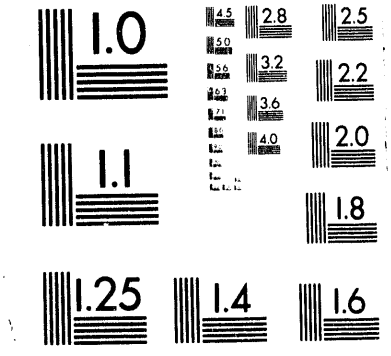
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PNL-9368
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WASTE TANK SAFETY PROGRAM

AEROSOL AND VAPOR CHARACTERIZATION OF TANK 241-C-103: DATA REPORT FOR IN-TANK OVS SAMPLES OBTAINED 12/02/93

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SUMMARY

Waste tank vapor space samples for a flammability analysis and characterization were obtained from Tank 241-C-103, referred to as C-103, in early December 1993. The purpose of this report is to describe the analytical results of these samples and the resulting concentration of normal paraffin hydrocarbons (NPH) in the tank vapor space.

Past reports of a thick fog in the vapor space of C-103 led to a concern that an NPH fog could supply fuel to the vapor space in a form that could not be resolved by standard flammability measurement procedures. The scope of this study was to utilize a previously validated method to determine actual NPH concentrations. In this method, NPH samples were collected in multi-layer aerosol/vapor sorbent tubes inserted into the tank vapor space and analyzed by gas chromotography/mass spectrometry.

Workers noted that no fog was present in C-103 when the samples were obtained. The NPH present in samples from C-103 contained primarily dodecane, tridecane, and tetradecane. The near lack of undecane, the most volatile analyte, was possibly the result of years of preferential evaporation of that analyte from the organic waste layer in the tank. The percentage contribution to total quantifiable NPH, by mass, was constant in all samples at 35.5 ± 1.8, 52.3 ± 2.0, and 12.2 ± 1.7%, for dodecane, tridecane, and tetradecane, respectively. Sampling and analytical uncertainty, based on a laboratory study, was estimated to be ± 21%. The concentration of NPH in the vapor space of C-103, based on the samples and estimated uncertainty, ranged from 0.55 to 1.31 mg/L. To be conservative, use of the 20-min samples was recommended, yielding an NPH concentration of 1.08 ± 0.23 mg/L. While the results indicate that NPH concentrations are low, they would not be representative of conditions that may be present should a fog form in the vapor space of the tank.

ACKNOWLEDGMENTS

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1.0 INTRODUCTION

A floating layer of organic materials on the surface of waste in Tank 241-C-103, referred to as C-103, and anecdotal evidence of a fog in the headspace of the tank have led to concern about potential flammability. This and other issues are the subject of work initiated by Westinghouse Hanford Company (WHC) to characterize the waste and vapor space in C-103 and other waste tanks. The impetus for the current work was provided by a justification of continued operations (JCO), submitted as Appendix A in the environmental assessment of C-103 vapor and liquid characterization activities (U.S. DOE 1993).

The use of flammability meters in the headspace of C-103 was not considered reliable because such instruments are not designed to collect and account for a fuel aerosol, and it was the unknown condensed-droplet component of the aerosol that was of primary concern. Therefore, it was proposed that a sample of the aerosol be collected directly from the headspace and analyzed to determine its composition and potential flammability. To support this effort, a sampling system and an analytical method were developed and validated by Pacific Northwest Laboratory (PNL)[a] to obtain samples for determining the concentration of normal paraffin hydrocarbon (NPH). Measurement of NPH was selected because NPH concentration was related to potential flammability in an assessment by Huckaby and Estey (1993), with an estimated lower flammability limit (LFL) of 46 mg/L.

Samples were obtained from the vapor space of C-103 by WHC on 12/2/93. Results of the samples are provided in this report. Although no dense fog was visible upon inspection of C-103 immediately before sampling, the samples were obtained as planned because the method was suitable for both vapor or vapor mixed with aerosol droplets.

The sorbent-vapor and aerosol-collection substrate and the field sampling system are described in Section 2.0. The analytical method is described in Section 3.0. The results of analyzing samples from C-103 are described in Section 4.0. Conclusions are summarized in Section 5.0. Ambient local meteorological conditions are listed in Appendix A. A summary list of gas chromatography/mass spectrometry (GC/MS) data is included in Appendix B. Actual GC/MS chromatograms are shown in Appendix C.

(a) Operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

2.0 SAMPLING SYSTEM AND OSHA VERSATILE SAMPLER

Because the presence of aerosol droplets might interfere with the use of flammability detectors, a field sampling system was used to measure the concentration of NPH in the headspace of C-103. Controlled flow rates and volumes of the headspace atmosphere were drawn through a sample tube containing a particle filter and two sorbent traps in series. Additional detailed information on the design and use of the sorbent trap and the sampler is available (Ligotke et al. 1993).

2.1 LAYERED-SORBENT SAMPLE COLLECTORS

The NPH content of aerosols in the vapor space of C-103 was measured using sorbent traps designated as Occupational Safety and Health Administration (OSHA) Versatile Samplers, also called OVS (SKC Inc., Eighty Four, Pennsylvania). The OVS, designed to collect particles and vapors in a single tube, contain a high-efficiency glass fiber filter and two XAD-2 sorbent layers, or packed-beds, as shown in Figure 2.1. The 74-mm-long OVS are open glass tubes consisting of two right-cylindrical smoothly joined sections having diameters of 13 mm at the inlet end and 7 mm at the outlet end. Collection media are contained in the larger section. From inlet to outlet, the tube contains a Teflon o-ring, filter, front sorbent layer, middle polyurethane foam (PUF) separator, back sorbent layer, and back PUF. Materials of construction and substrate are purified to ensure low background interference.

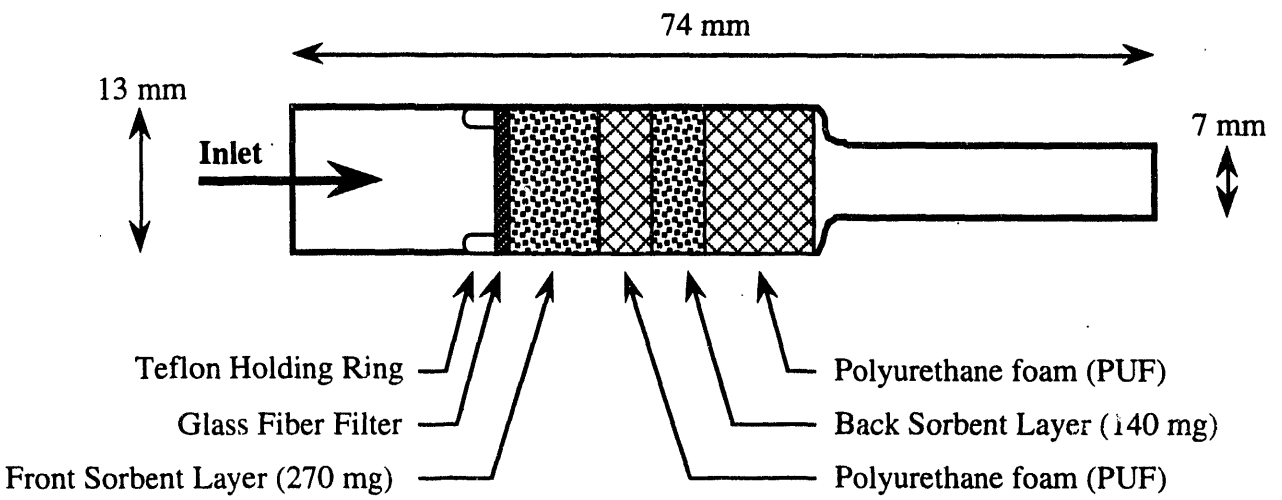

FIGURE 2.1 Schematic of the OSHA Versatile Sampler Used to Sample Normal Paraffin Hydrocarbon Aerosols (shown larger than full-scale)

2.2 PORTABLE FIELD SAMPLING SYSTEM

A portable field sampling system was designed and assembled for use at C-103. The system design provided a robust, redundant manual unit for controlling and verifying flow rate and sample volumes. Because a sample pump was used to draw flow through the OVS, all flow-control valve restrictions were located downstream of the flowmeters to avoid the need to make corrections for low sample line pressures. The system contained two complete sampling units to provide back-up capabilities. In addition to flow rate control, components were included to allow temperature measurement in the tank vapor space and system verification (vacuum leak testing).

