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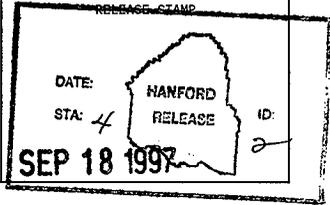
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Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks

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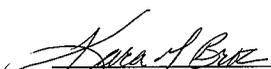
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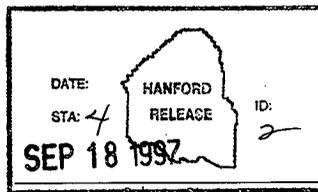
Abstract: This report documents the measurement of headspace gas concentrations and monitoring results from the Hanford tanks that have continuous flammable gas monitoring. The systems used to monitor the tanks are Standard Hydrogen Monitoring Systems. Further characterization of the tank off-gases was done with Gas Characterization Systems and vapor grab samples. The background concentrations of all tanks are below the action level of 6250 ppm. Other information which can be derived from the measurements (such as generation rate, release rate, and ventilation rate) is also discussed.

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TABLE OF CONTENTS

1.0	Introduction	1
1.1	Tri-Party Agreement (TPA) Milestone M-40-10	1
1.2	Public Law 101-510, Section 3137, the Flammable Gas Tank Watch List, and the Unreviewed Safety Question	2
1.3	Non-Watch List Tanks	2
2.0	Description of The Flammable Gas Monitoring Systems	3
2.1	Standard Hydrogen Monitoring Systems (SHMS)	4
2.2	Other Monitoring Systems	5
2.3	Monitoring System Performance	6
3.0	Gas Release Events	10
3.1	241-SY-101 Gas Release Events	10
3.2	Gas Release Events From Other Double Shell Tanks	12
3.3	Gas Release Events From Single-Shell Tanks	15
3.4	Correlation of Surface Level Drops With Peak Hydrogen Concentration	15
4.0	Gas Monitoring Results	22
4.1	Grab Sampling Method	22
4.2	Determination of Steady-State From Grab Sampling	22
4.3	Summary of Double-Shell Tank Grab Sampling	22
4.4	Summary of Single-Shell Tank Grab Sampling	29
4.5	Summary of SHMS Monitoring	30
4.6	Summary of Monitoring by Other Systems	30
4.6.1	Gas Monitoring System - 2	30
4.6.2	Gas Characterization System	32
4.6.3	Gas Chromatograph Results	33
4.6.4	Ammonia and Hydrogen Monitoring of Tank Farm Exhaust Vents	34
5.0	Determination of In-Tank Gas Composition	34
5.1	Composition of 241-SY-101 Waste Gas	34
5.2	Waste Gas Composition for Other Tanks	35
6.0	Hydrogen Generation Rates	38
6.1	Double-Shell Tanks	38
6.2	Single-Shell Tanks	41
7.0	Tank Ventilation Rates	43
7.1	GRE Behavior	43
7.2	GRE Model	44
7.3	GRE Data Evaluation	48
7.4	Tracer Gas Tests	49
8.0	Flammable Gas Action Levels for Hanford Waste Tanks	51
8.1	Description of Action Level	51
8.2	Action Level Response	51

HNF-SD-WM-TI-797, Rev. 2

8.3	Summary of Gas Release Events Exceeding the Action Level . . .	52
9.0	Action Plans for Continued Monitoring	53
9.1	Current System Issues and Corrective Actions Planned	53
9.1.1	Issue Resolution	54
9.2	Application of New Systems	55
10.0	Conclusions	57
11.0	References	58
Appendix A	A-1
Appendix B	B-1
Appendix C	C-1
Appendix D	D-1

LIST OF TABLES

Table 1-1. Flammable Gas Watch List Tanks	2
Table 1-2. Non-Watch List Tanks	3
Table 2-1. Gas Monitoring Instruments	3
Table 2-2. Vapor Grab Samples vs. SHMS	9
Table 3-1. Summary of Gas Release Events for Tank 241-SY-101	11
Table 3-2. Summary of Gas Release Events for Tank 241-SY-103	12
Table 3-3. Summary of Gas Release Events in Tank 241-AW-101	13
Table 3-4. Summary of Gas Release Events for Tanks 241-AN-103 and 241-AN-104	14
Table 3-5. Summary of Gas Release Events for Tank 241-AN-105	14
Table 3-6. Amount of Gas Released from GREs in Single-Shell Tanks	16
Table 4-1. 241-SY-103 Grab Samples	24
Table 4-2. 241-AW-101 Grab Samples	25
Table 4-3. 241-AN-103 Grab Samples	26
Table 4-4. 241-AN-104 Grab Samples	27
Table 4-5. 241-AN-105 Grab Samples	28
Table 4-6. Single-Shell Tank Grab Sample Summary	29
Table 4-7. Maximum SHMS Readings	31
Table 4-8. 241-SY-101 Gas Monitoring	32
Table 4-9. Gas Characterization System Results	33
Table 4-10. GCS Results during GREs	33
Table 4-11. Stack Gases	34
Table 5-1. Estimated Composition of Gases at 46°C in Tank 241-SY-101	35
Table 5-2. Retained Gas Sampler Results	36
Table 5-3. Waste Gas Sample Results from Drill String Grab Samples	37
Table 6-1. Hydrogen Generation Rates (DSTs)	40
Table 6-2. Other Gas Generation Rates	41
Table 6-3. Hydrogen Generation Rates (SSTs)	42
Table 7-1. Summary of GRE evaluation (preliminary)	48
Table 7-2. Ventilation rates from tracer gas tests	50
Table 9-1. New SHMS Installations in Fiscal Year 1997	56
Table 9-2. New SHMS Installations Planned for Fiscal Year 1998	56

LIST OF FIGURES

Figure 3-1. 241-SY-101 H ₂ Concentration vs. Level Drop	19
Figure 3-2. 241-SY-103 H ₂ Concentration vs. Level Drop	19
Figure 3-3. 241-AW-101 H ₂ Concentration vs. Level Drop	20
Figure 3-4. 241-AN-104 H ₂ Concentration vs. Level Drop	20
Figure 3-5. 241-AN-105 H ₂ Concentration vs. Level Drop	21
Figure 7-1. Tank 241-U-103 SHMS Data	45
Figure 7-2. Tank 241-SX-106 SHMS Data	46
Figure 7-3. GRE Model Applied to Tank 241-U-103	47

ACRONYMS

cfm	Cubic Feet per Minute
DACS	Data Acquisition and Control System
DOE	Department of Energy
DQO	Data Quality Objective
DST	Double-shell Tank
FGWL	Flammable Gas Watch List
FTIR	Fourier Transform Infra-red Spectrometer
GC	Gas Chromatograph
GCS	Gas Characterization System
GMS	Gas Monitoring System
GRE	Gas Release Event
GSC	Gas Sample Conditioner
HLAN	Hanford Local Area Network
IR	Infra-red
LFL	Lower Flammability Limit
NFPA	National Fire Protection Association
PNNL	Pacific Northwest National Laboratory
ppm	Parts Per Million
RGA	Reduction Gas Analyzer
RGS	Retained Gas Sampler
SACS	Surveillance Analysis Computer System
SHMS	Standard Hydrogen Monitoring System
SS	Steady State
SST	Single-shell Tank
TBD	To Be Determined
TCD	Thermal Conductivity Detector
TMACS	Tank Monitoring and Control System
TWINS	Tank Waste Information Network System
TPA	Tri-Party Agreement
USQ	Unreviewed Safety Question

1.0 Introduction

This report is being published to document the measurement of headspace gas concentration and monitoring results obtained to date using the systems described in section 2 of this report for the Hanford Flammable Gas Watch List tanks. This report will cover the data collection period from April 1990 to July 1997. These data will contribute to the closure of the unreviewed safety question for these tanks and eventually to the resolution of the flammable gas safety issue; however, it is the purpose of this report to present the data and not to interpret how the data represents the safety condition of the tanks. This task is left to the safety analysts.

This report will discuss the legal and administrative requirements which are driving the monitoring effort, the methods used for monitoring or measuring the headspace gas concentrations, the summary of the results of the measurements, the actions to be taken in the event concentrations reach action levels, and the plans for system improvements and future monitoring.

Additionally several applications of the data will be explored. These include the use of the data to determine the composition of the gas as it resides in the waste, the rate at which the gases are being generated, and the rate at which the tanks are naturally ventilated. The composition of the waste gas is important in the safety analysis of the tank to determine the potential energy of the stored gas; the generation rate is also useful in determining the magnitude of the safety issue; the ventilation rate is useful in calculating the time at risk following a gas release event. All of this information will be useful in developing and validating the models to be used to predict tank performance and support closure of the safety issue.

