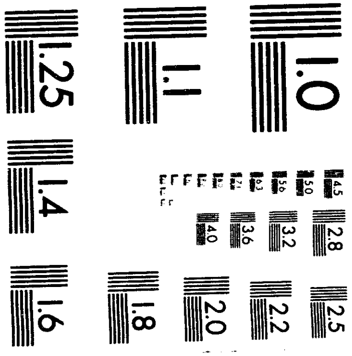
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Progress Toward Resolution of Vapor Problems Associated with Tank 241-C-103

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PROGRESS TOWARD RESOLUTION OF VAPOR PROBLEMS ASSOCIATED WITH TANK 241-C-103

J. L. Huckaby, H. Babad, and M. S. Story

ABSTRACT

Noxious and flammable gases and vapors associated with high-level radioactive waste storage tank 241-C-103 at the Hanford Site are discussed. Focus is on the Westinghouse Hanford Company strategy to characterize the tank headspace. The sampling and analysis methodology is described. Sampling limitations, devices, and equipment are discussed. Results to date are given.

INTRODUCTION

Westinghouse Hanford Company (WHC) has been investigating the potential hazards of noxious gases and vapors emanating from high-level radioactive waste underground storage tanks at the Hanford Site. Between July 1987 and May 1993, 19 health incidents occurred in which tank farm workers were exposed to unknown gases and vapors at unknown concentrations. These incidents involved 34 people, and 6 of the incidents were linked to tank 241-C-103.

To date, knowledge of the gases and vapors in the waste tank headspaces has been inadequate to design cost-effective mitigation. This lack of knowledge has meant that tank farm workers' health could be ensured only by using personal protective equipment that is restrictive, uncomfortable, and introduces its own safety hazards.

As the first step in resolving worker health and safety concerns about waste tank gases and vapors, WHC has developed and is implementing a tank headspace characterization strategy. Characterization of the gases and vapors in the waste tanks is complicated by an array of factors. These include: physical and procedural limitations on tank access; elevated headspace temperatures, which result in headspace air having a dewpoint higher than the ambient air temperature; and gas and vapor concentrations that differ by many orders of magnitude from tank to tank. In addition, for tank 241-C-103, the concentration range and number of analytes far exceed standard, accepted gas analysis methodologies.

BACKGROUND

Tank 241-C-103 will be the first tank to undergo vapor and gas characterization and issue resolution. This tank was constructed in 1943-44 and has a 2,020,000-L (533,000-gal) waste storage capacity. It is covered with approximately 2.13 m (7 ft) of soil, and is accessible only via flanged, vertical pipes (risers). Some of the 13 risers present on the tank are dedicated to instrumentation and equipment, and only 1 has been deemed suitable for installation of vapor sampling equipment.

Many types of radioactive wastes from a wide variety of Hanford Site processes have been stored in tank 241-C-103 during its 50-year history, with each type of waste leaving its signature. The waste storage and transfer history of tank 241-C-103 has been given by Anderson (1), and discussed by Jungfleisch (2) and Carothers (3). Of particular interest is that tank 241-C-103 is thought to be the only Hanford Site high-level waste tank to have a separate organic liquid phase.

The organic liquid phase in tank 241-C-103 is thought to have originated in the plutonium-uranium extraction (PUREX) process (3). Samples of the organic phase, collected in December 1993, appear to support this premise. Sample analysis indicates that roughly 64 weight percent of the organic liquid is tributyl phosphate (TBP), which was the principle extractant of the PUREX process. The PUREX process diluent for TBP, the $C_{11}H_{24}$ to $C_{15}H_{32}$ normal paraffinic hydrocarbons (NPH), make up most of the remaining 36 weight percent.

Recent measurements of the tank 241-C-103 waste level indicate the depth of sludge and aqueous supernate is about 168 cm (66 in.). The layer of organic liquid, which floats on top of the aqueous supernate, was measured in December 1993 and found to be between 3.8 and 5.0 cm (1.5 and 2.0 in.) thick. Using these measurements, the total current waste volume is calculated to be approximately 757,200 L (200,000 gal). The headspace volume is similarly calculated to be about 2,550 m^3 (90,000 ft^3).

Radioactive decay of waste stored in tank 241-C-103 generates heat. Consequently, the waste surface temperature is higher than the temperature of the walls or dome above the waste. This condition can give rise to the formation of an aerosol in the headspace, as warm moist air from near the waste surface rises and is cooled below its dewpoint. Though workers have in the past reported the headspace to be foggy, whether this fog was composed of organic liquid or water droplets is not known. Visual inspections of the headspace in December 1993 and January 1994 indicate that if any aerosol is present in the headspace, it is too diffuse to be observable.

