PNNL-15648

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Data Quality Issues Associated with the Presence of Chlorinated Hydrocarbons in Tank Vapor Samples

J.C. Evans
J. L. Huckaby

February 2006

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm


This document was printed on recycled paper.

PNNL-15648

Data Quality Issues Associated with the Presence of Chlorinated Hydrocarbons in Tank Vapor Samples

J.C. Evans
J.L. Huckaby

January 2006

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, WA 99352

Abstract

Characterization data for the gases and vapors in the Hanford Site high-level radioactive waste tank headspaces are compiled and available via the TWINS interface (TWINS 2006). A recent re-examination of selected data from TWINS has shown a number of anomalies with respect to compounds that are 1) not expected to be present in the tank based on operational knowledge and 2) not found consistently in the same tank by alternative analysis methods or repeat sampling. Numerous results for two chemicals in particular, cis- and trans-1,2-dichloropropane, are determined here to be suspect based on evidence that they were laboratory contaminants.

1.0 Introduction

Characterization data for the gases and vapors in the Hanford Site high-level radioactive waste tank headspaces are compiled and available via the TWINS interface (TWINS 2006). A recent re-examination of the data has shown a number of anomalies with respect to compounds which are 1) not expected to be present in the tank based on operational knowledge and 2) not found consistently in the same tank by alternative analysis methods or repeat sampling. A particular case in point involved the compounds cis (Z) and trans (E) 1,3-dichloropropene. Table 1 lists the 1,3-dichloropropene headspace data from TWINS, with the tank and date of sampling. While these compounds were observed in a number of tank samples by the U.S. EPA TO-14 analysis method, they were not observed in any sample using the triple sorbent trap (TST) method, an equivalent and equally sensitive analytical procedure.

In most cases, the erratic results were apparent in field blanks as well as in the tank samples. In particular, ambient air blanks, which should not contain the dichloropropenes, often showed a positive result. Ambient air blanks were of two types, those collected manually in the SUMMA sampling canister placed upwind of the tank being sampled, and those collected through the sampling manifold (valved to allow ambient air to enter instead of tank air). Table 1 lists the reported concentrations of both isomers in the ambient air blanks for each event, or indicates the data were previously flagged with a "B" to indicate laboratory blank contamination.

1,3-Dichloropropene was reported in only two tanks where direct measurements of ambient blanks did not indicate a contamination problem, specifically tank U-112 sampled on December 6, 1996 and BY-108 sampled on September 10, 1996. The archival data packages for those samples were examined and findings discussed in Sections 2.0 and 3.0.

2.0 U-112 Sample S6119-b31.255

The sample batch from the U-112 December 1996 sampling event consisted of 6 samples. Only the analysis of S6119-b31.255 (255) sample and its replicate showed any anomaly with respect to chlorinated compounds. There were no ambient air samples analyzed with this batch and the nitrogen continuing calibration blank (CCB) was clean. The 255 sample showed the presence of every single compound in the TO-14 standard with the sole exception of pyridine, a notoriously quirky compound because of its strongly polar character. Pyridine was the only non-detect. All other target compounds were either positive detects or J flagged. All other compounds were present at levels in the range of 10 ppbv except for a few compounds common waste vapors such as 1-butanol, which were at higher levels because they were genuinely present in the tank headspace. The majority of the TO-14 compounds were present at essentially constant levels in a pattern strongly suggestive of contamination by the calibration standard. The other five identical samples from the same sampling event did not show that pattern and, except for the tank associated species, the TO-14 target compounds were all non-detects in those samples.