1.1 Tri-Party Agreement (TPA) Milestone M-40-10

The Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) Milestone M-40-10 required the following work to be completed by January 31, 1997:

Design, procure, and fabricate Standard Hydrogen Monitoring Systems (SHMS) for all Unreviewed Safety Question (USQ) Flammable Gas Watch List tanks. Prepare all required safety and environmental documentation for tank intrusive work on a tank by tank, or group of tanks, basis. Install the SHMSs and obtain vapor space grab samples. Analyze samples using a high sensitivity mass spectrometer to determine the concentrations of flammable gases (hydrogen, nitrous oxide, ammonia) for all tanks. Report the background gas compositions for the double-shell tanks that entrap and periodically release gas. The vapor space of each tank will be observed over a sufficient period of time to make decisions regarding resolution of the safety issue. A report, with the analytical data for each tank, will be prepared, cleared for public release, and transmitted to RL for subsequent issuance to the Washington Department of Ecology and Environmental Protection Agency. Monitoring will continue after the initial report.

The continuous gas monitors have been installed on the FGWL tanks as listed in Table 1-1. Revision 1 of this report met the requirement for reporting of the monitoring results from these systems as stated in M-40-10. This revision (Rev. 2) addresses the requirement for continued monitoring plus monitoring results of other tanks of concern. This document is updated annually.

Table 1-1. Flammable Gas Watch List Tanks

Double - Shell	Single - Shell
241-AN-103, 104, 105	241-A-101
241-AW-101	241-AX-101, 103
241-SY-101, 103	241-S-102, 111, 112
	241-SX-101, 102, 103, 104, 105, 106, 109
	241-T-110
	241-U-103, 105, 107, 108, 109

1.2 Public Law 101-510, Section 3137, and the Flammable Gas Tank Watch List

In November 1990, the *National Defense Authorization Act for Fiscal Year 1991*, Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at the Hanford Nuclear Reservation," [the Wyden Amendment] was passed. It required the Secretary of Energy to identify within 90 days high-level nuclear waste tanks that could have a "serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure." The identified tanks contained flammable gas, ferrocyanide ions, organic chemicals, and high radioactive decay heat.

In January 1991, the Westinghouse Hanford Company formally submitted a Watch List of tanks subject to the law (Harmon 1991a). In February 1991, Westinghouse Hanford submitted a method for selecting flammable gas tanks (Harmon 1991b). The 1991 Flammable Gas Watch List identified 23 tanks. In 1992 and 1993, two additional tanks were added for a total of 25. These six DSTs and 19 SSTs are listed in Table 1-1. All of the Watch List tanks have had SHMS installed.

1.3 Non-Watch List Tanks

There are also other tanks that have operating SHMS. These tanks either show evidence of gas retention or have planned activities that require flammable gas monitoring. These tanks are listed in Table 1-2.

Table 1-2. Non-Watch List Tanks

Double-Shell	Single-Shell
241-AY-102	241-C-106
	241-BY-103, BY-106, BY-109

2.0 Description of The Flammable Gas Monitoring Systems

The tanks are monitored for hydrogen and other flammable gases to assure that the tank dome space is safe and to increase understanding of the mechanisms for gas release and dispersion. A number of different systems are in use. Depending upon the information desired from a tank, different monitoring instruments are combined into a tank specific system. These instruments are listed in Table 2-1, along with their measurement accuracies and ranges. The following sections describe how the instruments are applied in different monitoring systems.

Table 2-1. Gas Monitoring Instruments (2 Sheets)

Instrument	Gases Monitored	Range	Accuracy
Whittaker™ Electro-Chemical Cell and Transmitter	Hydrogen Specific	0-1% and 0-10% H ₂ by Volume	±0.2% by Volume Absolute (Resolution of 50 ppm)
Gas Chromatograph Reduction Gas Analyzer (GC-RGA)	Hydrogen Specific	Low Range 0-500 ppm H ₂ High Range 500-30,000 ppm H ₂	Low Range ±4 ppm <100 ppm and ±10% of Reading >100 ppm High Range ±10% of Reading
Gas Chromatograph Thermal Conductivity Detector (GC-TCD)	Hydrogen (H ₂) Nitrous Oxide (N ₂ O) Methane (CH ₄)	H ₂ 3 to 3000 ppm N ₂ O 10 to 20,000 ppm CH ₄ 10 to 4000 ppm	H ₂ , N ₂ O, CH ₄ ±3 ppm <30 ppm and ±10% of Reading >30 ppm
Fourier Transform Infra-Red Spectrometer (FTIR)	Ammonia (NH ₃) Nitrous Oxide (N ₂ O) IR spectra for other species	NH ₃ 10 to 30,000 ppm N ₂ O 10 to 30,000 ppm Other species TBD	N ₂ O, NH ₃ ±5 ppm < 100 ppm ±10% of Reading > 100 ppm
Infra-Red Photo Acoustic Multi-Gas Monitor	Ammonia (NH ₃) Selected filters for other species	NH ₃ 10 to 10,000 ppm Other species TBD	NH ₃ ±10 ppm < 100 ppm ±10% of Reading > 100 ppm

Table 2-1. Gas Monitoring Instruments (2 Sheets)

Instrument	Gases Monitored	Range	Accuracy
Grab Samples - Mass Spectrometer	Hydrogen (H ₂) Nitrous Oxide (N ₂ O) Methane (CH ₄) Argon (Ar) Nitrogen (N ₂) Oxygen (O ₂)	0 - 100% by volume	at least ± 10 ppm

2.1 Standard Hydrogen Monitoring Systems (SHMS)

The basic Standard Hydrogen Monitoring System monitors hydrogen continuously. Gas is vacuum pumped from the tank into a temperature controlled cabinet which contains the monitoring instrument. For double-shell tanks, the sample is obtained from the tank ventilation exhaust duct; for single-shell tanks, the sample is obtained from a probe which is inserted well into the tank dome space. The monitoring instrument is a Whittaker™ electrochemical cell which is hydrogen specific. The cell generates an electrical signal proportional to the volume percent hydrogen concentration. This signal is processed by a transmitter. The 4-20 mA output from the transmitter is sent to a digital data readout and to the data recorder. The recording channel of the data recorder is programmed to activate an alarm relay if a preset hydrogen concentration (currently 6250 ppm) is reached. The alarm relay opens a normally closed contact which serves as the input to a programmable logic controller, which controls the annunciation of a high hydrogen alarm and initiates an automatic vapor grab sample. Data are recorded by connection to the Tank Monitoring and Control System (TMACS) and by an on-board chart recorder.

The SHMS also has a grab sample station, which allows two 75 cc vapor samples to be taken simultaneously from the gas stream, isolated, and transported to a laboratory for analysis. Hydrogen and other gases can be measured from these samples.

These systems are calibrated quarterly. A mixture of 100 ppm hydrogen and air is used to adjust the low end of the hydrogen sensor, and a mixture of 5.0% hydrogen mixed with nitrogen is used to balance the high end of the sensor. A mid-range standard gas of 1000 ppm hydrogen is used as an on-line calibration check during system operation (Schneider 1996).

The first SHMS was developed for use in continuously monitoring hydrogen concentrations on waste tank 241-SY-101. There are currently three of the basic units installed and operating on this tank. One system monitors the vent header concentration and the other two monitor locations within the headspace. Based on the success of these instruments the system was upgraded by adding the capability to automatically obtain a grab sample on a high hydrogen reading. Also the Whittaker™ cells were configured so that one covers a high range (0-10% by volume) and one covers a low range (0-1% by volume). This modified version is called the SHMS-B.

The SHMS-B is the most widely used of the SHMS instruments. It is installed on all FGWL tanks other than 241-SY-101 and 241-AN-104. Data are recorded by connection to the TMACS and by the on-board chart recorder. As specific needs have arisen the SHMS-B has been modified to provide the needed capabilities. This has resulted in several variations which include models C, D, E, and E+. Table 4-7 lists the tanks and type of SHMS currently installed and Table 9-2 lists the tanks and types of SHMS planned for installation.

The SHMS-C is a SHMS-B which is modified to accommodate a dual column gas chromatograph with thermal conductivity detectors (GC-TCD). Data for the Whittaker™ cells are recorded by connection to the TMACS and by the on-board chart recorder. The data for the gas chromatograph are recorded by a resident computer and is retrieved via floppy disk for off-line analysis. The SHMS-C is designed to accurately record baseline hydrogen concentrations which are well below the range of the Whittaker™ cells.

The SHMS-D is a SHMS-B which is modified to accommodate an infra-red (IR) photo-acoustic multi-gas monitor, which measures ammonia. Data for the Whittaker™ cells are recorded by connection to TMACS and by the on-board chart recorder. The data for the infra-red photo-acoustic multi-gas monitor are recorded by a resident computer and is retrieved via floppy disk for off-line analysis. The SHMS-D was developed for use in monitoring ammonia concentrations in the ventilation exhaust of DSTs.

The SHMS-E is an updated version of the SHMS-B and accommodates (but they are not installed) a dual column gas chromatograph with a thermal conductivity detector and an infra-red photo-acoustic multi-gas monitor. Data are recorded by an on-board digital data logger with data retrieval via floppy disk. The upgrade in the design from the SHMS-B is in the data recording (the strip-chart is eliminated) and the programmable logic controller. The SHMS-E is intended for use in the same applications as a SHMS-B. The SHMS-E has the advantage of easily being upgraded to an E+.