Tank 241-C-103 is passively ventilated to the atmosphere through a high-efficiency particulate air filter, which removes any radiolytic particulates from the tank exhaust. Thus, the tank inhales and exhales as the atmospheric barometric pressure rises and falls. On an average day, about 0.46 percent of the headspace is exchanged with the atmosphere due to barometric pressure fluctuations (4). A small amount of dry air is also introduced at a riser-mounted instrument to prevent condensation and corrosion of the instrument. The rate of air exchange between the tank and the atmosphere is such that the headspace is nearly saturated with vapors from the waste. The fog reported to exist in this tank as late as 1987 could only exist if the headspace were saturated with vapor. Direct evidence from the December 1993 sampling event also supports this premise; vapor condensate was observed to be dripping from the tank dome and risers.

HEADSPACE FLAMMABILITY

Flammability of vapors from the semivolatile NPH and TBP layer, at the headspace temperature of approximately 40 °C, has been estimated by Van Tuyl (5) and Huckaby and Estey (6). They concluded that if these vapors were the only fuel present, the headspace would contain only a small fraction of the lower flammability limit (LFL), and could not support flame propagation. It has been argued, however, that an aerosol of organic liquid droplets could contain enough additional fuel to raise the fuel content of the headspace above the LFL (7). Kummerer (8) has recently employed the MAEROS (9) aerosol modeling program to place an upper bound of 0.22 mg/L on the aerosol mass density. Given the LFL for NPH is about 46 mg/L, this aerosol mass density would not appreciably affect the headspace flammability.

There has been, favorable flammability estimates notwithstanding, the need to measure the actual fuel content of the headspace in tank 241-C-103. Indeed, the flammability issue has had to be addressed before other intrusive activities needed for noxious gas and vapor characterization could proceed.

In addition to vapors from the semivolatile organic liquid waste, there are organic vapors associated with the chemical and radiolytic degradation of the sludge and organic liquid layers. For example, acetone, which is thought to be a degradation product of hexone in the sludge, and n-butanol, which is a degradation product of TBP, are known to be present. These and other volatile organic vapors, which may contribute to the tank 241-C-103 headspace flammability, must be addressed.

Hydrogen, methane, and ammonia are also generated by processes within tank 241-C-103. Complete assessment of the tank headspace flammability requires that concentrations of these gases be determined.

The WHC strategy for identifying and quantifying the tank 241-C-103 flammable headspace constituents involves three steps. The first step, performed in November 1993, was to initially evaluate the concentrations of flammable permanent gases present. The second step, performed in December 1993, was to evaluate the headspace flammability using a calibrated combustible gas meterto determine the total concentration of NPH in the aerosol and vapor phases. The third step, initiated in January 1994, requires that all headspace constituents of significance to the flammability issue be evaluated by collecting and analyzing representative headspace samples. Sampling methods and results to date are discussed below.

FUGITIVE EMISSIONS

The goal of the tank 241-C-103 headspace characterization effort is to determine which gases and vapors are present that could potentially endanger workers' health. Ultimately, characterization data will be used as needed to design mitigation of any noxious gas or vapor problem identified, and to provide WHC Health and Safety with worst-case worker exposure data.

Because of a variety of limitations, initial sampling and analysis efforts will not provide validated quantitative data on all constituents of interest. All data obtained (i.e., whether validated, preliminary, or semiquantitative) will be reviewed by a panel of experts in various fields of toxicology. This toxicology panel will determine which, if any, of the headspace constituents pose any potential risk to workers' health. Methods to quantitatively measure these constituents of toxicological concern will then be validated, and the tank will be resampled as needed to establish the concentrations of these constituents.

SAMPLING AND ANALYSIS METHODS

Characterization of the complex mixture of organic and inorganic components found in tank 241-C-103 represents a significant technical challenge. There are no U.S. Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), or National Institute of Occupational Safety and Health (NIOSH) validated methods for sampling or characterizing the composition of a complex mixture of vapors in a radioactive environment. Some existing EPA, OSHA, and NIOSH standard sampling methods, designed to sample ambient work space environments, have been modified to accommodate the harsher tank dome space conditions. Accepted ambient air analysis methods will be modified and validated to provide quantitative assessment of the headspace constituents.

The vapors and gases in the tank 241-C-103 headspace will be characterized by sampling air from the tank and sending the samples to appropriate laboratories for analysis. Alternative approaches (e.g., in situ analysis using spectroscopic methods, and analysis of sampled air using in-field analytical equipment) require a greater development of technology, and are not discussed here.

