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**HOLDING TIME STUDY OF VOLATILE ORGANIC COMPOUNDS  
IN SUMMA CANISTERS\***

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# What is TRU Waste?

The U.S. Department of Energy (DOE) is currently storing large quantities of radioactive waste resulting from defense activities conducted during the last fifty years. The radioactivity is largely due to  $^{239}\text{Pu}$  and other isotopes of elements with atomic number equal to or greater than that of uranium, hence the term "transuranic" or "TRU" waste. The radioactive half lives of isotopes in the TRU waste are on the order of 10,000 years making very long-term containment necessary. One plan for disposal of a large quantity of the waste involves permanent burial in a depository approximately 600 m below ground in southeast New Mexico. The burial site, known as the Waste Isolation Pilot Plant (WIPP), consists of large manmade cavities within a salt vein, and temporary buildings and transportation facilities at the site. Any TRU waste to be moved to the site must be characterized and shown to be free of hazardous chemical substances within limits set by regulatory agencies.

# **Headspace Gas Sampling as a Method of Characterizing Mixed Waste**

**A WIPP Quality Assurance Program Plan (QAPP) was established in 1991 for the characterization of waste destined for the WIPP site. According to the plan, gas phase measurements are to be made as a method for monitoring waste by drawing off a sample of air from the headspace intervening between the solid waste and the wall of its container. The sample of headspace gas needs to be analyzed for both combustible and incombustible inorganic gases, and for chemically hazardous volatile organic compounds (VOCs). This paper is concerned with the possible effects on the measured levels of VOCs due to holding the samples beyond four weeks, the normal limit on VOC sample holding times.**

# **What's Special About SUMMA Canisters?**

**The QAPP for sampling and analysis of VOCs is written according to guidelines provided by EPA Method TO-14, "The Determination of Volatile Organic Compounds in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis". The canisters used in this method, known by the trade name SUMMA, are canisters that have been chemically treated to provide an interior surface of chrome-nickel oxide. The treatment gives a surface that avoids the catalytic decomposition of organic compounds sometimes caused by metal surfaces. Inertness of the canister surface is a key consideration in setting holding time limits. Another is the extent of interaction between species in the gaseous matrix. The purpose of this study is to show any changes in VOC levels resulting from prolonged holding of the gas samples.**

# **Is 28 Days the Practical Limit for VOC Holding Time?**

**In sampling waste drums for WIPP, meeting allowable holding time can become a major concern. The difficulty in meeting holding time requirements arises because of preparations needed to relocate and access the drums, the extra precautions necessary when working with radioactivity, and the large number of minor bags contained within the drums needing to be sampled. It is generally necessary to conduct sampling in a batch-wise fashion where a relatively large number of samples is taken at one time. Frequently analysis for a batch of samples can not be completed within the 28 day holding time.**

**For this holding time study two headspace gas samples, together with a duplicate of each were taken from TRU waste drums at Idaho National Engineering Laboratory (INEL) in January 1993. One member of each duplicate pair was analyzed at INEL within one week of collection. The second member of each set was sent to Argonne National Laboratory East (ANL-E) in Illinois in May 1993. At ANL-E the samples were observed by two different pathways. For both the first and second samples, measurement were made of analyte levels throughout a period of three months. Following that period, additional analytes were added to Sample No. 1 and the level of the analytes in both sample 1 and 2 were monitored for an additional three months. The data that were obtained were used as input for statistical tests to detect any change in analyte levels.**

# Collecting the Holding Time Data

Starting from day zero as the day of collection, measurements were made on sample No. 1 on day five (the INEL measurement), then on days 131, 139, and 155. Four analytes above the program required quantitation limit (PRQL) were monitored for the period. In order to monitor the behavior of additional important analytes not present in the field canisters and to observe any rapid change in concentration occurring during the first few days following collection, field sample No. 1 was spiked with additional analytes. The analytes used for spiking were WIPP target compounds selected on the basis of their frequency of occurrence in previously analyzed field samples. The eight selected from a total of 29 WIPP headspace target analytes occurred with a frequency of 15% or greater in field samples at INEL. Following the addition of these analytes to field sample No. 1, a new set of measurements was started on the day of addition, or day zero, and then repeated on days 9, 22, 48, and 92. Measurements on sample No. 2 were made on day 7 (the INEL Measurement) and continued through day 327. Sample No. 2 was observed without the presence of additional analytes.

# Measurement Techniques

The analytical method involved passing an accurately measured volume of sample containing a known concentration of two internal standards through a multi-component Tenax trap (see diagram). The trapped analytes and internal standards were injected into a Hewlett-Packard 5890 gas chromatograph equipped with a wide bore DB624 column. The gas chromatograph was followed by a Hewlett-Packard 5971 mass selective detector. Quantitation of analytes is based on the ratio of the characteristic ion abundance for the analyte to the characteristic ion abundance for a spike internal standard (internal standard method). The quantitative relationship is established using dilutions of certified gas mixtures that give a calibration curve at five levels of concentration. For any given analyte the 5-point calibration curve spans a 25-fold range of concentration. For samples containing analytes at higher concentrations, one or more dilutions are made to bring each of the analytes within the 5-point calibration range.

On each day that measurements were made with the gas chromatograph/mass spectrometer system, instrument tuning was tested with bromofluorobenzene (BFB) and a continuing calibration was run with a standard mixture of the 29 WIPP target analytes.