The SHMS-E+ is a SHMS-E with the gas chromatograph and IR monitor installed. The GC monitors hydrogen, nitrous oxide, and methane, and the IR monitor detects ammonia. Data are recorded by an on-board digital data logger with data retrieval via floppy disk or by connection to a host computer via the Hanford Local Area Network (HLAN). The SHMS-E+ is intended for applications similar to those of the Gas Characterization System (GCS), which is described in Section 2.2. The SHMS-E+ provides nearly the same measurement capability as a GCS but at a significantly lower cost.

2.2 Other Monitoring Systems

The Gas Monitoring System - 1 (GMS-1) monitors hydrogen and tank vapor space pressure for waste tank 241-SY-101. The environmentally controlled enclosure contains one Whittaker™ electrochemical cell and a grab sample station. It also has a pressure transmitter. It initially had a mass spectrometer for multi-specie analysis that has since been removed. Data from GMS-1 are recorded by the 241-SY-101 Mixer Pump Data Acquisition and Control System (DACS).

The Gas Monitoring System - 2 (GMS-2) is an environmentally controlled enclosure containing a Fourier Transform Infra-red Spectrometer (FTIR), two hydrogen specific reduction gas analysis gas chromatographs and one infra-red photo-acoustic monitor. GMS-2 monitors the vapor space of waste tank 241-SY-101. The FTIR measures ammonia and nitrous oxide. One GC has a single column and monitors low concentrations of hydrogen, and the other GC has a dual column and monitors both low and high concentrations of hydrogen. The IR monitor samples the ventilation exhaust stack of the SY farm (combined exhaust of 241-SY-101, -102, and -103) for ammonia. The data are recorded by the 241-SY-101 DACS. GMS-1 and GMS-2 provide the detailed concentration history necessary to support the mixer pump operation, and the data from these systems have significantly contributed to the understanding of this tank and the closure of the USQ for this tank.

The Gas Characterization System (GCS) is an environmentally controlled enclosure with an FTIR, two dual column thermal conductivity gas chromatographs, and a grab sample station. The GCS is an upgraded version of the GMS-2. The FTIR monitors ammonia, one GC monitors hydrogen, and the other GC measures nitrous oxide and methane. The data are recorded by the resident computer system and can be remotely accessed over the HLAN. The GCS is used to provide the detailed history of gas concentration over a wide range in order to support the decision of whether additional measures are needed to mitigate the safety issue of a tank. These systems are currently installed on tanks 241-AN-105 and 241-AW-101.

2.3 Monitoring System Performance

Overall, the performance of the SHMS units has been mixed. The performance of many of the systems has been excellent. Several of the systems have severe operational problems which are discussed here and also in Section 9.0. Considering the harsh operating environment they have performed reliably.

The Whittaker™ electrochemical cells have proven to be very reliable. Few failures of these detectors have occurred over the nearly five years of operation. The advertised accuracy of the sensor is ± 2000 ppm. The sensors have proven to provide measurement of hydrogen with an accuracy better than 2000 ppm. This has been proven by comparison of the sensor output with concentrations measured by independent instruments such as the high resolution mass spectrometer or gas chromatographs installed in the GCS and GMS. For concentrations near steady-state in the tanks, the sensors do not provide an accurate measure of the absolute hydrogen concentration (nor are they intended to at this level); however, they are quite capable of resolving changes in hydrogen concentration as small as 50 ppm. The sensors respond specifically to hydrogen and are not significantly influenced by other gases which may be present in the sample stream such as ammonia, methane, nitrous oxide, or water vapor (Schneider 1993).

A phenomenon has occurred on four occasions where one Whittaker cell appears to detect high hydrogen concentrations, and the other cell shows only steady-state concentrations. This phenomenon was observed on the following tanks: 241-S-102 on December 7, 1995; 241-BY-103 on December 28, 1996 - January 14,

1997; 241-U-107 on April 21 - 28, 1997; and 241-AY-102 on June 10, 1997. The high hydrogen concentrations recorded on these dates are not considered to be real. For 241-AY-102, the narrow range cell recorded two hydrogen peaks of about 6000 ppm within one hour before stabilizing again at steady-state concentrations. For 241-U-107, the flow rate calculated based on the hydrogen decay curve recorded by the narrow range cell was an order of magnitude greater than the tank's estimated breathing rate. The wide range cell showed no response. A follow-up calibration of the detectors showed a normal response from both detectors. For 241-BY-103, the wide range detector detected a peak concentration of 0.197 vol% and the narrow range detector did not respond, showing only steady-state concentrations. The 241-S-102 SHMS was off-line (the sample pump was not operating) when a similar phenomenon was exhibited.

This phenomenon may be due to electrolyte leakage from the Whittaker cells. The 241-BY-103 leak may have been a result of cold weather (the temperature around December 26, 1996 dropped to about -10 °F) stiffening the seals leading to a loss of electrolyte. Another condition which affects seal integrity is chemical interaction with gases such as N_2O , a common component of the gases generated in the tanks, which may be the cause of the 241-U-107 SHMS failure. The Whittaker™ cell manufacturer has also suggested that the problem may be due to a main circuit board production problem and that changing the board may solve the problem (Schneider 1997).

System down time has been due almost exclusively to problems in the sample delivery system: clogging due to moisture (discussed in section 9.1) and failure of the sample pump. Failure of the sample pumps was traced to a faulty motor bearing design which has been corrected by the vendor. The SHMS on 241-A-101, 241-AX-101, 241-S-102, and 241-SX-102 have had limited operating time due to moisture clogs. The SHMS on 241-AX-103 has not operated regularly because the inlet was plugged with ammonium nitrate (see Appendix A).

For SHMS on tanks with a history or potential of high vapor space moisture, gas sample conditioners (GSCs) have been or are being installed. These systems consist of a condenser coil that separates moisture from the sample stream. These systems are intended to prevent moisture clogging of the SHMS sample lines.

The manual grab sampling system has worked very well and a total of 437 samples have been obtained. The automatic grab sampling system has activated a total of three times. Of these three events data were only obtained from the May 1996 event in waste tank 241-AN-105. The system did activate during the two other events; however, air in-leakage through the solenoid valve seats compromised the sample results.

Vapor grab samples are taken periodically from the tanks, and the hydrogen content is measured with a mass spectrometer, which has an accuracy better than ± 10 ppm. Table 2-2 compares the steady-state concentrations (when a GRE is not occurring in a tank) measured in vapor grab samples with the range of steady-state concentrations measured by the Whittaker™ cell.

The range of hydrogen concentrations measured with the SHMS is within 2000 ppm of the background concentrations measured with the mass spectrometer as illustrated in Table 2-2.

The GMS-2 has provided excellent data for tank 241-SY-101; however a significant effort is required to keep the system operational. GMS-2 is comprised of 1992 vintage laboratory grade analytical instruments, computers, and software operating in a field environment. This system was developed and installed on tank 241-SY-101 when there was an extreme urgency for data on the tank and there was not adequate time to perform the system development and testing required to ensure a robust system. The instruments themselves have performed well. The main difficulty in operating the system has been data acquisition. In order for the instruments to sample continuously they must be computer controlled. This control system must operate the instrument, obtain the raw data, reduce the raw data to gas concentration information, and then communicate the information to the host computer in the Data Acquisition and Control System (DACS). The GMS-2 must perform this function for four different instruments (two GC's, an FTIR, and a photo-acoustic IR - a total of 50-70 discrete measurements per hour) plus keep track of all the process variables such as sample flow rates, pressures, and temperatures. Initially, system shutdowns due to software failures were frequent (daily) after system start-up, but software modifications and system upgrades have greatly improved the reliability.

The GCSs have performed flawlessly since their start-up. This can be partly attributed to the advances in instrument, computer, and software technology, but is more importantly due to the disciplined engineering approach used in the development. All hardware and software were thoroughly tested in the laboratory prior to application in the field. Additional information on the performance of these systems is included in section 4.6.

Table 2-2. Vapor Grab Samples vs. SHMS

Tank	Vapor Sample Average Hydrogen (ppm)	SHMS Whittaker™ Cell Range Hydrogen (ppm)
241-AW-101	169	0 - 1100
241-SY-103	27	0 - 470
241-AN-103	53	0 - 700
241-AN-104	35	0 - 400
241-AN-105	70	0 - 700
241-AX-101	55	0 - 540
241-AX-103	26	0 - 380
241-S-102	617	0 - 2000
241-S-111	72	0 - 680
241-S-112	27	0 - 490
241-SX-101	8	0 - 400
241-SX-102	18	0 - 120
241-SX-103	30	0 - 310
241-SX-104	10	0 - 300
241-SX-105	13	0 - 710
241-SX-106	35	0 - 320
241-SX-109	9	0 - 310
241-T-110	7	0 - 200
241-U-103	614	0 - 1230
241-U-105	587	0 - 1440
241-U-107	352	0 - 1680
241-U-108	429	0 - 2000
241-U-109	324	0 - 1530
241-BY-103	101	0 - 770
241-BY-106	201	0 - 880
241-BY-109	75	0 - 650
241-C-106	23	0 - 756

3.0 Gas Release Events

In this document, a gas release event is defined as an increase in tank dome space hydrogen concentration from the steady-state level, followed by a decrease back to the steady-state concentration. The hydrogen increase from steady-state to a peak concentration can take minutes or hours in a double-shell tank and may take days in a single-shell tank. The gas release may be accompanied by a drop in waste level, indicating the waste volume has decreased due to the release of gas. However, the tanks do not consistently show a level drop with each release. If a release occurs in one small area of the tank, the level may drop in that small area but not affect the waste near the level measurement device. The level drop may also be too small to be detected with the level instrument installed in the tank. Some gas may be trapped in the waste crust, causing a temporary increase in waste level.