Table 1. SUMMA Canister cis- and trans-1,2-Dichloropropene TWINS Data

Tank Name	Chemical Name	Sample Date	Field Sample Id	Result Type	Conc. (ppmv)	Data Qualifier Code	Notes	Ref.
B-105	1-Propene, 1,3-dichloro-, (E)-	7/30/1996	S6075-A04.282	Primary	0.0016	J	present in field blank at 0.0014 ppm	1
			S6075-A05.323	Primary	0.0016	J		
			S6075-A06.324	Primary	0.0015	J		
B-105	1-Propene, 1,3-dichloro-, (Z)-	7/30/1996	S6075-A04.282	Primary	0.0016	J	present in field blank at 0.0015 ppm	1
			S6075-A05.323	Primary	0.0017	J		
			S6075-A06.324	Primary	0.0015	J		
B-107	1-Propene, 1,3-dichloro-, (E)-	7/23/1996	S6074-A04.182	Primary	0.0036	J	present in ambient sample at 0.0035 ppm and in field blank at 0.0038 ppm	2
			S6074-A05.208	Primary	0.0036	J		
			S6074-A06.211	Primary	0.0037	J		
B-107	1-Propene, 1,3-dichloro-, (Z)-	7/23/1996	S6074-A04.182	Primary	0.0036	B	B-flagged	2
			S6074-A05.208	Primary	0.0035	B		
			S6074-A06.211	Primary	0.0035	B		
BX-103	1-Propene, 1,3-dichloro-, (E)-	8/1/1996	S6081-A04.028	Primary	0.0020	J	present in ambient sample at 0.00077 ppm	3
			S6081-A05.035	Primary	0.0021	J		
			S6081-A05.035	Duplicate	0.0021	J		
			S6081-A06.060	Primary	0.0019	J		
BX-111	1-Propene, 1,3-dichloro-, (E)-	8/27/1996	S6083-A04.289	Primary	0.0037	J	present in ambient sample at 0.0018 ppm and in field blank at 0.0037 ppm	4
			S6083-A05.290	Duplicate	0.0037	J		
			S6083-A05.290	Primary	0.0035	J		
			S6083-A06.292	Primary	0.0036	J		
BX-111	1-Propene, 1,3-dichloro-, (Z)-	8/27/1996	S6083-A04.289	Primary	0.0037	B	B-flagged	4
			S6083-A05.290	Primary	0.0035	B		
			S6083-A05.290	Duplicate	0.0035	B		
			S6083-A06.292	Primary	0.0035	B		
BY-108	1-Propene, 1,3-dichloro-, (E)-	3/28/1996	S6021-A05.212	Primary	0.0030	BJH	B-flagged	5
			S6021-A06.215	Primary	0.0036	BJH		
BY-108	1-Propene, 1,3-dichloro-, (E)-	3/28/1996	S6021-A07.220	Primary	0.0100	JH	present in ambient sample at 0.0020 ppm and in field blanks at 0.0024 and 0.0019 ppm	5
BY-108	1-Propene, 1,3-dichloro-, (E)-	3/28/1996	S6022-A28.232	Primary	0.0048	BH	B-flagged	5
			S6022-A29.244	Primary	0.0036	BJH		
			S6022-A30.247	Primary	0.0130	BJH		
BY-108	1-Propene, 1,3-dichloro-, (Z)-	3/28/1996	S6021-A05.212	Primary	0.0035	JH	present in ambient sample at 0.0020 ppm and in field blanks at 0.0024 and 0.0019 ppm	5
			S6021-A06.215	Primary	0.0038	JH		
			S6021-A07.220	Primary	0.0100	JH		
			S6022-A28.232	Primary	0.0049	H		
			S6022-A29.244	Primary	0.0037	JH		
			S6022-A30.247	Primary	0.0140	JH		

Table 1. SUMMA Canister cis- and trans-1,2-Dichloropropene TWINS Data (cont'd)