Analysis of samples has been complicated by the need to quantitate different constituents that may be present in very high and very low concentrations. For example, it is important to quantitate certain constituents for flammability (such as NPH) which may be present in the hundreds of parts per million by volume (ppmv). It is also important to quantitate carcinogenic constituents (such as benzene) which may be present at less than 0.01 ppmv. This problem is twofold; first, different analytical methods must be employed to address the different concentration ranges, and second, the presence of large quantities of semivolatile organic vapors greatly complicated analysis of trace constituents.

The analytes of interest and their concentrations determine the analytical methods and sampling techniques employed. Organic vapors are analyzed by gas chromatographs in combination with a variety of detectors, such as a mass spectrometer (GC/MS), flame ionization detector (GC/FID), and nitrogen-phosphorous detector (GC/NPD). When applicable, EPA, OSHA, and NIOSH methodologies are applied, such as EPA TO-12 and TO-14 analyses for total non-methane hydrocarbons and speciation of toxic organic compounds, respectively.

Permanent gases such as nitrous oxide and hydrogen are also analyzed by gas chromatography. Acidic and basic inorganic gases, such as NO_2, NO, NH_3, and SO_2, are analyzed by liquid extraction and ion chromatography or ion-selective electrode methods.

SAMPLING DEVICES AND EQUIPMENT

Two general types of sampling devices will be used to characterize the tank 241-C-103 headspace. Whole air sampling devices, which literally collect a sample of the air for concentration and analysis at a laboratory, will be used to measure permanent gases and volatile organic compounds. Analyte trapping devices, which essentially concentrate analytes by adsorption or absorption of the target analytes in some sorbent media, will be used to measure inorganic acidic and basic gases, and vapors of both volatile and semivolatile organic species.

SUMMA canisters are whole air sampling devices, and consist of stainless steel vessels whose walls have been electrochemically and thermally passivated to minimize adsorption of analytes onto the walls. Prior to use, SUMMA canisters are cleaned by a special process and evacuated. Opening a valve on the canister fills the canister with sample air.

Several sorbent traps will be used on tank 241-C-103. These traps use a solid sorbent material packed into small glass or stainless steel tubes. Off-the-shelf analyte-specific sorbent traps will be used to sample acidic and basic inorganic gases (e.g., NO_2, NO, SO_x, and NH_3). OSHA versatile sampler (OVS) traps will be used to collect the vapors and any aerosol of the semivolatile organic compounds (e.g., NPH and TBP). A sorbent trap containing 3 beds of different organic vapor-trapping sorbent media, the triple-sorbent trap (TST), will also be used to sample vapors of volatile and semivolatile organic compounds. Phosphorous-containing organic compounds (e.g., TBP) will also be collected with Depot Area Air Monitoring System (DAAMS) traps.

Two methods will be used to collect representative gas and vapor samples from the waste tanks. The first method involves lowering individual sample-collecting devices into the tank headspace, and is referred to hereafter as in situ sampling (ISS). The second method employs a system of heated transfer tubing, valves, flow control equipment, and an air pump to transport a continuous stream of air from the tank to sampling devices that are located in a climate-controlled mobile laboratory. The equipment associated with this latter method is referred to hereafter as the vapor sampling system (VSS).

ISS has been used to measure the concentrations of NPH in tank 241-C-103. OVS traps were attached by plastic tubing to air flow metering equipment and an air pump. The OVS traps are essentially sorbent tube traps with a glass fiber filter at the inlet, so that any NPH aerosol droplets drawn into the trap would be stopped and coalesced on the filter. A bed of sorbent material, appropriate for adsorbing semivolatile organic vapors, follows the filter. This device was determined by laboratory testing to be effective at trapping NPH aerosols and vapors (10). After being lowered into the tank headspace, a measured amount of air was drawn through each trap, and the NPH removed by liquid extraction and analyzed on a GC/MS (11).

The ISS method has the advantages of being inherently simpler and less expensive than the VSS, and avoids certain potential problems of the VSS such as loss of trace analytes to wall adsorption. It is not currently a viable method for all needed samples, however, such as samples for permanent gases or volatile organic vapors.

The VSS employs: heated transfer tubing; a heated sampling manifold; relatively sophisticated temperature, flow control, and valving technology; and an air pump to draw air, gases, and vapors out of the waste tanks. Different types of sampling devices can be used at different stations of the manifold, all of which are housed with the measurement and control equipment in the mobile vapor sampling laboratory. Use of the VSS involves installation of a special vapor sampling probe into a riser of the tank, while actual sample collection with sampling devices occurs in the VSS mobile laboratory.