A sketch of the sampling system is shown in Figure 2.2. Gas flow was drawn through a sampler into one of two sampling units: Unit A, on the left or Unit B, on the right of the sampler. Unit A was used to sample C-103. Sample flow was passed through a filter-dryer-filter arrangement to contain possible contamination and prevent any condensation from collecting in the system. Color-indicating calcium carbonate was used in the dryers. The filters were high-efficiency Gelman Type AE glass fiber (Gelman Sciences, Ann Arbor, Michigan). The three-way valve was used to initiate sample flow or provide bypass flow from the vented system enclosure. Flow was measured in a precision flowmeter. A 0- to 10-in. H_2O gauge was used to monitor sample line pressure. Further downstream, metering and on-off valves were used to control flow rate. The sample pump was a metal-bellows sample pump (Model 29678M1 MB-302 XP MOD, Parker-Hannifin, Sharon, Massachusetts) approved by WHC for use in the waste tank farms.

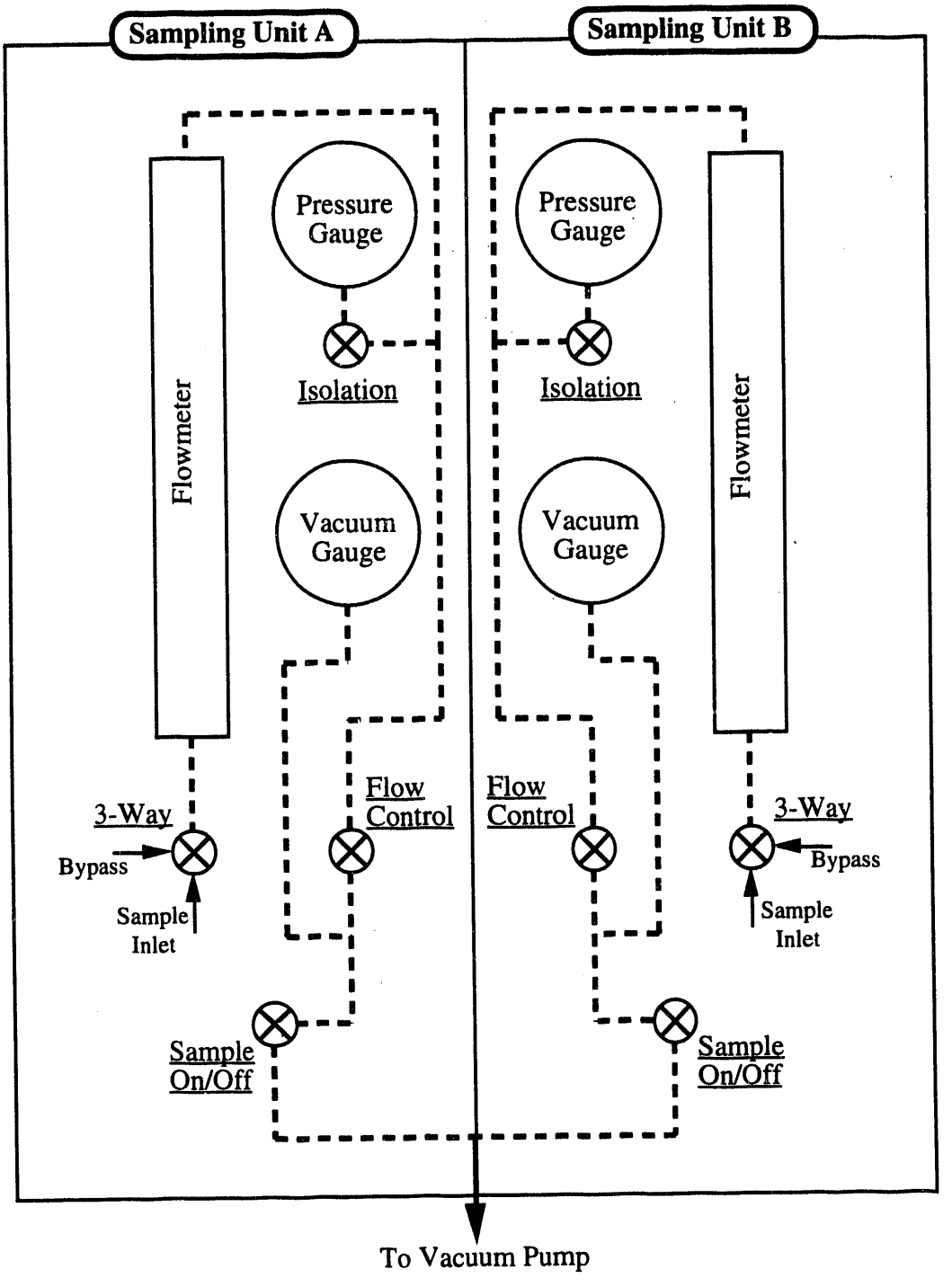

FIGURE 2.2 Portable Field Sampling System for Normal Paraffin Hydrocarbon Aerosols in Waste Tank C-103. Actual locations of sample inlets are in lower outer corners; the inlets are shown at the three-way valves for clarity.

3.0 ANALYTICAL APPROACH

Normal paraffin hydrocarbons are defined as straight chain or normal (n-) alkanes. For the purposes of a laboratory study completed before sampling C-103 (Ligotke et al. 1993), NPH was considered to consist of a mixture of n-alkanes ranging from C_{11} through C_{15}. The NPH data are reported in terms of n-alkanes and quantitated from calibration of n-alkanes using gas chromatography/mass spectrometry (GC/MS). Solutions used in the study were mixtures of C_{11} through C_{15} normal hydrocarbons. These alkanes were chosen because a preliminary analysis of NPH lots showed them to make up about 85% of the total NPH. The GC/MS was calibrated using a solution of mixed n-alkanes ranging from C_{11} to C_{16}. The same mixed n-alkane solution was used to spike known quantities of each analyte onto OVS tubes to evaluate desorption efficiency.

Samples obtained in the vapor space of C-103 were removed from plastic (outer) and aluminum foil (inner) wrappings and each OVS was divided into two portions. The front portion contained the glass fiber filter and the front XAD-2 sorbent bed. The back portion contained the PUF separator, the second XAD-2 sorbent bed, and the PUF plug. Each portion was placed in a labeled 4-mL vial fitted with a Teflon®-lined screw cap.

Samples corresponding to a 4-min sampling time (OVS 4, 5, and 6) were analyzed by GC/MS first. Front and back portions of OVS 4, 5, and 6 were desorbed by adding 1 mL of carbon disulfide to each vial, recapping the vials, and sonicating for 30 min. Portions of the extract were transferred to an auto-sampler vial, to which portions of naphthalene-d_8 internal standard were also added. The remainder was archived against future analyses. Sample OVS 5 was screened by GC/MS to determine if sample analyte concentrations were within the instrument calibration range. From this screening, it was determined that front portions of samples OVS 4, 5, and 6 needed to be diluted 1:5 for quantitative analysis. The back portions of these samples were not diluted.

Samples OVS 1, 2, and 3 were desorbed as above and analyzed without additional dilution. Concentrated samples OVS 9 and 10 were screened by GC/MS to look at undecane (C_{11}) concentrations relative to the dodecane (C_{12}), tridecane (C_{13}), and tetradecane (C_{14}) levels. Undecane (C_{11}) levels seen were significantly low, contributing < 5% to the total analyte found on the sample. Samples OVS 8, 9, and 10 were diluted 1:20 for quantitation by GC/MS. Tributyl phosphate (TBP) was analyzed using GC/MS and selected ion monitoring (SIM) mode.

