

## Characterization of Hanford Waste Tank Headspace Samples Using Autosampler Coupled with Preconcentrator and Analyzed by Gas Chromatography/Mass Spectrometry

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### Background

From the 1940s to the 1990s, approximately 210,000 m<sup>3</sup> (55 million gal) of radioactive byproduct from plutonium processing was deposited in 177 underground storage tanks on the US Department of Energy's Hanford Nuclear Reservation in Washington State. The majority of the storage tanks have exceeded their design lives, and many of them are suspected or known to be leaking. The composition of the waste varies among the tanks and is known to be approximate. In addition to highly caustic concentrated inorganic compounds, many tanks contain radioactive and organic mixed waste. The fugitive emissions from these tanks may pose a safety hazard due to flammability and an occupational exposure hazard due to the presence of toxic chemicals.

### Objectives

The primary objective is to develop an analytical methodology for characterization of volatile organic compounds (VOCs) collected from headspace of underground waste storage tanks. Since the analytical procedure is to be used on a routine basis with a relatively short turn-around time, an autosampler has been incorporated in the analytical system. Federal and Washington State regulatory programs govern the management of the tank waste, the analytical results have to meet data quality objectives (DQO) for regulatory requirements for hazardous and radioactive air emissions sampling and analysis. In addition, the DQO process has to identify the regulatory drivers that include:

- The analytes which are needed to address regulatory air emission issues. Analytes include those which are known or potentially present in vapor phase,
- Which analytes to test via sampling and laboratory analyses, and
- The appropriate analytical methods that provide acceptable detection capability and quality.



Hanford Site Double-Shell Tank Farm Under Construction

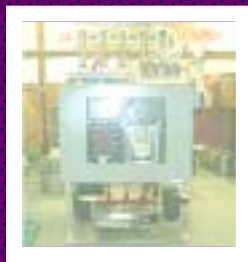


Inside Double-Shell Tank

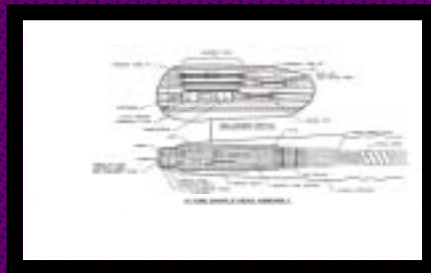
# Instrumentation and Analysis

## Sample Collection

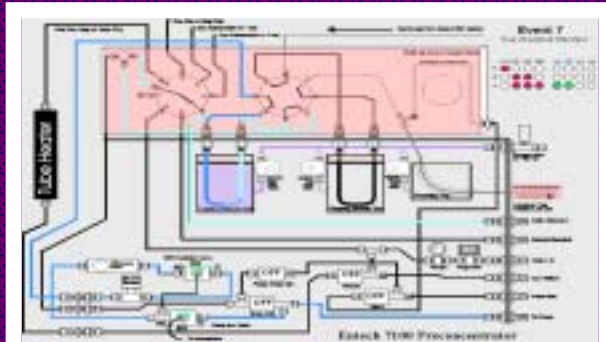
The In Situ Vapor Sampling System (ISVSS) was used to collect VOCs in SUMMA™ canisters from the waste tanks. The ISVSS is portable and consists of two principal sections: the sample head assembly and a cart-mounted sampling manifold. The sample head assembly, which houses transfer lines connected to SUMMA canisters, is lowered into the tank's headspace to obtain vapor samples. The sampling manifold draws tank headspace vapor through the sample head assembly and measures the volume of gas drawn through the sampling system.



In Situ Vapor Sampling System



Typical Sampling Head Arrangement of Sorption Tubes and Filters



Sequentially, a fixed volume (20 to 200 ml) of tank headspace sample and a fixed volume (100 ml) of a multi-component internal standard are withdrawn from the SUMMA canisters by an autosampler (Entech 7032-L) for analysis. The VOCs in the vapor sample are concentrated by a preconcentration system (Entech 7100). The preconcentrator consists of three cryogenic traps (glass beads, Tenax™ TA, and Silonite coated tubing). In addition to cryogenic focusing of VOCs, the preconcentrator also provides water management (microscale purge and trap) and carbon dioxide removal (purging Tenax trap sub-ambiently). Subsequently, the VOCs were transferred to a gas chromatograph (GC) column (60 m x 0.25 mm ID, 5% diphenyldimethyl polysiloxane) and analyzed by gas chromatography/mass spectrometry (Agilent model 5973 Mass Detector/6890 GC). The GC oven temperature is programmed as follows: hold at 0°C for 10 min, then heated to 230°C at 4°C/min.