The VSS was specifically designed to collect representative samples from warm, moist tanks, even if a fog is present in the headspace. The mobile vapor sampling laboratory has: a SUMMA canister air sampling station that can hold up to 6 SUMMA canisters; a sorbent trap sampling station, which has a 9-sorbent-trap capacity; and a GC/FID used to monitor the sampling event. Advantages of the VSS include the ability to perform sampling in adverse weather conditions, to house a modicum of real-time analytical equipment, and to address high concentrations of organic vapors.

RESULTS

Results of the first 3 tank 241-C-103 vapor sampling events indicate that the fuel content of the headspace is well below levels of concern. The November 1993 sampling event established that the hydrogen concentration in the headspace is about 800 ppmv. This corresponds to about 2 percent of the LFL for hydrogen. Methane was found to be present at about 15 ppmv, or about 0.03 percent of the LFL for methane. The combustible gas meter measurements, obtained during the December 1993 sampling event, were between 4 and 7 percent of the LFL. NPH samples, also collected in December 1993, indicated an average of 0.85 mg/L of NPH in the headspace, or roughly 2 percent of the LFL for NPH. Samples collected using the VSS in January 1994: 1) confirmed earlier hydrogen and methane measurements; 2) established ammonia concentrations of 300 to 500 ppmv, which is well below the ammonia LFL; and 3) lent support to the earlier conclusion that total organic vapor concentrations are moderate relative to the LFL. The December sampling event also established that no aerosol was visibly present in the headspace.

The tank 241-C-103 headspace, however, has been determined to contain high levels of potentially harmful vapors and gases. Preliminary results from vapor sampling for compounds near or above their NIOSH 8-hour time weighted average (TWA) recommended exposure limit (REL) are summarized in Table 1. As indicated in Table 1, NH_3, N_2O, and TBP were found to be above their NIOSH RELs. Analysis for volatile organic compounds in the January 1994 samples has not been completed, so Table 1 should not be considered as complete.

Table 1

Compound	Estimated Concentration (ppmv)	NIOSH 8-hour TWA REL (ppmv)
Ammonia, NH_3	300 - 500	25
Carbon monoxide, CO	23.9	35
Nitrous oxide, N_2O	775 - 947	25
Tributyl phosphate (TBP)	4 - 14	0.2

Table 1. Gas and vapor concentrations observed in the tank 241-C-103 headspace.

Though concentrations of some compounds are higher in the headspace than recommended for a worker's breathing zone, this does not mean that an eminent hazard to tank workers exists. First, tank workers are required to use supplied breathing air when working in the vicinity of tank 241-C-103 or tank 241-C-102, to which the former tank is connected. Second, in-tank gas and vapor concentrations are reduced by dilution with ambient air as tank air is exhausted. And third, workers are typically in the vicinity of any given tank for only short periods of time (several minutes to several hours), and long-term exposure (daily over an extended period) does not occur.

CONCLUSIONS

Purpose, strategy, methodology, and equipment for high-level waste tank headspace characterization at the Hanford Site have been discussed. Specific attention has been given to application of the characterization strategy to tank 241-C-103, the first tank to be characterized. The gas and vapor issues associated with tank 241-C-103 were defined as: 1) the potential flammability of the headspace; and 2) the potential for exposing tank workers to fugitive emissions from the tank.

The tank 241-C-103 headspace flammability was discussed. The basis for concern that the headspace could be flammable, and how headspace sampling has provided strong evidence that the headspace is well below the lower flammability limit, were described. Methods and equipment employed to evaluate the headspace flammability were enumerated. The current estimate of the fuel content of the tank 241-C-103 headspace was given as being between 5.7 and 8.4 percent of the lower flammability limit.

The strategy and equipment needed to characterize the potentially hazardous gases and vapors associated with tank 241-C-103 were described. Two methods of sample collection were identified and discussed: 1) collection of samples by lowering sampling devices into the tank headspace; and 2) transport of air from the headspace to remotely located sampling devices via heated transfer lines. Sample collection devices and their analyses were described. Results obtained to date were presented, though caveated as preliminary. NH_3, N_2O, and tributyl phosphate were measured to be significantly above their NIOSH 8-hour time weighted average recommended exposure limits (TWA/RELs). It was concluded that though potential toxic levels of some compounds are being observed in the tank headspace, current worker protection, chiefly the use of supplied breathing air, is adequate to ensure worker health.

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