4.0 RESULTS OF C-103 VAPOR SPACE SAMPLES

Unopened OVS were prepared and provided by PNL to WHC and used to sample the vapor space of C-103. On receipt of exposed samples and data sheets, PNL determined sample volumes and analyzed samples, NPH concentrations, and sampling uncertainty.

4.1 SAMPLE PREPARATION AND FIELD DATA

The tank farm work procedure by Huckaby and Edwards (1993) and a report by Ligotke et al. (1993) provided the basis for the sampling and analysis associated with the "aerosol sampling" task of Sample Job 6 (SJ 6). Minor changes to the tank farm procedure included increasing the sample flow rate to 200 mL/min. These and other changes were recommended and provided to WHC in August 1993 and again shortly before the sampling effort. The electrical grounding procedure, which was covered under a different tank farm procedure, was deleted by WHC.

Sample Preparation: A total of 20 OVS were prepared and provided to WHC on 11/30/93. Label tape, found to withstand a 30-min exposure to 50°C, was used to identify three blanks, three controls, ten samples, and four spares. Each OVS was also labeled by pen on the manufacturer's paper tag. The OVS were labeled "C103/BLK1...3" for Tank Blank 1 to 3, "C103/CTL1...3" for Control 1 to 3, "C103/OVS 1...10" for Sample 1 to 10, and "C103/Spare 1...4" for Spare 1 to 4. Each OVS was placed with a piece of 10- by 15-cm aluminum foil and one set of end caps into a sealed 18- by 20-cm zip-lock plastic bag. The OVS were placed in coolers to avoid inadvertent heating. A second bag with aluminum foil was prepared for each OVS and placed into a second cooler. Each plastic bag was labeled with the code of an OVS sample.

Field Data: The sampling system was checked and provided to WHC for testing during the week of 11/22/93, and sampling was performed on 12/2/93. The system was returned to PNL after sampling for final system checks. In addition to the sampling system, spare parts, including one complete sample line and OVS holder, were provided to ensure that equipment or procedural failure would not compromise the sampling effort. Modifications made to the sampling system in November 1993 included 1) upgrading the sample line driers located on the sampling unit, 2) adding two redundant HEPA filters in stainless holders upstream of each sampling unit's drier, and 3) fabricating and installing new, larger flange plates needed to accommodate changes in the diameter of the tank-riser opening and new electrical grounding requirements.

Samples were obtained from C-103 between 1428 and 1702 h on 12/2/93. Controls were obtained by sampling air in the vicinity of C-103 shortly before the tank was sampled and before 1500 h when it began to rain (ambient meteorological data are listed in Appendix A). Sampling

was performed using the left side (Unit A) of the sampling system. The flowmeter used was a precision valveless variable area rotameter (Aalborg 112-02, serial number 062364, 150-division) having a maximum air flow rate of 374 mL/min. The target flow rate was 200 mL/min, nominally achieved at a centered float reading of 96. Calibration data provided by the WHC Standards Laboratory at 21°C indicated flow rates of 198, 201, and 204 mL/min at float readings of 95, 96, and 97, respectively. Air pressure in the sample line downstream of the flowmeter was always 1 or 2 in. H_2O less than ambient; this indicated that no saturation or overloading of the OVS occurred, and that pressure corrections to sample volume data would not be significant. The temperature indicated by the dial thermometer (T0) located on the sampling system gradually decreased from 10 to 5°C as the sampling progressed, slightly reducing measured flow rates.

Data written on pages 24 through 36 of the field work procedure were provided to PNL. Results of pre-test vacuum checks were not provided, but were prerequisite to performing the sample job. A summary table of sample data was also provided. The correlation used to calculate flow rate based on flowmeter reading was confirmed.

The temperature of the vapor space was measured using two platinum resistance temperature devices (RTD) probes. One probe, T1, was located 9.3 m below the riser flange and about 9 cm above the inlet of the OVS. The second probe, T2, was located 5.5 m below the riser flange. Because of response time, the temperatures measured during 20-min samples likely reflect actual conditions. However, measurements made during the 4-min samples should also have been accurate within about 0.5°C, suggesting that the vapor space temperature was not perfectly stable.

One of the 20-min OVS samples, OVS 7, was destructively sampled by WHC to confirm contamination levels. The remaining samples were received by PNL on 12/3/93, one day after sampling occurred. Sample analysis was initiated on that day. Upon receipt of the samples in ice-cooled containers, the bag containing OVS 8 was removed from the plastic container, placed in another plastic bag, and submitted for gamma energy analysis (GEA). The gamma survey found essentially no gamma-emitting isotopes above background. For ^{60}Co and ^{137}Cs, the results were < 1.2 and < 1 pCi per sample, respectively.

4.2 SAMPLE VOLUMES

Sampling data are summarized in Table 4.1 and Appendix B. Standard conditions represent atmospheric pressure and 21°C, the flowmeter calibration temperature. Actual sample volume refers to the volume of air sampled at actual tank conditions, presuming one atmosphere and a temperature of 40°C, as described in Section 4.1. The difference between T1 and 40°C was

TABLE 4.1 Summary of Sample Job 6 OVS Sampling Data in C-103. Samples were obtained from the tank on 12/2/93.

Sample	Start Time (h)	T0, T1, T2[a] (°C)	Sample Δt (min)	Flowmeter Reading (div)	Actual Flow Rate (L/min)	Sample Volume Actual (L)	Sample Volume Uncertainty (± L)
Ctl 1	1337	10, 12, 12	10.0	96	0.199	1.99	0.11
Ctl 2	1352	10, 13, 12	10.0	95	0.197	1.97	0.11
Ctl 3	1408	10, 12, 11	10.0	97	0.202	2.02	0.11
OVS 1	1428	10, 38, 37	1.0	96	0.219	0.219	0.016
OVS 2	1439	8, 38, 38	1.0	97	0.223	0.223	0.016
OVS 3	1446	8, 38, 38	1.0	97	0.223	0.223	0.016
OVS 4	1452	8, 38, 38	4.0	96	0.219	0.877	0.045
OVS 5	1501	7, 38, 38	4.0[b]	96	0.220	0.878	0.045
OVS 6	1510	7, 38, 38	4.0	96	0.220	0.878	0.045
OVS 7[c]	1519	6, 40, 40	20.0	96	0.220	4.40	0.22
OVS 8	1550	6, 40, 40	20.0	96	0.220	4.40	0.22
OVS 9	1616	5, 40, 40	20.0	96	0.221	4.41	0.22
OVS 10	1642	5, 40, 39	20.0	96	0.220	4.41	0.22

(a) RTD locations described in Section 4.1.
(b) Seconds were not listed on time-of-day at end of 4-min sample, sample duration presumed to be 4.0 min.
(c) OVS 7 was destructively sampled by WHC. No analytical results available.

not significant (< 1%). Uncertainty in sample volume refers to actual conditions and was based on sample duration and flowmeter readings; uncertainties in temperature and pressure measurements were not expected to have had significant impact and were ignored.

4.3 NPH ANALYTE DISTRIBUTION

The GC/MS chromatograms showing analyte distributions of selected samples are included in Appendix C. A summary of the distribution of NPH analytes, from Appendix B, differed from that used in calculations of saturated vapor concentrations and laboratory experiments described by Ligotke et al. (1993). The near lack of C_{11}, the most volatile analyte, was possibly the result of years of preferential evaporation from the waste tank. While C_{11} and C_{15} were present at less than quantifiable levels (< 0.015 mg per sample), the distribution of C_{12}, C_{13}, and C_{14} was constant in all nine analyzed samples. The percentage contribution to total quantifiable NPH, by mass, was 35.5 ± 1.8, 52.3 ± 2.0, and 12.2 ± 1.7%, for C_{12}, C_{13}, and C_{14}, respectively. The high degree of consistency between analyte distribution results from all sample durations (1, 4, and 20 min) provided an indication that both sampling and analytical procedures were performed consistently. The distribution of NPH analytes present in each sample is shown in Figure 4.1.