Reproducibility of Analytical Methodology (%RSD)							
Target Analyte	CAS Number						
	4 ppbv	10 ppbv	20 ppbv	30 ppbv	60 ppbv	120 ppbv	
n-Propane	74-98-6	23.67	2.17	4.72	3.54	2.26	5.52
Methyl chloride	74-87-3	11.74	4.29	3.86	4.05	3.40	5.20
n-Butane	106-97-8	13.22	3.28	3.58	2.96	2.37	4.74
Dichloromethane	75-09-2	19.54	2.53	3.44	2.49	2.43	4.71
n-Hexane	110-54-3	16.82	2.89	8.15	1.74	2.28	9.94
Chloroform	67-66-3	16.93	3.33	4.23	3.42	3.64	4.26
Benzene	71-43-2	17.64	3.28	5.35	1.76	0.77	5.45
n-Heptane	79-01-6	19.18	6.77	6.50	0.80	0.96	5.68
Toluene	108-88-3	18.82	7.39	5.11	0.54	0.82	5.05
m,p-Xylene	106-42-3	21.21	8.02	3.93	2.11	3.61	1.86
n-Nonane	111-84-2	16.69	8.88	3.26	1.41	0.89	5.75
1,1,2,2-Tetrachloroethane	95-47-6	18.74	7.26	4.60	1.30	2.29	2.75
n-Decane	124-18-5	18.08	8.60	3.70	3.00	3.07	2.24
Hexachloro-1,3-butadiene	87-68-3	17.97	7.16	2.11	5.98	2.79	1.82
Acetaldehyde	75-07-0	20.96	10.36	10.80	5.09	5.28	14.06
Methanol	67-56-1	25.53	11.74	7.97	2.95	10.99	8.13
Acetone	67-64-1	2.84	6.36	14.81	7.60	8.37	2.80
2-Propanol	67-63-0	21.72	13.24	12.06	7.34	5.33	4.22
Propanenitrile	107-12-0	11.07	8.77	10.80	3.06	1.04	1.91
2-Butanone	78-93-3	22.88	12.50	16.40	5.25	3.59	2.08
1-Butanol	71-36-3	19.79	6.24	10.43	11.38	14.17	0.95
2-Hexanone	591-78-6	26.87	10.71	7.36	2.99	2.70	8.07
2-Octanone	111-13-7	42.43	8.28	5.20	8.86	5.40	7.70

\*Based on the average of response factors measured at concentrations of 4, 10, 20, 30, 60, and 120 ppbv of multiple calibration curves (3-5 replicates over a period of 12 months)

Linearity of Calibration Curves			
Selected Target Analyte	CAS Number		
	Minimum and Maximum of R <sup>2</sup>		
n-Propane	74-98-6	1.000	1.000
Methyl chloride	74-87-3	1.000	1.000
n-Butane	106-97-8	0.999	1.000
Dichloromethane	75-09-2	1.000	1.000
n-Hexane	110-54-3	1.000	1.000
Chloroform	67-66-3	0.997	1.000
Benzene	71-43-2	0.996	1.000
n-Heptane	108-88-3	1.000	1.000
Toluene	108-88-3	0.968	1.000
m,p-Xylene	106-42-3	0.916	0.994
n-Nonane	111-84-2	0.998	1.000
1,1,2,2-Tetrachloroethane	95-47-6	0.958	1.000
n-Decane	124-18-5	0.962	0.988
Hexachloro-1,3-butadiene	87-68-3	0.946	0.981
Acetaldehyde	75-07-0	0.993	0.999
Methanol	67-56-1	0.962	0.986
Acetone	67-64-1	0.999	1.000
2-Propanol	67-63-0	0.962	1.000
Propanenitrile	107-12-0	0.999	1.000
2-Butanone	78-93-3	0.999	1.000
1-Butanol	71-36-3	0.948	0.995
2-Hexanone	591-78-6	0.995	1.000
2-Octanone	111-13-7	0.947	1.000