Gas releases have several causes. Gas trapped in the waste can build up until the waste becomes buoyant. As the waste floats up, gas is released, and the waste resettles after the waste returns to less than neutral buoyancy. Such waste movement can be monitored with thermocouples installed at different elevations in the waste. Temperature changes of several degrees occur within hours when warm waste rises and is replaced by the cooler supernatant liquid. This type of gas release is called "buoyant displacement" and occurs in the DSTs (Stewart et al. 1996a). It is believed that buoyant displacements (historically called "rollovers") do not occur in SSTs (Stewart et al. 1996b).

Gas releases in the SSTs have been observed to be associated with changes in barometric pressure. These releases have been very small compared to those seen in the DSTs. It is believed that when low barometric pressure decreases the pressure on the trapped gas, the gas expands and percolates to the surface of the waste.

Small gas releases have also occurred in a few cases when the waste was disturbed during work activities. A gas release occurred in tank 241-AW-101 that can be correlated with the insertion of an instrument into the waste (the void fraction of the waste was being measured) (Stewart et al. 1996a). However, over forty locally waste disturbing activities have been conducted in the DST FGWL tanks, and with the exception of the 241-AW-101 activity mentioned, none have resulted in gas releases large enough to be detected by surface level change or SHMS (if a SHMS was installed at the time of the activity). In the SSTs, few locally waste disturbing activities have been conducted since the SHMS were installed.

3.1 241-SY-101 Gas Release Events

Table 3-1 lists the gas release events that have been detected in 241-SY-101 since 1990. This tank was mitigated with a mixer pump that was installed in July 1993. During nine of the eleven gas releases, hydrogen concentrations in the dome space were above 25% of the lower flammability limit (LFL) for hydrogen. The LFL for hydrogen in air is 4% or 40,000 ppm. Three releases increased the dome space hydrogen concentration beyond the LFL.

Gas releases in this tank were accompanied by level drops ranging from 12.7 to 33.5 cm. The number of days between gas releases averaged 116 days \pm 25. The gas releases in this tank were somewhat predictable based on the number of days between gas releases.

The peak hydrogen concentrations listed for GREs that occurred during 1990 were measured with a thermal conductivity analyzer (which is no longer used). The February 1991 GRE was very slow and barely registered above background levels for hydrogen on the monitoring instruments. The peak concentration listed was measured with an on-line mass spectrometer (which is no longer used). GMS-1 was installed in April 1991, and its Whittaker cell measured the peak concentrations listed for the May, August, and December 1991 GREs. Two SHMS and GMS-2 were installed during 1992. The peak hydrogen concentrations listed since 1991 were measured with Whittaker cells or the on-line mass spectrometer. Further details on 241-SY-101 gas instrumentation before 1992 are available in Babad et al. (1991).

Table 3-1. Summary of Gas Release Events for Tank 241-SY-101

Date	Maximum H ₂ Concentration ^a (ppm)	Level drop ^{b,c} (cm)	Days since previous GRE
4/19/90	35,000	23.6	
8/5/90	12,000	13.2	108
10/24/90	47,000	25.4	80
2/16/91	400	12.7	115
5/16/91	28,000	18.3	89
8/27/91	3800	15.2	103
12/4/91	53,000	33.0	99
4/20/92	14,800	18.3	138
9/3/92	51,200	33.5	136
2/2/93	27,400	21.6	152
6/26/93	34,000	24.8	144
Average number of days between GREs = 116			
Standard deviation (days) = 25			

a - SHMS data

b - SACS (Surveillance Analysis Computer System) data

c - Level drop is measured from the pre-GRE level to the minimum level following the GRE. The waste level may not stabilize until a few days after the GRE.

3.2 Gas Release Events From Other Double Shell Tanks

Tables 3-2, 3-3, 3-4, and 3-5 list the gas releases detected with gas monitoring in the other double-shell tanks. Only two other double-shell tanks, 241-AW-101 and 241-AN-105, have had gas releases that have exceeded 25% of the LFL. None of these releases have exceeded the LFL. Level drops in these tanks following gas releases are generally less than one inch. These measurements show that the GREs in these tanks are much smaller than those seen in tank 241-SY-101. The average number of days between gas releases is less than 100 in tanks 241-AW-101, 241-AN-104, and 241-SY-103. However, the standard deviations of these averages are almost as large as the averages themselves. Using the time period to predict future gas releases for these tanks does not appear feasible from existing data. A gas release in a tank on one day does not guarantee another gas release will not happen the next day. During October 1995, three definite hydrogen increases occurred in 241-AN-104 during a nine day period. However, the hydrogen concentration in the dome space remained low. The only tank with consistent hydrogen increases above 25% of the LFL is 241-AN-105. Based on the size of the releases seen in these tanks, it appears that events in these tanks are localized and do not involve the entire tank contents.

Table 3-2. Summary of Gas Release Events for Tank 241-SY-103

Date	Maximum H ₂ Concentration ^a (ppm)	Level drop ^{b,c} (cm)	Days since previous GRE
1/22/95	1090	1.5	
3/1/95	2230	3.0	38
5/2/95	2940	2.2	62
8/23/95	1260	0.9	113
9/6/95	1890	2.5	14
12/3/95	740	0.7	88
6/6/96	1090	1.0	186
7/14/96	2170	1.8	38
12/20/96	5110	6.1	159
Average number of days between GREs = 87			
Standard deviation = 61			

a - SHMS data

b - SACS (Surveillance Analysis Computer System) data

c - Level drop is measured from the pre-GRE level to the minimum level following the GRE. The waste level may not stabilize until a few days after the GRE.

Table 3-3. Summary of Gas Release Events in Tank 241-AW-101

Date	Maximum H ₂ Concentration ^a (ppm)	Level drop ^{b,c} (cm)	Days since previous GRE
10/1/94	8800	1.9	
10/21/94	2980	0.25	20
11/27/94	5000	0	37
2/22/95	5800	0	87
5/8/95	1800	0	75
5/17/95	1000	0.9	9
7/8/95	2000	0	52
7/12/95	900	0	4
8/2/95	3300	0	21
9/15/95	1900	+0.2	44
9/22/95	4660	+2.0	7
10/16/95	1750	0.3	24
12/12/95	2110	0.3	57
12/29/95	6000	+0.7	17
2/5/96	3200	+0.5	38
5/14/96	1455	0.2	99
6/5/96	2500	0.2	22
Average number of days between GREs = 38			
Standard deviation = 29			

a - SHMS data

b - SACS (Surveillance Analysis Computer System) data

c - Level drop is measured from the pre-GRE level to the minimum level following the GRE. The waste level may not stabilize until a few days after the GRE.

Table 3-4. Summary of Gas Release Events for Tanks 241-AN-103 and 241-AN-104

Tank	Date	Maximum H ₂ Concentration ^a (ppm)	Level drop ^{b,c} (cm)	Days since previous GRE
241-AN-103	8/22/95	3000	0.6	
241-AN-104	11/6/94	3000	5.3	
	2/16/95	2088	0.2	102
	8/3/95	480	0	168
	10/2/95	3200	+0.8	60
	10/5/95	1000	0	3
	10/8/95	5000	0.7	3
	5/3/96	6109	1.4	235
	5/1/97	2250	0.4	363
241-AN-104	Average number of days between GREs = 133			
	Standard deviation = 132			

a - SHMS data

b - SACS (Surveillance Analysis Computer System) data

c - Level drop is measured from the pre-GRE level to the minimum level following the GRE. The waste level may not stabilize until a few days after the GRE.

Table 3-5. Summary of Gas Release Events for Tank 241-AN-105

Date	Maximum H ₂ Concentration ^a (ppm)	Level drop ^{b,c} (cm)	Days since previous GRE
8/21/95	17,000	3.8	
5/30/96	14,500	2.5	283
4/5/97	6890	0.8	310
	Average number of days between GREs = 296		
	Standard deviation = 19		

a - SHMS data

b - SACS (Surveillance Analysis Computer System) data

c - Level drop is measured from the pre-GRE level to the minimum level following the GRE. The waste level may not stabilize until a few days after the GRE.

3.3 Gas Release Events From Single-Shell Tanks

Single-shell tanks appear to have small, localized gas release events that are mostly due to changes in barometric pressure. No surface level drops have been associated with these events and the hydrogen concentrations following the events have been below 1500 ppm.