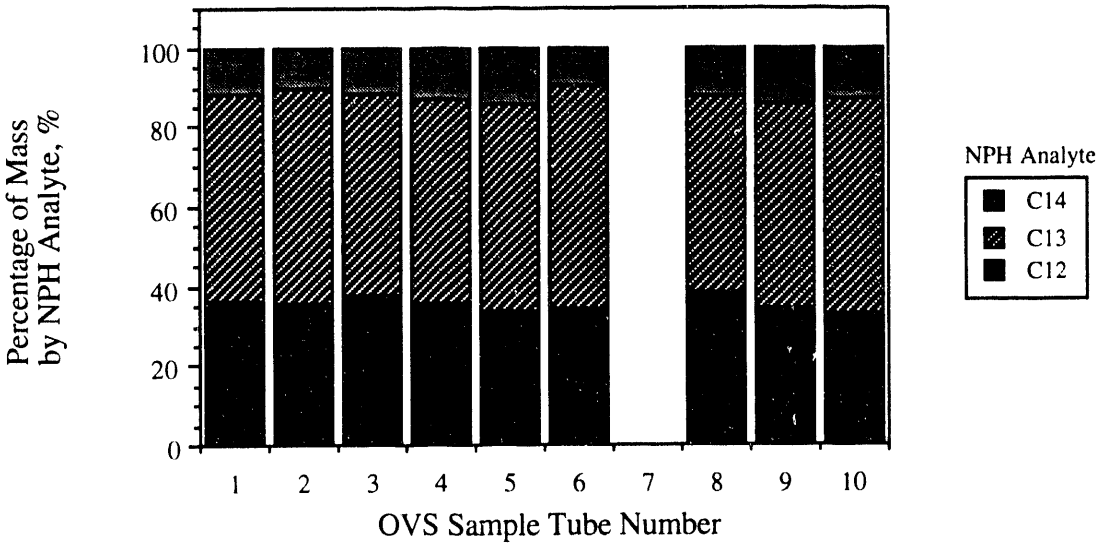

FIGURE 4.1 Distribution of Normal Paraffin Hydrocarbon Analytes Collected in OSHA Versatile Samplers. Results of in-tank samples of the vapor space of C-103 on 12/2/93. Sample OVS 7 was not analyzed.

4.4 NPH MASS COLLECTED IN OVS

The total mass of NPH analytes present in exposed OVS was determined by adding the contributions of C_{12}, C_{13}, and C_{14}. A summary of analytical results, based on information in Appendix B, is shown in Table 4.2. The results were corrected for experimentally-determined adsorption of NPH in the OVS. The majority of NPH was found in the front sections of the exposed OVS; only 0 to 6% of total NPH was found in the back sections. This indicates that no breakthrough of NPH occurred, confirming the results of a laboratory study (Ligotke et al. 1993).

Sample durations of 1 to 20 min were selected to yield useful data whether NPH concentrations in the tank vapor space were dilute or concentrated. (For example, the 1-min samples were obtained to provide a source of data if very high NPH concentrations actually caused the 20-min samples to overload.) Because NPH levels in C-103 were not highly concentrated, NPH analytes were collected in OVS at levels within the range of the analytical procedure. No analyte was detected in any of the controls that exceeded the limit of quantifiable detection (0.015 mg/sample), and only one analyte, C_{12}, was clearly observed in a single control. Masses of C_{11} and C_{15} in the samples were ≤ 0.015 mg and were ignored. Based on greatest levels of NPH collected (during the 20-min samples), the contribution of C_{11} and C_{15} was less than 1%. Masses of C_{12} through C_{14} ranged from 0.02 to 2.5 mg/sample, and total NPH ranged from 0.15 to 4.9 mg/sample.

TABLE 4.2 NPH Mass in OVS Samples from C-103. Samples were obtained from the tank on 12/2/93. Corrected for adsorption efficiency. Uncertainty = ± 20%.

Sample	NPH Mass in Sample (mg)					Total (mg)	Uncertainty (mg)
	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}		
Ctl 1	NQ[a]	NQ	NQ	NQ	NQ		
Ctl 2	NQ	NQ	NQ	NQ	NQ		
Ctl 3	NQ	NQ	NQ	NQ	NQ		
OVS 1	NQ	0.067	0.094	0.022	NQ	0.183	0.037
OVS 2	NQ	0.064	0.097	0.019	NQ	0.180	0.036
OVS 3	NQ	0.055	0.075	0.017	NQ	0.147	0.029
OVS 4	NQ	0.244	0.352	0.090	NQ	0.686	0.14
OVS 5	NQ	0.206	0.314	0.087	NQ	0.607	0.12
OVS 6	NQ	0.189	0.306	0.051	NQ	0.546	0.11
OVS 7[b]							
OVS 8	NQ	1.81	2.32	0.566	NQ	4.69	0.94
OVS 9	NQ	1.69	2.53	0.698	NQ	4.91	0.98
OVS 10	NQ	1.54	2.55	0.619	NQ	4.71	0.94

(a) NPH Analyte mass in sample was "NQ", less than quantifiable (< 0.015 mg).
(b) OVS 7 was destructively sampled by WHC. No analytical results are available.

4.5 NPH CONCENTRATION AND UNCERTAINTY

The concentration of NPH in the vapor space of C-103, based on the OVS samples obtained on 12/2/93, were determined by ratioing the mass of NPH present in each OVS to the volume of air sampled from the tank vapor space using Equation (4.1):

$$C_m = MQ^{-1}t^{-1} \tag{4.1}$$

where C_m is NPH mass concentration in mg/L, M is NPH mass in mg, Q is actual sample flow rate in L/min, and t is sample duration in min. The total sampling and analysis uncertainty, W_C, for the OVS samples, as determined by Ligotke et al. (1993) under laboratory conditions, was determined as

$$W_C = [(W_M/Qt)^2 + (-MW_Q/Q^2t)^2 + (-MW_t/Qt^2)^2]^{1/2} \tag{4.2}$$

where W_M, W_Q, and W_t are uncertainties in NPH mass (± 20%), flow rate (± 0.011 L/min), and sample duration (± 3 s), respectively. The overall uncertainty was 21% for each sample obtained from C-103. Differences in sampling duration were overshadowed by the analytical uncertainty and caused the overall calculated uncertainty to vary by less than 1%.

The range of NPH concentrations was 0.62 to 1.11 mg/L, as shown in Table 4.3. Average NPH concentrations were 0.77 ± 0.10, 0.70 ± 0.08, and 1.08 ± 0.02 mg/L, based on each set of three OVS obtained using sample durations of 1, 4, and 20 min, respectively. Considering the estimated combined sampling and analysis uncertainty, the range of average concentrations would be 0.61 to 0.93, 0.55 to 0.85, and 0.85 to 1.31 mg/L for sample durations of 1, 4, and 20 min, respectively. While this analysis would indicate that the NPH concentration was about 0.85 mg/L (the only concentration common to all three sets of samples), we believe that extrapolating the laboratory-derived uncertainty to field samples may not be entirely appropriate because of possible unknown sources of errors present in the field. Consequently, and to provide conservative results, we recommend that the 20-min samples be selected for the determination of NPH concentration. Doing so, the concentration of NPH in the vapor space of C-103, based on the OVS samples obtained on 12/2/93, was 1.08 ± 0.23 mg/L.

4.6 OTHER ANALYTICAL RESULTS

Based on screenings of concentrated and diluted extracts of OVS, C_{12} through C_{14} concentrations that have been reported constitute about 90% of the portion of the material present on the OVS that can be detected by GC/MS. Compounds other than NPH analytes were also indicated in the OVS sample GC/MS chromatograms. Except for TBP, these other compounds were not quantified. The most abundant compounds eluted near the retention times of C_{12} and C_{13}. An initial screening of the spectra indicated that the compounds were branched alkanes. Concentrated samples of OVS 9 and 10 were screened on a second GC/MS to look for TBP, but no quantitation was performed. Ions used to identify TBP could not be distinguished from the background instrument noise. However, front and back portions of samples OVS 8, 9, and 10 were also analyzed using the selected ion monitoring mode to increase the sensitivity for the ions used to identify TBP.