C correlation Coefficients based on 3 to 5 individual calibration curves

Accuracy of the Analytical Methodology			
Com pound	Average % recovery	STDEV	% RSD
Chloroethane	108.66	6.89	6.34
Tetrahydrofuran	106.78	5.87	5.50
n-Pentane	102.13	6.33	6.20
Methyl isobutyl ketone	100.60	5.88	5.85
Chlorobenzene	104.17	6.11	5.87
1,2,4-Trimethylbenzene	115.97	7.63	6.57

Accuracy was measured by the % recovery of selected analytes. This is BEST traceable standard was obtained from an independent supplier. 26 m ethanol was obtained over a period of 12 months.

# Performance of Analytical Methodology

Holding Times for VOCs Stored in 6 Litre Siloxane Canisters for 4 Months									
Analysis	Day 7	Day 14	Day 21	Day 28	Analysis	Day 7	Day 14	Day 21	Day 28
Propene	103	99	97	99	Carbon Tetrachloride	96	95	94	92
Dichlorodifluoromethane	100	94	95	92	Cyclohexane	102	98	97	92
Chloroethane	98	93	93	90	2,2,4-Trimethylpentane	101	97	98	97
Dichloromethane	91	87	91	91	n-Heptane	100	97	98	97
n-Butane	100	99	96	96	1,2-Dichloroethane	99	95	97	97
n-Pentane	100	95	93	90	Trichloroethene	97	95	95	95
3-Pentanone	100	96	94	86	Bromochloromethane	99	97	97	95
Bromochloroethane	103	96	95	94	1,4-Dioxane	110	110	105	74
Chloroform	100	95	95	90	1,2-Dichloropropane	95	91	92	81
Bromodichloromethane	101	94	95	91	4-Methyl-2-Pentanone	102	101	101	86
Trichlorofluoromethane	100	95	95	92	1,2-Dichlorobenzene	98	92	91	62
Acetone	94	91	91	83	Toluene	98	96	96	96
Propene	97	90	92	82	1,2,4-Trichlorobenzene	96	96	96	97
1,2,4-Trichlorobenzene	100	96	95	90	2-Methyl-2-Butanol	98	96	97	93
Bromochloroethane	99	95	95	91	1,2-Dichloroethane	95	92	91	83
Methylchloroethane	85	86	86	82	Tetrahydrofuran	97	95	95	78
1,1-Dichloroethane	75	85	84	85	Chlorobenzene	97	95	95	93
Cyclohexane	101	98	97	92	n-Heptane	98	97	96	96
1,2-Dichloroethane	98	95	94	88	Bromochloroethane	97	96	100	90
Methylchloroethane	94	89	90	84	Styrene	94	93	92	81
1,2,4-Trichlorobenzene	100	95	95	91	n-Butane	98	98	98	99
Vinylacetate	84	88	87	76	1,1,2,2-Tetrachloroethane	99	100	100	100
2-Pentanone	91	89	87	77	4-Methyl-2-Pentanone	97	97	100	92
n-Heptane	102	97	95	89	1,1,3,3-Tetraethylbenzene	97	99	97	100
1,2,4-Trichlorobenzene	98	94	93	88	1,2,4-Trichlorobenzene	96	99	97	100
n-Butane	94	88	87	78	1,2,4-Trichlorobenzene	96	99	98	91
Chlorobenzene	99	95	95	92	n-Heptane	87	93	96	65
Tetrahydrofuran	96	91	91	81	1,4-Dichlorobenzene	94	94	91	80
1,1,2,2-Tetrachloroethane	97	91	95	92	1,2,4-Trichlorobenzene	99	104	101	101
1,2,4-Trichlorobenzene	98	94	93	89	1,2,4-Trichlorobenzene	99	102	92	110
Bromochloroethane	97	95	94	90	Bromochloroethane	108	102	102	120