Tank Name	Chemical Name	Sample Date	Field Sample Id	Result Type	Conc. (ppmv)	Data Qualifier Code	Notes	Ref.
BY-108	1-Propene, 1,3-dichloro-, (E)-	9/10/1996	S6092-A04.147	Primary	0.0100	J	ambient samples show contamination of most target analytes	6
			S6092-A05.148	Primary	0.0099	J		
			S6092-A06.150	Primary	0.0110	J		
C-107	1-Propene, 1,3-dichloro-, (Z)-	12/17/1996	S7010-A04.246	Primary	0.0005	B	B-flagged	7
			S7010-A04.246	Duplicate	0.0004	B		
			S7010-A05.254	Primary	0.0005	B		
			S7010-A06.256	Primary	0.0006	B		
S-103	1-Propene, 1,3-dichloro-, (E)-	6/12/1996	S6060-A04.080	Primary	0.0057		present in ambient sample at 0.0030 ppm and in field blank at 0.0047 ppm	8
			S6060-A05.082	Primary	0.0040			
			S6060-A06.083	Primary	0.0040			
S-103	1-Propene, 1,3-dichloro-, (Z)-	6/12/1996	S6060-A04.080	Primary	0.0044	J	present in ambient sample at 0.0031 ppm and in field blank at 0.0034 ppm	8
			S6060-A05.082	Primary	0.0036	J		
			S6060-A06.083	Primary	0.0041	J		
S-106	1-Propene, 1,3-dichloro-, (Z)-	6/13/1996	S6061-A04.097	Primary	0.0032	J	present in ambient sample at 0.0026 ppm	9
			S6061-A05.108	Primary	0.0034	J		
			S6061-A06.120	Primary	0.0033	J		
U-112	1-Propene, 1,3-dichloro-, (E)-	7/9/1996	S6071-A04.093	Primary	0.0041	JH	present in field blank at 0.0042 ppm	10
			S6071-A05.183	Primary	0.0041	JH		
			S6071-A06.333	Primary	0.0045	JH		
U-112	1-Propene, 1,3-dichloro-, (Z)-	7/9/1996	S6071-A04.093	Primary	0.0040	BH	B-flagged	10
			S6071-A06.333	Primary	0.0043	BH		
U-112	1-Propene, 1,3-dichloro-, (E)-	12/6/1996	S6119-b31.255	Primary	0.0093	H	sample shows uniform contamination of all target analytes except pyridine	11
			S6119-b31.255	Duplicate	0.0090	H		
U-112	1-Propene, 1,3-dichloro-, (Z)-	12/6/1996	S6119-b31.255	Primary	0.0092	H		
			S6119-b31.255	Duplicate	0.0087	H		

References:

1. Pool et al. (1997a).
2. Evans et al. (1997a).
3. Evans et al. (1997b).
4. Pool et al. (1997b).
5. Thomas et al. (1997).
6. Evans et al. (1997c).
7. Pool et al. (1997c).
8. Evans et al. (1997d).
9. Evans et al. (1997e).
10. Evans et al. (1997f)
11. Sklarew et al. (1997).

3.0 BY-108 Samples S6092-A04.147, 148, and 150

This package showed essentially the same effect, that of the standard gas mixture components being present at a low level, except that it occurred in all samples in the batch run after the calibration blank (which was clean). Both ambient air samples showed the presence of most target compounds at very low levels near the instrument detection limits. It should be noted that the two compounds of concern for this review were not detected in the ambient samples; however, the pattern of other compounds detected is indicative of contamination by the calibration standard. cis- and trans-1,2-Dichloropropene may simply be detectable with somewhat less sensitivity. The concentration levels shown in the 2 ambient samples were lower than in the tank samples but that is consistent with the fact that the ambient sample aliquots used in the analyses were 5 times larger. The mass recovery was essentially the same on average for most target compounds in the ambient air samples as in the four tank samples, suggesting that the source of contamination was independent of the sample size. That, in turn, suggests a constant source of very low level cross-contamination unrelated to the canisters. Differences in concentration thus would be a calculational artifact tied to the value for sample size.

4.0 Discussion

There is overwhelming evidence that the reported chlorinated compounds were not present in either tank BY-108 or U-112, and that the results were an artifact of contamination associated with the analytical sample introduction system. Thus, there is nothing special about the cis- and trans-1,2-dichloropropene other than the extra attention tied to toxicity. This problem was previously observed in many other samples.

The exact cause remains somewhat unclear. At face value, the results could suggest the canisters themselves had been contaminated somehow. However, the method used to prepare the canisters maintained a very rigorous isolation of the canisters from the TO-14 standard even to the point of being carried out in a different building. Many of the compounds of concern are very volatile and memory effects under vacuum pumping and nitrogen flushing are simply not credible. In any case, most of those canisters had never been exposed to the gas standard at all.

The likely culprit is the Entech® sample introduction system which did have a TO-14 standard plumbed in as a dedicated line for use in running continuing calibration verifications (CCVs) prior to the start of each batch run. Thus, it is likely the source of the contamination was valve leakage within the multiport canister sampling valve feeding the Entech. The reason it does not typically show up in the CCBs is undoubtedly again related to plumbing issues. The CCBs were not run from canisters but rather from a nitrogen line plumbed into the system directly via a completely different pathway. By contrast, ambient air blanks were run as samples and thus represent a better measure of internal blank contamination within the sample introduction system itself. The leakage thus must have occurred between the canister sampling valve and the CCV

input line. The question of why some batches show this effect in all samples and others in only one or two remains but valve leakage is an inherently erratic process.