Quantities of TBP greater than the 50 µg per sample detectability limit only exceeded background in the front portions of the 20-min samples. The maximum measured quantity of TBP was 180 µg, collected in OVS 9. This is equivalent to 41 mg/m^3 (3.9 ppm). *(Conversion from concentration in mg/m^3 to ppm was made as $C_{ppm} = (C_{mg/m^3})(R)/(MW)$, where R is 25.7 L/mole at 40°C and MW is 266.3.)* Sample OVS 8 contained 80 µg TBP, resulting in an air concentration of 18 mg/m^3 (1.7 ppm), and OVS 10 contained 120 µg TBP for 27 mg/m^3 (2.6 ppm).

It should be noted that n-butanol, a known degradation product of TBP, could not be determined by the methods used in this study. This is because the OVS tubes were desorbed using carbon disulfide, which masks the GC/MS response of n-butanol.

TABLE 4.3 Total NPH Mass Concentration in OVS Samples from C-103. Based on data listed in Tables 4.1 and 4.2 and described in Appendix B.

Sample	Actual Sample Volume (L)	Total NPH Mass (mg)	NPH Concentration (mg/L)	Uncertainty (mg/L)
Ctl 1	1.99	NQ[a]	ND[b]	ND
Ctl 2	1.97	NQ	ND	ND
Ctl 3	2.02	NQ	ND	ND
OVS 1	0.219	0.183	0.84	0.18
OVS 2	0.223	0.180	0.81	0.17
OVS 3	0.223	0.147	0.66	0.14
OVS 4	0.877	0.686	0.78	0.16
OVS 5	0.878	0.607	0.69	0.14
OVS 6	0.878	0.546	0.62	0.13
OVS 7[c]	4.40	ND	ND	ND
OVS 8	4.40	4.69	1.07	0.22
OVS 9	4.41	4.91	1.11	0.23
OVS 10	4.41	4.71	1.07	0.22

(a) NPH analyte mass in sample was "NQ", less than quantifiable (< 0.015 mg).
(b) Result was "ND", not determined.
(c) OVS 7 was destructively sampled by WHC. No analytical results are available.

5.0 CONCLUSIONS

The vapor space of waste tank C-103 was sampled and analyzed for normal paraffin hydrocarbon (NPH) analytes using a method developed and validated in a previous laboratory study. The measurements were performed based in part on the possibility for aerosol NPH to increase the potential fuel load present in the tank's vapor space. Despite past reports of a thick fog in the tank, no fog other than a localized light mist near the riser, and perhaps near the waste surface, was noted during the sampling effort on 12/2/93. Sample data are reported to assist the flammability assessment and chemical characterization of the tank vapor space. Samples were obtained by inserting multi-stage aerosol/vapor sorbent traps called OVS to within 1 m of the waste surface and drawing known volumes of air from the vapor space through the OVS. Sampling was controlled using a manual flow control system constructed to meet quality and safety requirements.

The amount of NPH analytes present in the sample was determined using a gas chromatography/mass spectrometry technique developed during the laboratory study. That the NPH was effectively collected in the OVS sorbent layers was demonstrated in the laboratory study and in the samples obtained from C-103 in which only 0 to 6% of the total NPH mass was collected in the back (or secondary) sorbent layers. The NPH present in the OVS from C-103 contained primarily C_{12}, C_{13}, and C_{14} analytes. The near lack of C_{11}, the most volatile analyte, was possibly the result of years of preferential evaporation of that analyte from the organic waste layer in the tank. While C_{11} and C_{15} were present at less than quantifiable levels (< 0.015 mg per sample), the analytes C_{12}, C_{13}, and C_{14} were present in all nine samples. The percentage contribution to total quantifiable NPH, by mass, was constant in all samples at 35.5 ± 1.8, 52.3 ± 2.0, and 12.2 ± 1.7%, for C_{12}, C_{13}, and C_{14}, respectively.

Including an overall laboratory-derived sampling and analysis uncertainty of ± 21%, and based on the OVS samples, the concentration of NPH in C-103 was 0.55 to 1.31 mg/L. To be conservative, use of the 20-min samples was recommended, resulting in an NPH concentration of 1.08 ± 0.23 mg/L. The concentration of NPH in C-103 was similar to the 1.3 mg/L saturation concentration estimated, based on vapor pressure estimates at 40°C and an analyte distribution of NPH that included C_{11}. Because analytical results indicated that less C_{11} was actually present in the tank vapor space, the actual saturation concentration of NPH in C-103 was likely less than the estimated value, indicating that the vapor space is saturated or nearly saturated with NPH.

While present results indicate that NPH concentrations are low, they would not be representative of conditions that may be present should a fog form in the vapor space of C-103.

6.0 REFERENCES

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APPENDIX A

AMBIENT LOCAL METEOROLOGICAL CONDITIONS

APPENDIX A

AMBIENT LOCAL METEOROLOGICAL CONDITIONS

Meteorological data obtained during 12/02/93 are shown in Table A.1. Data listed in the table in bold type were obtained during the actual sampling period. Included in the list are data collected at the portable meteorological station located at the C tank farm (just northwest of the boundary fence), the 200 East Area meteorological station southwest of the tank farm, and surface measurements at the Hanford Meteorological Station several kilometers northwest of the tank farm. Data are hourly averages of wind speeds (m/s), wind directions (degrees, true north), air temperatures (°C), sea level pressure (mb and in. Hg), relative humidity (%), precipitation (hourly totals, mm), and solar energy (W/m^2). Wind measurement was made at an elevation of 2 m at the C tank farm, and 10 m at the Hanford station in 200 East Area.

The wind speeds were light and the direction variable during most of the day. During the afternoon, the direction shifted from easterly to southwesterly, and rain began during the hour ending 1500 Pacific Standard Time (PST). The rain totaled 3.5 mm (0.14 in) for the day. The temperature, about 9 °C in early afternoon, dropped to about 7 °C with the rain. The barometric pressure was relatively high and steady throughout the day, and the solar radiation data suggest heavy overcast.

Table A.1 Hourly Average Meteorological Data Obtained at and Near Tank C-103, 12/2/93 (Julian Date 336). Data listed in bold type were obtained during the actual tank sampling interval.

PST	C-Tank Farm Met. Station:						200E Met. Station:			Hanford Met. Station:	
Hour Ending (h)	Air Temperature (°C)	Relative Humidity (%)	Wind Direction (deg.)	Wind Speed (m/s)	Air Pressure (mb)	Air Pressure (in.Hg)	Air Temperature (°C)	Wind Direction (deg.)	Wind Speed (m/s)	Precipitation (mm)	Solar Radiation (W/m^2)
0100	6.4	70	296	3.0	1025	30.25	7.2	290	5.8	0.0	0
0200	6.9	65	264	4.6	1025	30.28	7.8	260	7.6	0.0	0
0300	7.2	59	269	4.5	1027	30.33	6.7	270	7.2	0.0	0
0400	6.1	60	257	3.4	1028	30.36	5.0	260	6.3	0.0	0
0500	4.8	64	242	1.9	1030	30.40	6.7	250	3.6	0.0	0
0600	4.7	63	255	1.7	1031	30.43	3.9	260	3.1	0.0	0
0700	4.1	66	241	1.4	1031	30.45	3.3	280	1.8	0.0	0
0800	3.7	68	213	0.8	1032	30.48	2.2	160	1.3	0.0	14
0900	5.1	65	227	0.4	1033	30.51	4.4	100	0.9	0.0	35
1000	4.9	71	228	1.1	1033	30.51	4.4	220	1.3	0.0	42
1100	5.7	67	222	0.9	1034	30.52	6.7	220	1.3	0.0	63
1200	7.3	59	202	1.0	1033	30.50	7.2	200	1.8	0.0	15
1300	8.6	54	96	0.5	1033	30.50	8.9	160	0.4	0.0	16
1400	**8.8**	**56**	**136**	**0.9**	**1033**	**30.49**	**9.4**	**150**	**1.8**	**0.0**	**77**
1500	**8.6**	**59**	**195**	**1.2**	**1033**	**30.49**	**8.9**	**190**	**2.2**	**0.1**	**21**
1600	**7.0**	**80**	**240**	**1.5**	**1033**	**30.51**	**6.7**	**240**	**3.1**	**1.0**	**0**
1700	**6.0**	**87**	**240**	**1.6**	**1033**	**30.51**	**6.7**	**230**	**2.7**	**1.5**	**0**
1800	5.5	91	96	0.4	1033	30.50	6.7	100	1.3	0.3	0
1900	5.1	94	61	0.3	1033	30.49	6.7	120	0.9	0.3	0
2000	5.4	91	159	1.0	1032	30.49	6.1	140	2.2	0.3	0
2100	5.9	87	167	1.9	1032	30.47	5.0	150	3.1	0.1	0
2200	6.0	85	168	1.7	1031	30.46	5.0	160	3.1	0.0	0
2300	5.8	86	152	1.6	1031	30.44	5.0	140	2.7	0.0	0
2400	4.4	93	13	0.6	1031	30.43	3.9	70	1.3	0.0	0
	C-farm: Portable meteorological station just outside of fence to the northwest, wind measured at an elevation of 2 m.						200E: Hanford Meteorology Station southwest of C-farm, wind at 10 m.			HMS: Hanford Meteorology Station at 622R, surface conditions.	