% Recovery of VOCs from the original concentration of 10 ppbv

Stability of Calibration Curves Over 12 Months					
Selected Target Analyte	CAS Number	Average % Dev	Minimum % Dev	Maximum % Dev	
n-Propene	74-98-6	4.9	0.0	14.2	
Methylchloride	74-87-3	5.3	0.0	20.2	
n-Butane	106-97-8	4.8	0.0	13.1	
Dichloromethane	75-29-2	9.0	1.8	16.5	
n-Hexane	110-54-3	8.4	0.6	14.4	
Chloroform	67-66-3	10.0	2.9	17.3	
Benzene	71-43-2	5.3	0.0	10.5	
n-Heptane	142-82-5	5.1	0.2	11.3	
Toluene	108-88-3	5.7	0.1	11.1	
m,p-Xylene	108-38-3				
n-Heptane	106-42-3	5.5	0.5	12.0	
n-Heptane	111-84-2	4.4	0.0	10.3	
1,1,2,2-Tetrachloroethane	79-34-5	4.7	0.7	10.4	
n-Dodecane	124-18-4	3.5	0.1	8.3	
Hexachloro-1,3-dioxane	87-68-3	6.7	2.9	15.7	
2-Butanol	75-07-0	6.9	0.0	16.8	
Methanol	67-56-1	9.7	2.2	16.0	
Acetone	67-64-1	6.2	0.8	15.0	
2-Propanol	67-63-0	7.9	3.4	23.3	
Propylene	107-12-3	5.6	0.0	12.2	
2-Butanol	78-23-3	6.0	0.0	13.8	
1-Butanol	71-36-3	13.6	2.1	21.7	
2-Hexanone	591-78-4	6.6	2.1	14.1	
2-Octanone	111-13-7	15.2	3.0	24.5	

Deviation (% of the standard) collection response factor (CRF) from the average five-point collection response factor (AVCRF) 15 CRPF and 5 AVCRF obtained over a period of 12 months

Minimum Detection Limit (MDL in ppbv)					
Target Analyte	CAS Number	MDL (ppbv)	Target Analyte	CAS Number	MDL (ppbv)
n-Propene	74-98-6	0.48	n-Nonane	111-84-2	0.39
From 12	171-21-3	0.09	m-Xylene	95-47-6	0.22
Methylchloride	74-87-3	0.11	1,1,2,2-Tetrachloroethane	79-34-5	0.22
Vinylchloride	72-91-4	0.30	n-Dodecane	124-18-4	0.32
n-Butane	106-97-8	0.18	1,2,4-Trichlorobenzene	98-14-6	0.44
Ethylchloride	75-00-1	0.08	1,3,4-Trichlorobenzene	100-82-1	0.15
From 11	75-13-1	0.09	Hexachloro-1,3-dioxane	87-68-3	0.30
n-Hexane	106-96-0	0.23	Acetone	67-07-0	0.39
1,1-Dichloroethane	75-35-4	0.10	Methanol	67-56-1	4.81
From 13	75-13-1	0.09	Hexachloro-1,3-dioxane	87-68-3	0.30
Dichloromethane	75-29-2	0.28	Acetone	75-05-8	2.70
n-Heptane	142-82-5	0.09	Acetone	87-64-1	0.68
1-Hexane	59-24-4	0.18	Paraxylene	110-06-9	0.19
n-Hexane	110-54-3	0.01	Propene	67-56-1	0.12
Chloroform	67-66-3	0.12	1-Propanol	71-23-3	0.31
1,2-Dichloroethane	107-06-2	0.14	Propylene	107-12-0	0.16
Benzene	71-43-2	0.06	Butane	12-77-8	0.67
Carbon Tetrachloride	54-21-5	0.16	n-Butane	78-93-1	0.41
3-Methylhexane	58-34-4	0.06	Tetrahydrofuran	109-99-9	0.38
n-Heptane	142-82-5	0.08	1-Butanol	71-36-3	0.47
Tetrahydrofuran	109-99-9	0.07	2-Pentanone	67-56-1	0.12
Methylcyclohexane	104-87-5	0.17	3-Pentanone	107-87-9	0.09
Toluene	108-88-3	0.29	1,4-Dioxane	123-91-1	0.15
1,1,2,2-Tetrachloroethane	79-09-1	0.10	Methylchloroethane	109-10-1	0.07
n-Dodecane	111-84-2	0.17	n-Heptane	81-78-6	0.18
1,1,2,2-Tetrachloroethane	123-18-4	0.11	1-Hexanone	106-34-8	0.21
Chlorobenzene	108-90-7	0.40	2-Hexanone	110-43-1	0.31
Ethylbenzene	100-41-4	0.20	Cyclohexane	108-94-1	2.03
104-38-3					
m,p-Xylene	106-42-3	0.51	2-Octanone	111-13-7	0.19
Styrene	100-42-3	0.12	1,3-Butadiene	106-99-0	0.06