The SHMS data were examined for evidence of gas releases by two independent analysts. The hydrogen signature of a gas release shows a rise from a steady-state concentration followed by a steady decrease back to the steady-state concentration. The volume of gas released was estimated by

$$V = (H_p - H_s)(V_d)$$

where H_p = peak hydrogen concentration
 H_s = steady-state concentration
 V_d = dome space volume.

The dates of gas releases as well as their duration, peak concentrations, and amount of gas released are listed in Table 3-6. Not all single-shell tanks have gas releases. Sixty-one percent of the single-shell tanks equipped with SHMS exhibit gas release behavior.

The results of hydrogen release volume calculations, Table 3-6, are indicative of what can be expected from these tanks. However, a thorough analysis has not been completed. The estimation of hydrogen gas release volumes is sensitive to the selected starting point of the release, the SHMS baseline offset and calibration, the magnitude of the SHMS concentration peak, and any drift that may occur in the SHMS data over the period of several months. This results in uncertainties of 2 to 3 times the calculated value in Table 3-6. Nevertheless, these releases are very small and are spread out over long periods of time (3 or more days). Further work will be done to improve these calculations as more data are accumulated.

3.4 Correlation of Surface Level Drops With Peak Hydrogen Concentration

To see if a linear correlation exists between the peak hydrogen concentration during a gas release and the correlating level drop, a linear regression was performed on the data from the double-shell tanks. Each tank was studied separately. No attempt has been made to interpret the meaning of these correlations. The level drop is measured from the pre-GRE level to the minimum level following the GRE. The waste level may not stabilize until a few days after the GRE.

Figure 3-1 shows the results for tank 241-SY-101. The relationship between the peak hydrogen concentration and the level drop seems to be linear. The slope of the line is 0.6 vol.% H_2 /in. level drop.

Figure 3-2 shows the results for tank 241-SY-103. Again, the peak H_2 concentration and waste level drop may be related. The slope of the line is 0.16 vol.% H_2 /in. level drop.

Figures 3-3 and 3-4 show the results for tanks 241-AW-101 and 241-AN-104. Hydrogen concentration and level drop are not related in these tanks. Many gas releases have occurred in these tanks that have not had a corresponding waste level drop. Sometimes, a rise in waste level occurs during the release, and the level returns to its previous height after a few days.

Figure 3-5 shows the results for tank 241-AN-105. The relationship between the peak hydrogen concentration and the level drop seems to be linear. The slope of the line is 0.88 vol.% H₂/in. level drop. This slope is larger than the slope for tank 241-SY-101.

Tank 241-AN-103 has had only one gas release since gas monitoring began. An analysis was not done on this tank. No similar analysis was attempted for the SSTs because no level drops or significant releases have been observed.

Table 3-6. Amount of Gas Released from GREs in Single-Shell Tanks
(3 Sheets)

Tank	GRE Start Date	GRE End Date	Peak Date	Event Length (days)	Time to peak (days)	Peak GRE H ₂ (ppm)	Steady-state H ₂ (ppm)	H ₂ released (m ³)
241-AX-101	12/3/96	12/7/96	12/4/96	5	2	430	300	0.25
	12/8/96	12/12/96	12/10/96	3.5	1.5	540	300	0.46
	12/19/96	12/22/96	12/20/96	3.5	2.5	360	270	0.17
	12/25/96	12/28/96	12/27/96	3	1.5	390	250	0.27
	12/31/96	1/3/97	1/1/97	3	0.5	420	240	0.35
	1/24/97	1/27/97	1/25/97	2.5	1	320	250	0.13
	2/11/97	2/14/97	2/12/97	3	1	340	250	0.17
	2/15/97	2/18/97	2/16/97	2.5	1	360	250	0.21
	2/26/97	2/28/97	2/26/97	2.5	0.5	370	200	0.33
241-BY-103	12/26/96	1/4/97	12/19/96	9	3	200	50	0.38
241-BY-106	6/1/96	6/5/96	6/3/96	4	2	300	0	0.43
241-BY-109	2/24/96	3/10/96	3/2/96	15.5	7.5	280	0	0.77
241-S-111	11/7/95	11/24/95	11/9/95	17	2.2	750	500	0.48
	11/24/95	12/11/95	12/4/95	17.2	9.6	710	470	0.46
	12/11/95	12/31/95	12/14/95	19.2	2.5	1270	470	1.55
	4/18/96	4/19/96	4/19/96	1	0.75	1160	200	1.86
	11/19/96	11/30/96	11/20/96	11.2	1	700	400	0.58
	12/9/96	12/25/96	12/11/96	15.9	2	690	300	0.76
	12/30/96	1/28/97	1/2/97	28.9	3.1	320	0	0.62
	2/26/97	3/13/97	3/3/97	14.8	4.7	320	30	0.56
241-SX-103	10/22/95	10/28/95	10/25/95	6.3	3.5	210	50	0.38

Table 3-6. Amount of Gas Released from GREs in Single-Shell Tanks
(3 Sheets)

Tank	GRE Start Date	GRE End Date	Peak Date	Event Length (days)	Time to peak (days)	Peak GRE H ₂ (ppm)	Steady-state H ₂ (ppm)	H ₂ released (m ³)
241-SX-103	11/6/95	11/10/95	11/8/95	4.4	2.2	160	60	0.24
	11/30/95	12/7/95	12/3/95	6.8	3.3	170	60	0.26
	12/8/95	12/17/95	12/12/95	9.2	3.9	640	50	1.41
	1/25/96	2/7/96	2/1/96	12.9	6.8	180	30	0.36
	2/7/96	2/8/96	2/8/96	0.88	0.87	360	40	0.77
	12/5/96	12/12/96	12/10/96	7	5	170	70	0.24
	12/27/96	1/5/97	12/31/96	9.1	4.5	230	60	0.41
241-SX-104	12/11/95	12/15/95	12/12/95	3.9	0.7	80	0	0.21
	1/25/96	2/7/96	2/1/96	12.9	6.9	200	0	0.52
	11/22/96	11/27/96	11/26/96	4.8	3.5	110	60	0.13
241-SX-105	12/10/95	12/13/95	12/12/95	3.7	2.5	320	0	0.75
	1/25/96	2/7/96	1/31/96	12.4	5.4	120	0	0.28
	12/26/96	1/8/97	12/28/96	13.3	1.4	710	200	1.2
241-SX-106	10/24/95	10/28/95	10/25/95	3.4	1.3	130	0	0.37
	12/12/95	12/15/95	12/12/95	3	0.6	330	0	0.93
	11/18/96	11/22/96	11/19/96	3.8	0.7	210	0	0.59
	12/9/96	12/12/96	12/10/96	2.7	0.3	200	0	0.56
	3/15/97	3/17/97	3/16/97	3.1	0.6	160	0	0.45
241-SX-109	12/11/95	12/19/95	12/12/95	7.7	0.8	110	0	0.43
241-U-103	12/9/95	12/24/95	12/12/95	14.3	3	1080	200	1.27
	2/12/96	3/5/96	2/20/96	22.4	8	990	0	1.43
	12/7/96	12/17/96	12/10/96	9.6	2.5	690	400	0.42
	2/16/97	2/23/97	2/17/97	7.6	1	630	300	0.48
	2/25/97	3/9/97	2/27/97	11.9	2	670	320	0.51
	3/14/97	3/21/97	3/16/97	6.3	1.7	750	320	0.62
241-U-105	12/10/95	12/26/95	12/12/95	15.7	2	740	170	0.92
	1/31/96	2/9/96	2/7/96	8.6	6.4	540	0	0.87
	2/18/96	2/29/96	2/20/96	11	1.8	450	80	0.60
	11/14/96	12/1/96	11/20/96	16.9	6	1440	800	1.04
	12/3/96	12/17/96	12/10/96	14	7	1050	570	0.78
	1/8/97	1/11/97	1/10/97	3.3	2	850	590	0.42
	2/25/97	3/10/97	2/27/97	12.4	1.5	540	160	0.62

Table 3-6. Amount of Gas Released from GREs in Single-Shell Tanks
(3 Sheets)