APPENDIX B

ANALYTICAL GC/MS DATA AND NPH QUANTITIES IN OVS

TABLE B.1 Aerosol Sample Data Summary (Sample Job 6a)

Sample	Date	Sample Conditions: T Ambient (°C)	T1 (°C)	T2 (°C)	~ RH Tank (%)	Calculated Saturated Water (mg/L)	Estimated Saturated NPH (mg/L)
Controls (Ambient Air Above Riser):							
Ctl 1	12/2/93	10	12	12	nd	10.7	nd
Ctl 2	12/2/93	10	13	12	nd	11.4	nd
Ctl 3	12/2/93	10	12	11	nd	10.7	nd
Aerosol Samples (In-Tank Vapor Space):							
OVS 1	12/2/93	10	38	37	nd	46.3	1.15
OVS 2	12/2/93	8	38	38	nd	46.3	1.15
OVS 3	12/2/93	8	38	38	nd	46.3	1.15
OVS 4	12/2/93	8	38	38	nd	46.3	1.15
OVS 5	12/2/93	7	38	38	nd	46.3	1.15
OVS 6	12/2/93	7	38	38	nd	46.3	1.15
OVS 7	12/2/93	6	40	40	nd	51.3	1.34
OVS 8	12/2/93	6	40	40	nd	51.3	1.34
OVS 9	12/2/93	5	40	40	nd	51.3	1.34
OVS 10	12/2/93	5	40	39	nd	51.3	1.34

Note: nd = "not determined".

TABLE B.1 (contd.)

Sample	Sampling System Data: Δt (min)	Flowmeter Reading (divisions)	Sample Line Δp (in.-H2O)	Indicated Sample Flow Rate (mL/min)	Actual Sample Flow Rate (mL/min)	Actual Sample Volume (L)	Volume Uncertainty (± L)
Controls (Ambient Air Above Riser):							
Ctl 1	10.0	96	-1	201	199	1.99	0.11
Ctl 2	10.0	95	-1	198	197	1.97	0.11
Ctl 3	10.0	97	-2	204	202	2.02	0.11
Aerosol Samples (In-Tank Vapor Space):							
OVS 1	1.0	96	-2	201	219	0.219	0.016
OVS 2	1.0	97	-2	204	223	0.223	0.016
OVS 3	1.0	97	-2	204	223	0.223	0.016
OVS 4	4.0	96	-1	201	219	0.877	0.045
OVS 5	4.0	96	-1	201	220	0.878	0.045
OVS 6	4.0	96	-1	201	220	0.878	0.045
OVS 7	20.0	96	-2	201	220	4.40	0.22
OVS 8	20.0	96	-2	201	220	4.40	0.22
OVS 9	20.0	96	-2	201	221	4.41	0.22
OVS 10	20.0	96	-1	201	220	4.41	0.22

Note: Actual conditions during aerosol sampling were determined using 40 °C.

TABLE B.1 (contd.)

Sample	Analytical Results: C11 (mg)	C12 (mg)	C13 (mg)	C14 (mg)	C15 (mg)	Total NPH (mg)	20% Analytical Uncertainty (± mg)	Actual NPH (mg/L)
Controls (Ambient Air Above Riser):								
Ctl 1	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	nd	nd	nd
Ctl 2	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	nd	nd	nd
Ctl 3	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	nd	nd	nd
Aerosol Samples (In-Tank Vapor Space):								
OVS 1	< 0.015	0.067	0.094	0.022	< 0.015	0.183	0.037	0.84
OVS 2	< 0.015	0.064	0.097	0.019	< 0.015	0.180	0.036	0.81
OVS 3	< 0.015	0.055	0.075	0.017	< 0.015	0.147	0.029	0.66
OVS 4	< 0.015	0.244	0.352	0.090	< 0.015	0.686	0.137	0.78
OVS 5	< 0.015	0.206	0.314	0.087	< 0.015	0.607	0.121	0.69
OVS 6	< 0.015	0.189	0.306	0.051	< 0.015	0.546	0.109	0.62
OVS 7	nd	nd	nd	nd	nd	nd	nd	nd
OVS 8	< 0.015	1.808	2.320	0.566	< 0.015	4.694	0.939	1.07
OVS 9	< 0.015	1.688	2.527	0.698	< 0.015	4.913	0.983	1.11
OVS 10	< 0.015	1.542	2.547	0.619	< 0.015	4.708	0.942	1.07

Note: OVS 7 was destructively sampled before analysis.

TABLE B.1 (contd.)

Sample	Mass/Time Ratio	% C12	% C13	% C14
Controls (Ambient Air Above Riser):				
Ctl 1	nd	nd	nd	nd
Ctl 2	nd	nd	nd	nd
Ctl 3	nd	nd	nd	nd
Aerosol Samples (In-Tank Vapor Space):				
OVS 1	0.18	36.7	51.4	11.9
OVS 2	0.18	35.6	53.9	10.5
OVS 3	0.15	37.5	51.2	11.3
OVS 4	0.17	35.6	51.3	13.1
OVS 5	0.15	33.9	51.7	14.3
OVS 6	0.14	34.6	56.1	9.3
OVS 7	nd	nd	nd	nd
OVS 8	0.23	38.5	49.4	12.1
OVS 9	0.25	34.4	51.4	14.2
OVS 10	0.24	32.8	54.1	13.1
	Average:	35.5	52.3	12.2
	± 1 Std Dev:	1.8	2.0	1.7