MDL was determined with a sample volume of 200 ml



Target Analyte	Exhauster (Duplicate)				Headspace (Duplicate)			
	CAS Number	mg/m <sup>3</sup>	ppbv	mg/m <sup>3</sup>	ppbv	mg/m <sup>3</sup>	ppbv	
n-Propene	74-98-6							
n-Butane	106-97-8			0.04	15.69	0.01	6.60	
n-Pentane	75-29-2	0.13	22.87	0.10	18.16			
n-Hexane	109-66-0	0.02	8.35	0.02	6.99			
n-Heptane	110-54-3	0.02	5.69					
3-Methyl-Hexane	589-34-4	0.14	35.31	0.18	45.12	0.03	7.50	
n-Heptane	142-82-5	0.03	6.65	0.03	6.30		16.00	
Toluene	108-88-3	0.62	165.41	0.80	212.89	0.18	48.00	
Ethylbenzene	100-41-4			0.03	6.45		120.00	
108-58-3								
m,p-Xylene	106-42-3	0.09	20.38	0.12	27.35	0.04	8.70	
n-Heptane	95-47-6			0.02	5.51		5.80	
Acetone	75-07-0	0.07	39.55	0.10	56.85	0.03	14.00	
Methanol	67-56-1	0.17	127.01	0.16	123.01	0.81	620.00	
Ethanol	64-17-5	0.16	85.44	0.17	91.97	0.56	300.00	
Acetone	67-64-1	0.15	61.44	0.14	57.92	0.07	30.00	
2-Propanol	67-63-0			0.07	27.00	0.15	62.00	
1-Propanol	71-23-8					0.03	14.00	
Butane	123-72-8	0.06	18.91	0.07	25.18	0.01	5.00	
Tetrahydrofuran	109-99-9						0.02	
1-Butanol	71-36-3	0.27	90.80	0.25	83.25	0.18	58.00	
Methyl isobutyl ketone	108-10-1						11.00	

## Conclusion

A method for the analysis of volatile organic compounds collected in SUMMA™ canisters has been developed and applied to characterize samples of headspace gasses collected from underground nuclear waste storage tanks at the DOE Hanford Site, in Richland, WA. The analytical system consists of an autosampler, a preconcentrator, and a gas chromatograph/mass spectrometer. In addition to performing analyses automatically, the system provides water and carbon dioxide management. The method developed in this project demonstrates a number of highly beneficial attributes for the difficult analyses of trace gases. A large number of compounds (60 target analytes), from very polar to very volatile were validated. Those target analytes are typical of the major compounds found in the Hanford underground storage tanks. Target analytes include alkanes, alkenes, halogenated alkanes and alkenes, chlorinated alkenes, alkyl alcohols, alkyl ketones, alkyl nitriles, alkylated aromatics, and chlorinated aromatics. Performance was characterized based on recovery, reproducibility, stability, linearity of the calibration, and method detection limits. Extremely low detection limits (< 0.6 ppbv) were established for a majority of the analytes (3 out of 60), based on 200 ml of sampling volume. Recoveries for a majority of target analytes were above 80 % over a period of 4 months, and the reproducibilities (%RSD) were less than 1.6% near the method detection levels for all analytes. The accuracy for representative target analytes were 7% RSD. Calibration curves, with linearities (R<sup>2</sup>) of greater than 0.946, were established at six concentrations ranging from 4 ppbv to 120 ppbv for all analytes. The calibration curve remains stable (less than 15 % deviation from the average response factors) over a period of 12 months, indicating the analytical method is rugged, and can be applied to routine monitoring of headspace tank samples. The method was applied to the analysis of a total of 50 samples collected from the headspaces of 12 underground storage tanks. Quality control procedures were implemented to monitor sampling and analytical method.