# Data Analysis

The data collected for Sample 1 and Sample 2 were analyzed using the MINITAB statistical software package (Minitab, Inc., State College, PA). Individual regression analyses were performed for each compound in both samples. Regression analysis assumes that the relationship between holding time, expressed in terms of days, and sample concentration can be described by a straight line. The model for this relationship is expressed as Eq. 1,

$$y_i = \beta_0 + \beta_1 x_i \quad (1)$$

where  $y_i$  is the sample concentration observed after  $x_i$  days,  $\beta_0$  is the  $y$ -axis intercept of the line, and  $\beta_1$  and  $\beta_2$  are determined such that the sum of the squares of the distances from all  $y_i$ 's to the straight line defined by the parameters is minimized. Using this method, a regression model was constructed for each target compound in Sample 1 and Sample 2.

# F-test and t-test

For each regression model, an F-test was performed to see if the slope  $\beta_1$ , is significant. The F-statistic is computed using Eq. 2, where  $SYY$  is the total sum of squares of the  $y_i$ 's,  $RSS$  is the residual sum of squares, and  $n$  is the number of samples.

$$F = \frac{(SYY-RSS)}{\frac{RSS}{(n-2)}} \quad (2)$$

The computed value is then compared with an appropriate value from an F distribution table; if the computed statistic is greater than the table value,  $\beta_1$  is significant to the model, and if it is less than the table value,  $\beta_1$  is not significant.

A second statistic applied to each regression model was the t-test. The t-test checks the specific hypothesis,  $\beta_1 = 0$ . The t-statistic is computed using Eq. 3, where  $SXX$  is the sum of squares for the  $x_i$ 's, and  $RSS$  and  $n$  are as defined above.

$$t = \frac{\beta_1 \sqrt{SXX}}{\sqrt{\frac{RSS}{(n-2)}}} \quad (3)$$

The computed value is then compared with the appropriate value from a t distribution table. If the absolute value of the computed t-value is less than the table value, then  $\beta_1 = 0$ , otherwise,  $\beta_1 \neq 0$ . In cases where  $\beta_1 = 0$ , this indicates that concentration is constant and not related to holding time. Both the F-tests and t-tests performed for each regression model were performed at the 99% confidence level.

# Regression Analysis

<b>Sample 1 Matrix</b> No. of Measurement Sets = 5 Total Days Observation = 92			
Compound Name	$\beta_0$ ppm	$\beta_1$ ppm/day	$\Delta/100$ days %
Methanol	262	-0.0057	-2
Cyclohexane	20.5	-0.0081	-4
Acetone	171	-0.033	-2
1,1-Dichloroethene	8.45	0.00046	+0.5
Methylene Chloride	23.5	-0.0040	-2
1,1-Dichloroethane	11.5	-0.0019	-1.6
Toluene	27.0	0.0046	+1.7
1,1,1-Trichloroethane	228	-0.090	-4
Trichloroethylene	133	0.079	6

<b>Sample 2 Matrix</b> No. of Measurement Sets = 7 Total Days Observation = 327			
Compound Name	$\beta_0$ ppm	$\beta_1$ ppm/day	$\Delta/100$ days %
Methanol	69.7	0.012	1.6
Cyclohexane	2.8	-0.00038	-1.4
Methylene Chloride	9.14	-0.00076	-.08
1,1,1-Trichloroethane	17.7	-0.0050	-2.8

# Statistical Tests

<b>Sample 1 Matrix</b>		
<b>Compound Name</b>	<b>F-test Table Value = 21.20</b>	<b>t-test Table Value = 4.60</b>
<b>Methanol</b>	<b>0.005</b>	<b>-0.07</b>
<b>Cyclohexane</b>	<b>2.91</b>	<b>-1.71</b>
<b>Acetone</b>	<b>1.18</b>	<b>-1.35</b>
<b>1,1-Dichloroethene</b>	<b>0.22</b>	<b>0.47</b>
<b>Methylene Chloride</b>	<b>2.88</b>	<b>-1.70</b>
<b>1,1-Dichloroethane</b>	<b>1.21</b>	<b>-1.10</b>
<b>Toluene</b>	<b>0.79</b>	<b>0.89</b>
	<b>Table Value = 34.12</b>	<b>Table Value = 5.84</b>
<b>1,1,1-Trichloroethane</b>	<b>8.70</b>	<b>-2.95</b>
<b>Trichloroethylene</b>	<b>6.49</b>	<b>2.55</b>

<b>Sample 2 Matrix</b>		
<b>Compound Name</b>	<b>F-test Table Value = 13.75</b>	<b>t-test Table Value = 3.71</b>
<b>Methanol</b>	<b>0.58</b>	<b>0.76</b>
<b>Cyclohexane</b>	<b>0.88</b>	<b>-0.94</b>
<b>Methylene Chloride</b>	<b>0.69</b>	<b>-0.83</b>
<b>1,1,1-Trichloroethane</b>	<b>8.75</b>	<b>-2.96</b>

# Conclusions

When the data for each compound are examined by regression analysis low values of  $\beta_1$  corresponding to changes in concentration with time are observed. However, when statistical tests (F-test and t-test) are applied in each case, the slopes are seen to be not significantly different from zero. That is, the headspace gas sample composition is not measurably changing with time. According to the QAPP the allowable uncertainty in the level of target analytes in the waste storage drums is  $\pm 30\%$ . No appreciable uncertainty is added when the sample gases are stored in SUMMA canisters for periods exceeding the customary 28-day holding time.