Tank	GRE Start Date	GRE End Date	Peak Date	Event Length (days)	Time to peak (days)	Peak GRE H ₂ (ppm)	Steady-state H ₂ (ppm)	H ₂ released (m ³)
241-U-105	3/15/97	3/23/97	3/16/97	7.8	0.9	550	130	0.68
241-U-107	12/11/95	12/24/95	12/11/95	11.6	0.6	640	50	1.00
	2/18/96	3/2/96	2/21/96	12.5	2.7	400	0	0.68
	9/11/96	9/18/96	9/14/96	6.8	3.4	480	300	0.30
	10/22/96	11/14/96	10/27/96	22.5	4.4	680	400	0.47
	11/14/96	11/27/96	11/19/96	13	5.4	810	430	0.64
	12/4/96	12/18/96	12/10/96	14	5.6	770	600	0.29
	12/28/96	1/16/97	12/28/96	19.3	0.4	1900	470	2.42
	4/2/97	4/9/97	4/5/97	6.7	2.5	1230	230	1.69
	4/12/97	4/20/97	4/15/97	8.2	2.8	1220	220	1.69
241-U-108	8/31/95	9/21/95	9/16/95	21.7	15.8	680	280	0.58
	9/24/95	9/30/95	9/27/95	6.3	2.8	620	340	0.41
	12/11/95	12/27/95	12/12/95	15.3	0.8	1000	300	1.02
	9/25/96	10/13/96	9/30/96	18	5.1	850	500	0.51
	10/17/96	11/6/96	10/26/96	19.8	8.6	1220	500	1.05
	11/11/96	11/28/96	11/20/96	16.2	9.3	1530	530	1.46
	12/8/96	12/26/96	12/10/96	18.2	2.5	1290	820	0.68
	2/15/97	2/24/97	2/21/97	9.1	5.6	790	490	0.44
241-U-109	12/11/95	12/25/95	12/13/95	13.8	1.4	2190	1480	1.05
	1/2/96	1/8/96	1/6/96	5.8	3.8	1510	1170	0.50
	1/9/96	1/12/96	1/10/96	2.8	0.3	1850	1030	1.21
	1/15/96	1/23/96	1/19/96	7.5	3.9	1300	980	0.47
	2/8/96	2/14/96	2/10/96	6.3	2.2	850	680	0.25
	2/18/96	2/23/96	2/22/96	4.7	4	1110	660	0.66
	2/28/96	3/4/96	3/1/96	5.6	2.3	1390	780	0.90
	1/10/97	1/18/97	1/12/97	8.1	2.5	630	210	0.62
	1/26/97	1/28/97	1/27/97	1.9	0.7	540	280	0.38

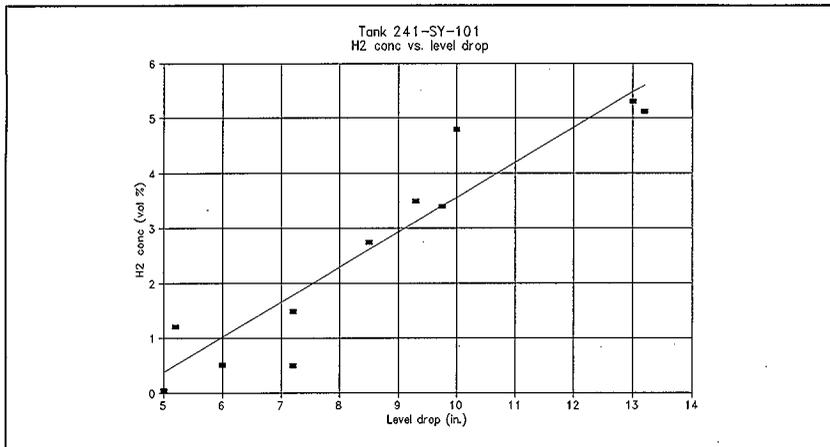


Figure 3-1. 241-SY-101 H₂ Concentration vs. Level Drop

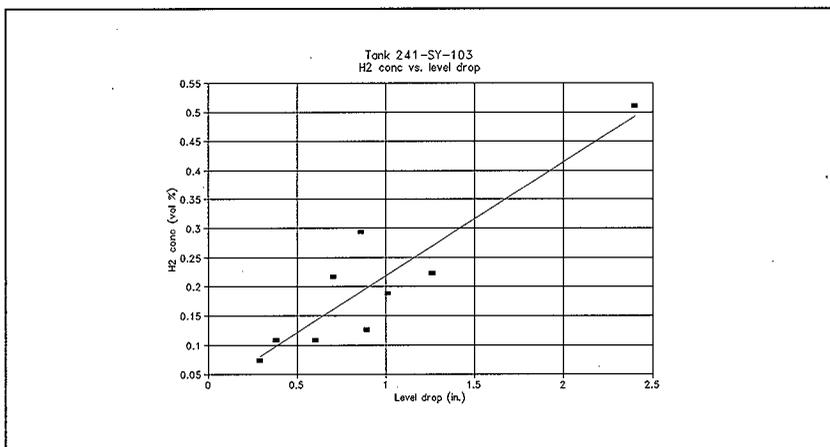


Figure 3-2. 241-SY-103 H₂ Concentration vs. Level Drop

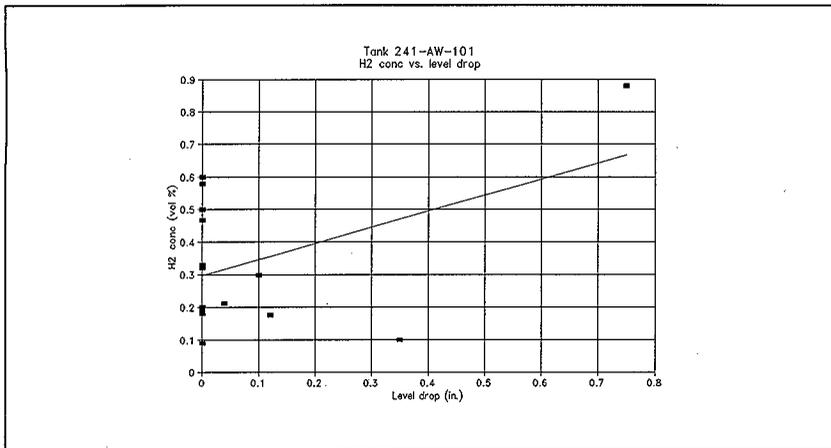


Figure 3-3. 241-AW-101 H₂ Concentration vs. Level Drop

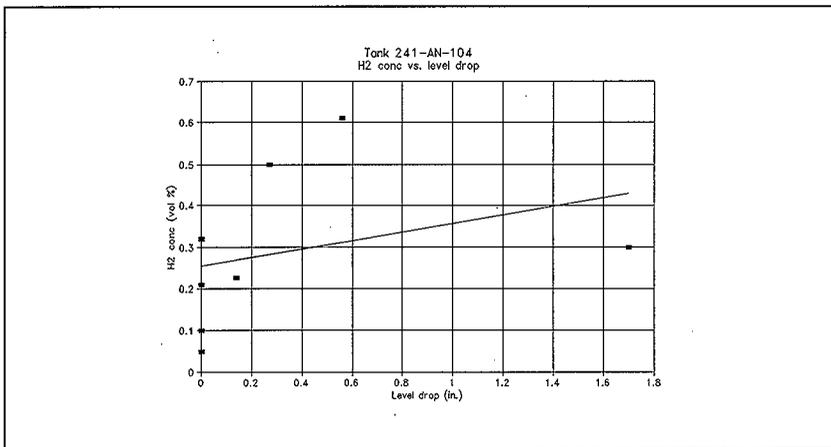


Figure 3-4. 241-AN-104 H₂ Concentration vs. Level Drop

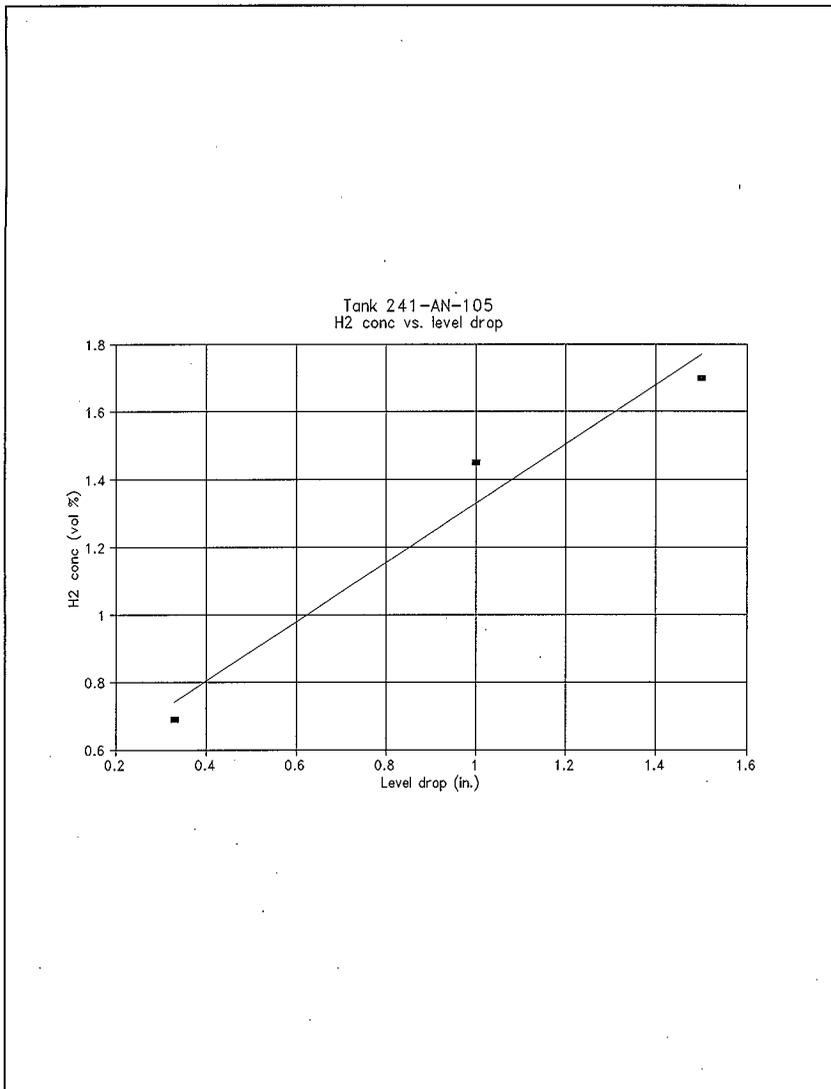


Figure 3-5. 241-AN-105 H₂ Concentration vs. Level Drop

4.0 Gas Monitoring Results

Gas monitoring is accomplished using SHMS, vapor grab samples, and the other systems described in section 2.2. Vapor grab samples are taken periodically to confirm SHMS hydrogen readings and to obtain additional information about other gases in the tanks. The other gases measured are nitrous oxide, which is an oxidizer, and methane, which is flammable. The samples are taken at the SHMS. The following is a summary of the monitoring results from the different methods.