APPENDIX C

ACTUAL GC/MS CHROMATOGRAMS FROM OVS SAMPLES

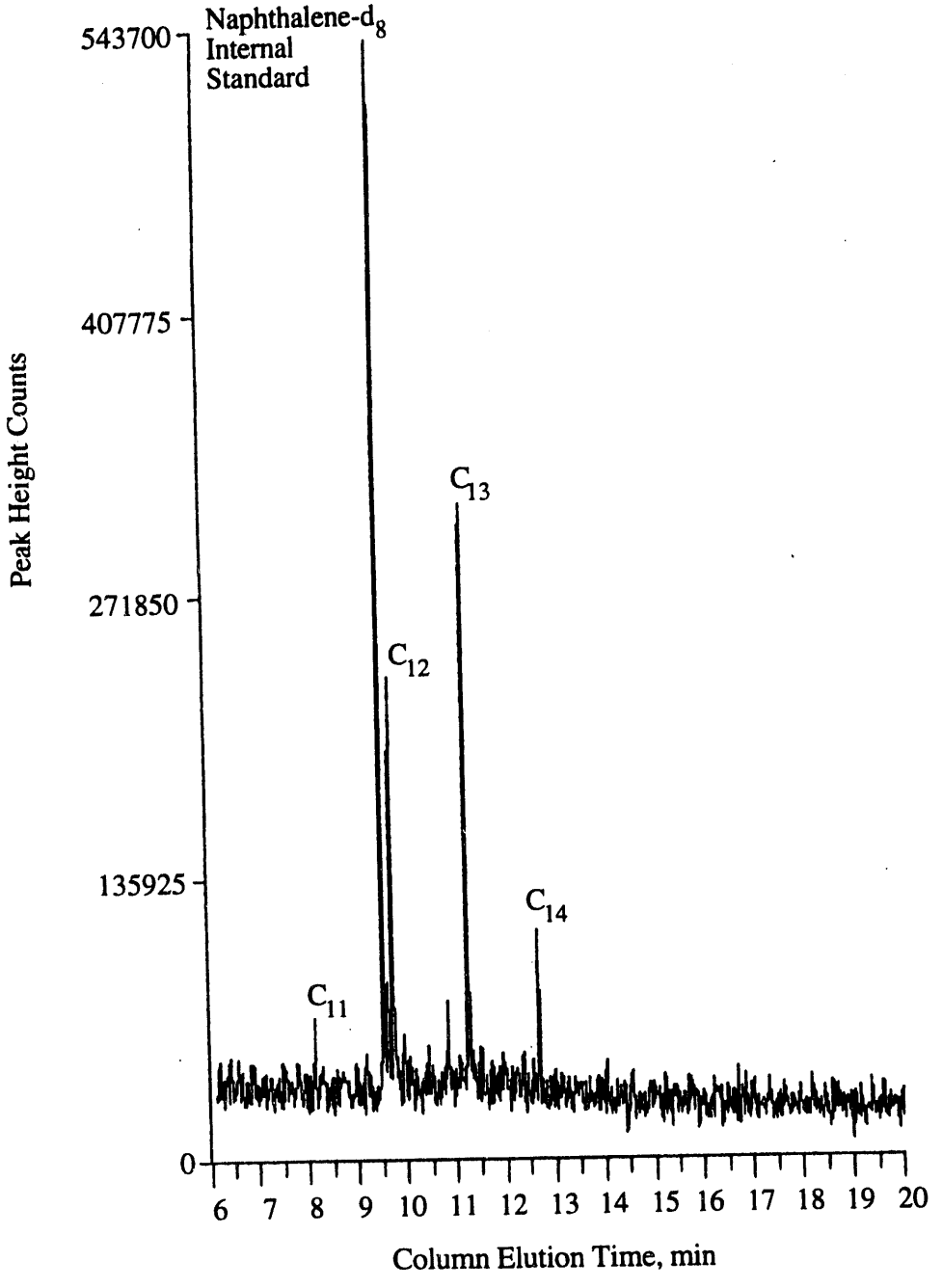

FIGURE C.1 GC/MS Total Ion Chromatogram of Waste Tank 241-C-103 Sample C103/OVS 6, Front OVS Portion, Extract Diluted 1:5 in CS_2. After initial screening by GC/MS, the sample was diluted into the calibration range for quantitation. The internal standard, Napthalene-d_8, was used to quantitate chromatographic peaks associated with NPH analytes with responses greater than 2.5 times the level of background noise (C_{12}, C_{13}, and C_{14}).

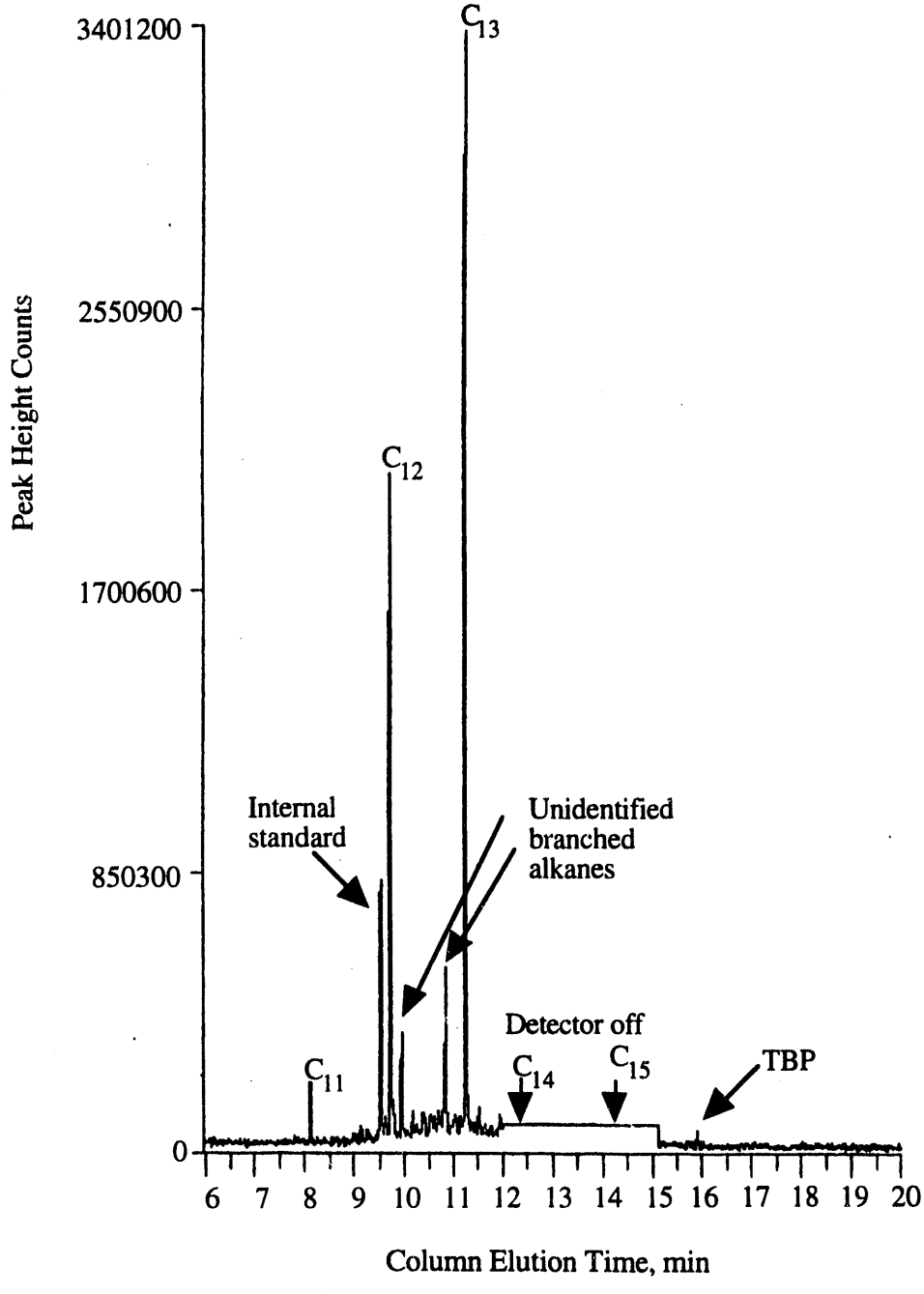

FIGURE C.2 GC/MS Total Ion Chromatogram of Waste Tank 241-C-103 Sample C103/OVS 6, Front OVS Portion, Undiluted Extract. The sample (the same as Figure C.1) was screened by GC/MS to look for evidence of quantifiable tributyl phosphate.