Based on the examination of data presented, it is recommended that the data for cis- and trans-1,2-dichloropropene listed in Table 1 be indicated as "suspect" in TWINS.

5.0 References

Evans, JC, KH Pool, BL Thomas, KB Olsen, JS Fruchter, and KL Silvers. 1997a. *Headspace Vapor Characterization of Hanford Waste Tank 241-B-107: Results from Samples Collected on 7/23/96*. PNNL-11268. Pacific Northwest National Laboratory, Richland, Washington.

Evans, JC, KH Pool, BL Thomas, DS Sklarew, AV Mitroshkov, JA Edwards, JL Julya, BM Thornton, JS Fruchter, and KL Silvers. 1997b. *Tank 241-BX-103 Headspace Gas and Vapor Characterization Results from Samples Collected on August 1, 1996*. PNNL-11469. Pacific Northwest National Laboratory, Richland, Washington.

Evans, JC, KH Pool, BL Thomas, DS Sklarew, AV Mitroshkov, JA Edwards, JL Julya, BM Thornton, JS Fruchter, and KL Silvers. 1997c. *Tank 241-BY-108 Headspace Gas and Vapor Characterization Results from Samples Collected on September 10, 1996*. PNNL-11503. Pacific Northwest National Laboratory, Richland, Washington.

Evans, JC, KH Pool, BL Thomas, KB Olsen, JS Fruchter, and KL Silvers. 1997d. *Headspace Vapor Characterization of Hanford Waste Tank 241-S-103: Results from Samples Collected on 6/12/96*. PNNL-11259. Pacific Northwest National Laboratory, Richland, Washington.

Evans, JC, KH Pool, BL Thomas, KB Olsen, JS Fruchter, and KL Silvers. 1997e. *Headspace Vapor Characterization of Hanford Waste Tank 241-S-106: Results from Samples Collected on 6/13/96*. PNNL-11260. Pacific Northwest National Laboratory, Richland, Washington.

Evans, JC, KH Pool, BL Thomas, KB Olsen, JS Fruchter, and KL Silvers. 1997f. *Headspace Vapor Characterization of Hanford Waste Tank 241-U-112: Results from Samples Collected on 7/9/96*. PNNL-11265. Pacific Northwest National Laboratory, Richland, Washington.

Pool, KH, JC Evans, BL Thomas, KB Olsen, JS Fruchter, and KL Silvers. 1997a. *Headspace Vapor Characterization of Hanford Waste Tank 241-B-105: Results from Samples Collected on 7/30/96*. PNNL-11299. Pacific Northwest National Laboratory, Richland, Washington.

Pool, KH, JC Evans, BL Thomas, DS Sklarew, AV Mitroshkov, JA Edwards, JL Julya, BM Thornton, JS Fruchter, and KL Silvers. 1997b. *Tank 241-BX-111 Headspace Gas and Vapor Characterization Results from Samples Collected on August 27, 1996*. PNNL-11469. Pacific Northwest National Laboratory, Richland, Washington.

Pool, KH, JC Evans, KB Olsen, JC Hayes, AV Mitroshkov, JA Edwards, JL Julya, BM Thornton, JS Fruchter, and KL Silvers. 1997c. *Tank 241-C-107 Fourth Temporal Study: Headspace Gas and Vapor Characterization Results from Samples Collected on December 17, 1996*. PNNL-11597. Pacific Northwest National Laboratory, Richland, Washington.

Sklarew, DS, KH Pool, JC Evans, JC Hayes, AV Mitroshkov, JA Edwards, JL Julya, BM Thornton, JS Fruchter, and KL Silvers. 1997. *Tank 241-U-112 Headspace Gas and Vapor Characterization: Results for Homogeniety Samples Collected on December 6, 1996*. PNNL-11607. Pacific Northwest National Laboratory, Richland, Washington.

Thomas, BL, KH Pool, JC Evans, KB Olsen, JS Fruchter, and KL Silvers. 1997. *Headspace Characterization of Hanford Waste Tank 241-BY-108: Second Comparison Study Results from Samples Collected on 3/28/96*. PNNL-11271. Pacific Northwest National Laboratory, Richland, Washington.

TWINS 2006. Tank Waste Information Network System. http://twins.pnl.gov.