4.1 Grab Sampling Method

A grab sample is taken automatically at the SHMS if the hydrogen concentration is above 6250 ppm. Grab samples are also taken manually on an as needed basis. To take a grab sample manually, the air flow through the SHMS is diverted to a side loop that contains the sample cylinders. The internal volume of each cylinder is 75 cc. The air flow through the loop is set between 0.22 and 0.44 cfm. The air stream passes through the cylinders for at least five minutes. The valves leading to the side loop and the sample cylinders are then closed, and the sample cylinders are removed and sent to Pacific Northwest National Laboratory (PNNL) for analysis. The samples are analyzed using a Finnigan MAT high sensitivity quantitative gas mass spectrometer.

These SHMS grab samples are taken in addition to vapor characterization samples. Characterization of the gases and vapors in the tank headspaces is needed to identify potentially hazardous waste storage conditions and for environmental protection regulatory compliance. Ongoing efforts include measuring the total organic vapor concentrations in all SSTs to estimate if a tank has a large liquid organic surface area (which could be a safety hazard), measuring the headspace water vapor concentrations to estimate evaporation rates, measurement of tank ventilation rates, and quantification of regulated emissions. Samples are collected in SUMMA™ canisters and sorbent traps. These samples are analyzed using ion chromatography (Brown et al. 1996). Data are archived in the Tank Waste Information Network System (TWINS).

4.2 Determination of Steady-State From Grab Sampling

Vapor grab samples are taken periodically from the tanks. If the hydrogen concentration measured by the SHMS is judged to not be changing rapidly, then the tank is at a steady state. Most of the grab samples were taken while the tank was at steady-state.

4.3 Summary of Double-Shell Tank Grab Sampling

Tank 241-SY-103: Table 4-1 is a list of gas concentrations measured in vapor grab samples. A "steady-state" sample was taken while the SHMS hydrogen measurements were steady, and a "GRE" sample was taken after SHMS hydrogen measurements had increased rapidly. The average hydrogen steady-state concentration was 27 ppm, and the average steady-state nitrous oxide

concentration was 18 ppm. Values preceded by a "less than" sign were omitted when averages and ratios were calculated. H_2/N_2O ratios ranged from 1 to 6. H_2/N_2O ratios from the grab samples taken during gas release events ranged from 1 to 2.

Tank 241-AW-101: Grab samples were taken from 1994 to 1997. Table 4-2 summarizes the results. The average hydrogen concentration in the samples was 169 ppm, and the average nitrous oxide concentration was 7 ppm. The H_2/N_2O ratios range from 24 to 58 for steady-state grab samples. These ratios are much higher than the gas ratios from the SY tanks. The ratios from the grab samples taken during gas releases ranged from 29 to 62.

The hydrogen concentration in these samples decreased to below 100 ppm in 1996. A ventilation flow controller began operating in March 1996, and the air flow through 241-AW-101 is now $3.5 \text{ m}^3/\text{min}$ (125 cfm). Before this controller was operating, the flow through the tank was estimated to be only about $0.6 \text{ m}^3/\text{min}$ (20 cfm).

Tank 241-AN-103: Grab sample data are listed in Table 4-3. In these grab samples, the average steady-state H_2 concentration was 53 ppm and the average N_2O concentration was 14 ppm. The H_2/N_2O ratios ranged from 10 to 16 for steady-state grab samples. The H_2/N_2O ratio from the grab sample taken during the August 1995 gas release was 20.

Tank 241-AN-104: Table 4-4 lists the vapor grab sample results. The average hydrogen concentration in the steady-state samples was 35 ppm, and the average nitrous oxide concentration was 8 ppm. The H_2/N_2O ratios ranged from 6 to 8 for steady-state grab samples. The H_2/N_2O ratio from the sample taken during a GRE was 8.

Tank 241-AN-105: Table 4-5 lists the results from the vapor grab samples. The average hydrogen concentration from the grab samples is 70 ppm. The average N_2O concentration is 17 ppm. The H_2/N_2O ratio ranges from 5 to 7 from steady-state grab samples. The H_2/N_2O ratios from the samples taken during the May 1996 GRE were both 5.

Table 4-1. 241-SY-103 Grab Samples

	Date	H ₂ , ppm	N ₂ O, ppm	CH ₄ , ppm
Steady-state	8/18/94	19	<10	<10
Steady-state	8/18/94	19	<10	<10
Steady-state	8/25/94	16	<10	<10
Steady-state	8/25/94	38	18	<10
Steady-state	9/1/94	63	39	11
Steady-state	9/1/94	3	<10	<10
Steady-state	9/7/94	<40	<10	<10
Steady-state	9/7/94	38	32	<10
Steady-state	9/15/94	27	23	<10
Steady-state	9/15/94	15	<10	<10
Steady-state	9/23/94	28	12	<10
Steady-state	9/23/94	48	23	<10
Steady-state	10/6/94	16	<5	<10
Steady-state	10/6/94	22	5	<10
Steady-state	10/19/94	22	4	<10
Steady-state	10/19/94	28	6	<10
GRE	3/2/95	1070	630	20
GRE	3/2/95	1440	900	20
GRE	8/24/95	750	450	12
GRE	8/24/95	890	540	15
GRE	6/7/96	1130	860	23
GRE	6/7/96	1160	860	22
GRE	6/7/96	1070	800	20
GRE	6/7/96	360	150	<10
GRE	7/15/96	1810	1330	40
GRE	7/15/96	1810	1300	40

Table 4-2. 241-AW-101 Grab Samples

	Date	H ₂ , ppm	N ₂ O, ppm	CH ₄ , ppm
Steady-state	9/28/94	467	8	<10
Steady-state	9/28/94	465	9	<10
Steady-state	10/27/94	240	<10	<10
Steady-state	11/2/94	173	<10	<10
Steady-state	11/10/94	400	<10	<10
Steady-state	11/16/94	380	10	<10
Steady-state	11/22/94	170	5	<10
Steady-state	12/7/94	120	5	<10
Steady-state	12/14/94	260	6	<10
Steady-state	12/21/94	400	8	<10
Steady-state	12/8/95	220	<10	<10
Steady-state	12/8/95	230	<10	<10
Steady-state	9/4/96	62	<5	<10
Steady-state	9/4/96	47	<5	<10
Steady-state	10/21/96	30	<10	<10
Steady-state	10/21/96	22	<10	<10
Steady-state	12/12/96	39	<10	<10
Steady-state	12/12/96	38	<10	<10
Steady-state	1/29/97	34	<10	<10
Steady-state	1/29/97	35	<10	<10
Steady-state	3/12/97	20	<10	<10
Steady-state	3/12/97	23	<10	<10
Steady-state	7/13/97	20	<10	<10
Steady-state	7/13/97	<10	<10	<10
GRE	10/6/94 (leaky canister)	12	5	<10
GRE	10/6/94 (leaky canister)	13	5	<10
GRE	10/21/94	2960	94	31
GRE	10/21/94	2980	93	30
GRE	11/30/94	910	31	<10
GRE	8/2/95	2850	46	25
GRE	8/2/95	2850	47	23

Table 4-3. 241-AN-103 Grab Samples

	Date	H ₂ , ppm	N ₂ O, ppm	CH ₄ , ppm
Steady-state	11/2/94	77	<10	<10
Steady-state	11/10/94	34	<10	<10
Steady-state	11/16/94	81	6	<10
Steady-state	11/22/94	22	<5	<10
Steady-state	11/30/94	230	14	<10
Steady-state	12/7/94	10	<5	<10
Steady-state	12/14/94	25	<5	<10
Steady-state	12/21/94	120	<10	<10
Steady-state	1/4/95	24	<10	<10
Steady-state	2/29/96	15	<5	<10
Steady-state	2/29/96	13	<5	<10
Steady-state	3/27/96	22	<5	<10
Steady-state	3/27/96	23	<5	<10
Steady-state	5/30/96	<5	<5	<10
Steady-state	5/30/96	<5	<5	<10
Steady-state	9/10/96	22	<10	<10
Steady-state	9/10/96	23	<10	<10
Steady-state	10/23/96	37	<10	<10
Steady-state	10/23/96	32	<10	<10
Steady-state	11/7/96	21	<10	<10
Steady-state	11/7/96	19	<10	<10
Steady-state	12/19/96	18	<10	<10
Steady-state	12/19/96	19	<10	<10
Steady-state	1/29/97	197	19	<10
Steady-state	1/29/97	197	19	<10
Steady-state	3/12/97	20	<10	<10
Steady-state	3/12/97	13	<10	<10
GRE	8/23/95	800	39	<10