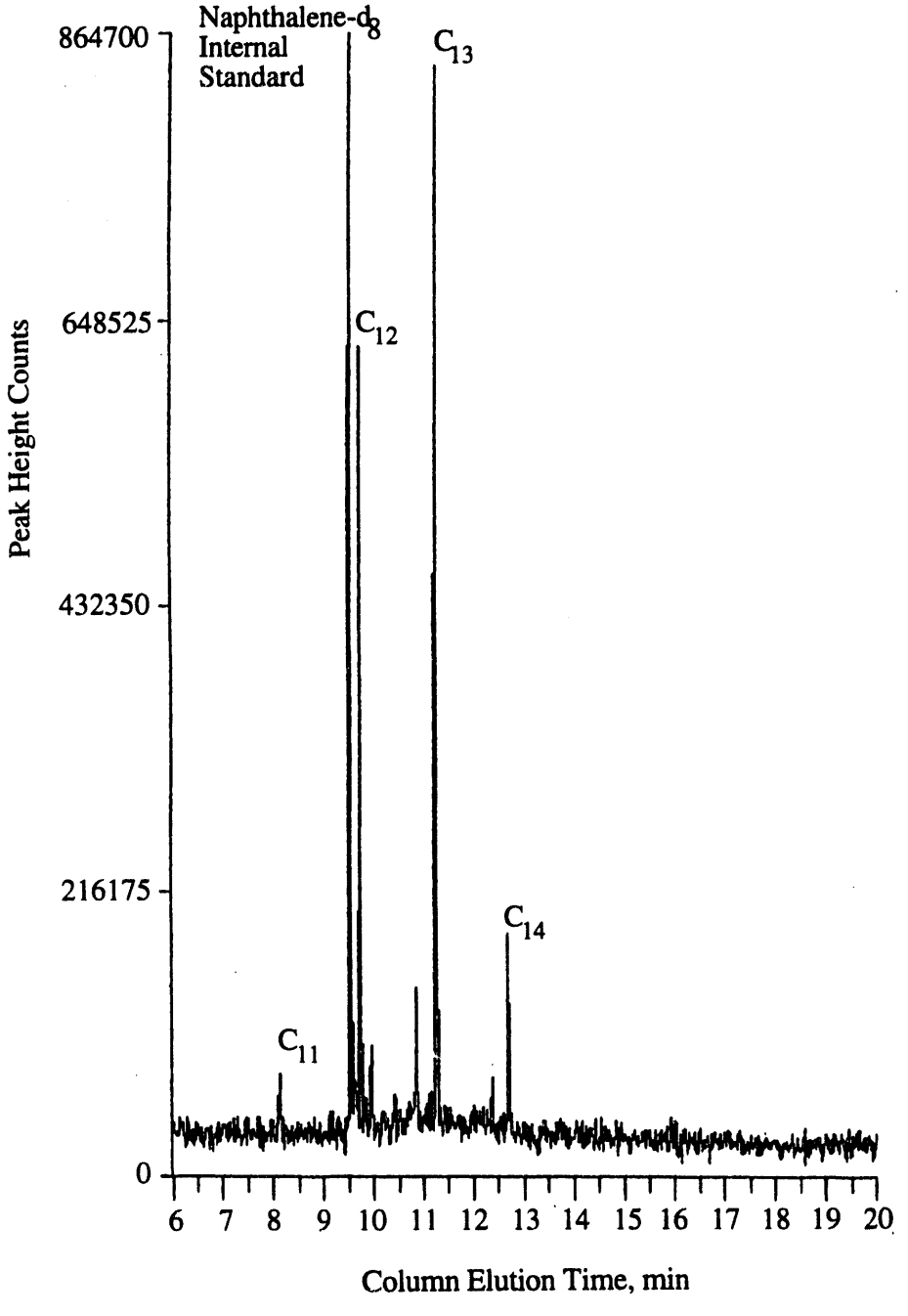

FIGURE C.3 GC/MS Total Ion Chromatogram of Waste Tank 241-C-103 Sample C103/OVS 1, Front OVS Portion, Undiluted Extract. Quantitation of NPH analytes for 1-min duration samples did not require dilution as chromatographic peaks were within the calibration range.

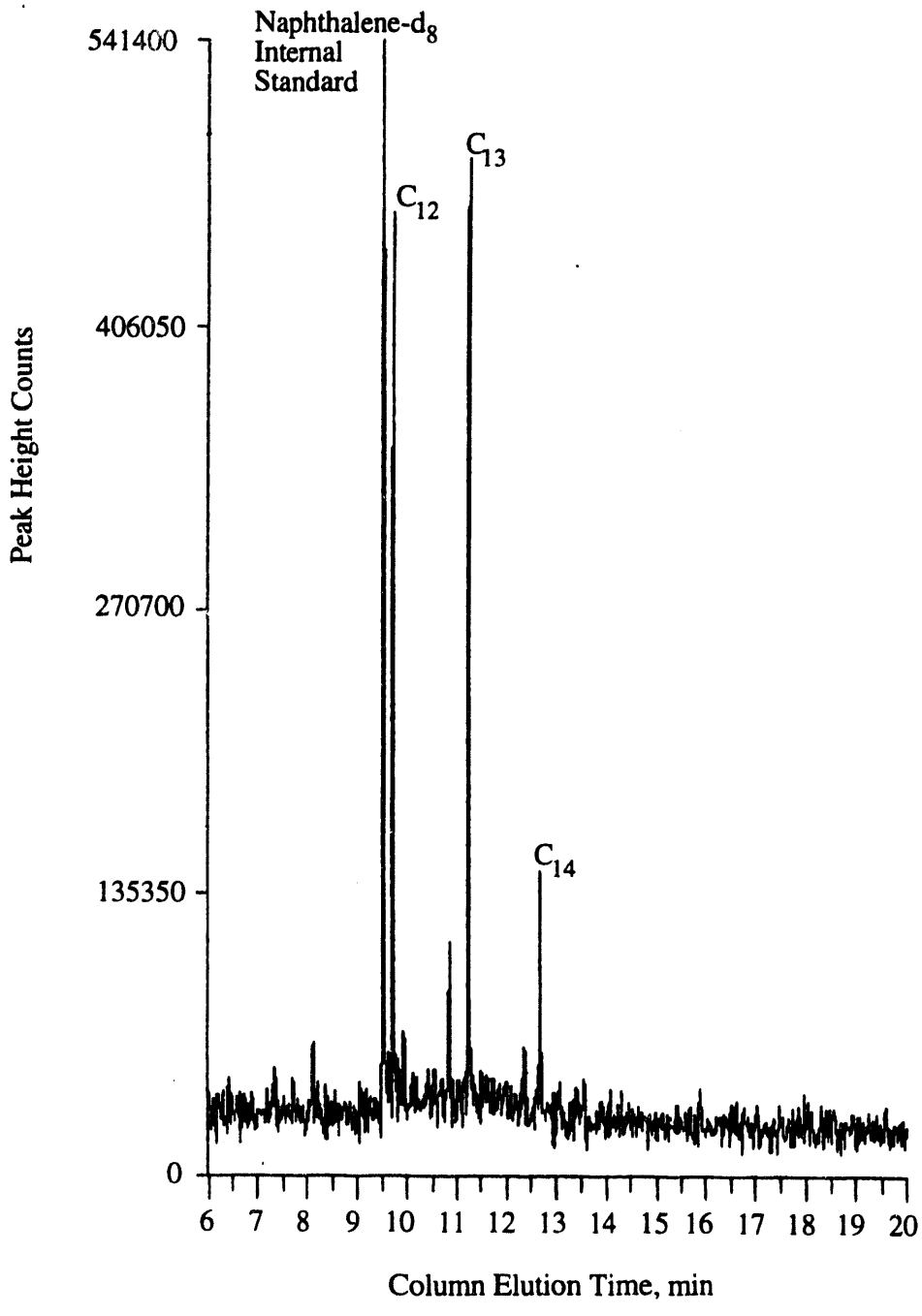

FIGURE C.4 GC/MS Total Ion Chromatogram of Waste Tank 241-C-103 Sample C103/OVS 8, Front OVS Portion, Extract Diluted 1:20 in CS_2. After initial screening by GC/MS, the sample was diluted into the calibration range for quantitation. The internal standard, Napthalene-d_8, was used to quantitate chromatographic peaks associated with NPH analytes with responses greater than 2.5 times the level of background noise (C_{12}, C_{13}, and C_{14}).

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