parallel provided good assurance that results obtained were representative of the tank atmosphere.

Acknowledgments

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