Table 4-4. 241-AN-104 Grab Samples

	Date	H ₂ , ppm	N ₂ O, ppm	CH ₄ , ppm
Steady-state	11/2/94	47	<10	<10
Steady-state	11/16/94	59	7	<10
Steady-state	11/22/94	32	5	<10
Steady-state	11/30/94	67	8	<10
Steady-state	12/7/94	52	8	<10
Steady-state	12/14/94	58	10	<10
Steady-state	12/21/94	66	<10	<10
Steady-state	1/4/95	62	<10	<10
Steady-state	2/29/96	27	<5	<10
Steady-state	2/29/96	25	<5	<10
Steady-state	3/27/96	49	8	<10
Steady-state	3/27/96	51	8	<10
Steady-state	5/30/96	20	<5	<10
Steady-state	5/30/96	21	<5	<10
Steady-state	9/10/96	39	<10	<10
Steady-state	9/10/96	35	<10	<10
Steady-state	10/23/96	31	<10	<10
Steady-state	10/23/96	26	<10	<10
Steady-state	11/7/96	13	<10	<10
Steady-state	11/7/96	14	<10	<10
Steady-state	12/19/96	17	<10	<10
Steady-state	12/19/96	19	<10	<10
Steady-state	1/29/97	26	<10	<10
Steady-state	1/29/97	23	<10	<10
Steady-state	3/12/97	14	<10	<10
Steady-state	3/12/97	13	<10	<10
GRE	11/9/94	154	19	<10

Table 4-5. 241-AN-105 Grab Samples

	Date	H ₂ , ppm	N ₂ O, ppm	CH ₄ , ppm
Steady-state	11/2/94	101	19	<10
Steady-state	11/9/94	220	31	<10
Steady-state	11/16/94	96	20	<10
Steady-state	11/22/94	98	20	<10
Steady-state	11/30/94	114	20	<10
Steady-state	12/7/94	69	14	<10
Steady-state	12/14/94	173	26	<10
Steady-state	2/29/96	40	8	<10
Steady-state	2/29/96	66	11	<10
Steady-state	3/27/96	40	8	<10
Steady-state	3/27/96	59	8	<10
Steady-state	5/30/96	49	10	<10
Steady-state	5/30/96	134	27	<10
Steady-state	9/10/96	<5	<10	<10
Steady-state	9/10/96	20	<10	<10
Steady-state	10/23/96	23	<10	<10
Steady-state	10/23/96	15	<10	<10
Steady-state	11/7/96	<10	<10	<10
Steady-state	11/7/96	<10	<10	<10
Steady-state	12/19/96	15	<10	<10
Steady-state	12/19/96	16	<10	<10
Steady-state	1/30/97	37	<10	<10
Steady-state	1/30/97	37	<10	<10
GRE	8/23/95 (leaky canister)	<5	<5	<10
GRE	8/23/95 (leaky canister)	<5	<5	<10
GRE	5/30/96	4200	860	60
GRE	5/30/96	10,700	2000	110
GRE	4/6/97 (leaky canister)	180	240	7
GRE	4/6/97 (leaky canister)	110	140	5

4.4 Summary of Single-Shell Tank Grab Sampling

Vapor grab samples have also been taken from the single-shell tanks. Table 4-6 summarizes the gas content. Individual grab samples are listed in Appendix B.

Table 4-6. Single-Shell Tank Grab Sample Summary^a

Tank	H ₂ Avg (ppm)	H ₂ Range (ppm)	N ₂ O Avg (ppm)	N ₂ O Range (ppm)	H ₂ /N ₂ O Range (ppm)	CH ₄ Avg (ppm)	CH ₄ Range (ppm)
241-A-101	1043	360 - 1540	192	53 - 250	3 - 7	10	<10 - 14
241-AX-101	55	17 - 103	7	5 - 13	1 - 11	<10	<10
241-AX-103	26	17 - 36	24	13 - 40	0.9 - 1.4	<10	<10
241-S-102	617	280 - 760	446	210 - 560	1.2 - 1.5	<10	<10 - 10
241-S-111	72	<5 - 210	28	17 - 38	4.5 - 5.5	<10	<10
241-S-112	27	16 - 233	8	7 - 9	3 - 4	<10	<10
241-SX-101	8	<5 - 10	<5	<5	N/A	<10	<10
241-SX-102	18	<5 - 42	10	5 - 30	0.5 - 6	<10	<10
241-SX-103	30	6 - 66	9	5 - 15	3 - 6	<10	<10 - 10
241-SX-104	10	2 - 28	<5	<5	N/A	<10	<10
241-SX-105	13	5 - 54	<5	<5	N/A	<10	<10
241-SX-106	35	12 - 89	12	6 - 25	1 - 13	<10	<10
241-SX-109	9	<5 - 17	4	3 - 5	2.7 - 3	<10	<10
241-T-110	7	<5 - 9	<5	<5 - <10	N/A	<10	<10
241-U-103	614	360 - 840	804	500 - 1240	0.6 - 1	14	<10 - 21
241-U-105	587	460 - 670	1360	830 - 1670	0.4 - 0.6	19	16 - 24
241-U-107	352	256 - 505	494	280 - 703	0.5 - 1	<10	<10 - 10
241-U-108	429	145 - 530	438	120 - 600	0.8 - 1.4	11	<10 - 20
241-U-109	324	212 - 460	372	272 - 520	0.8 - 1.2	<10	<10 - 11
241-BY-103	101	21 - 230	36	19 - 70	0.4 - 8	3	<10
241-BY-106	201	40 - 1,110	182	17 - 1,140	0.5 - 12	7	<10
241-BY-109	75	10 - 154	6	<5 - 40	2 - 14	3	<10
241-C-106	23	1.8 - 100	24	8 - 55	1.8 - 2.2	3	<10

^aIndividual grab sample data are given in Appendix B.

All 134 passively ventilated single-shell tanks have been vapor sampled as of August 12, 1996. The tank that had the highest percentage of the LFL was 241-C-103, which had 13% of the LFL. The next highest tank was 241-S-101 at 7% of the LFL. Only 27 tanks showed flammable gas concentrations above 1% of the LFL. These results are found in Appendix C.

4.5 Summary of SHMS Monitoring

As discussed previously, continuous monitoring of hydrogen concentration is performed using SHMS. Most of the tanks being continuously monitored have a SHMS-B, which has two Whittaker™ electrochemical cells. Tank 241-AN-104 has a SHMS-C, which adds a gas chromatograph. The GC was tested at this tank to see how well it would perform in field conditions. See Section 4.6.3 for measurements from the GC. Tanks 241-C-106 and 241-AY-102 also have SHMS-C cabinets with gas chromatographs. A SHMS-D has been installed at the exhaust vents of AN and AW Farms. The SHMS-D can measure both hydrogen and ammonia, and the ammonia results are listed in Section 4.6.4. A full description of the various monitoring systems is in section 2.0. Table 4-7 lists the tank, the type of SHMS, the date the SHMS was installed, and the maximum hydrogen reading the SHMS has measured. Most of the maximum readings occurred during gas release events. Tanks 241-SX-101, 241-SX-102, and 241-T-110, have not exhibited any GRE behavior to date, and the maximums listed are maximum steady-state readings. Appendix D contains plots of data from the SHMS.

4.6 Summary of Monitoring by Other Systems

Some double-shell tanks are monitored with other systems in addition to SHMS. Results are summarized in the following sections.

4.6.1 Gas Monitoring System - 2

The Gas Monitoring System -2 (GMS-2) has been sampling from the vent header (riser 7A) of tank 101-SY since November 1992. This system is a combination of an FTIR, two hydrogen specific reduction gas analysis gas chromatographs (GC-RGA), and one photo-acoustic infra-red (IR) analyzer. The FTIR measures NH_3 and N_2O , one GC measures low concentrations of hydrogen, the other GC has a dual column and can measure both low and high concentrations of hydrogen, and the IR analyzer monitors the SY farm exhaust stack for ammonia. The GCs, FTIR, and IR analyzer are used to support mixer pump administrative controls. The data are sent to the 241-SY-101 Data Acquisition and Control System (DACS).

Steady state concentrations prior to mixer pump operation were measured using this system (Wilkins 1993). Table 4-8 lists monthly averages leading up to the last major GRE and the peak concentrations during the last major GRE in this tank. Mixer pump operations began in July 1993. Gas concentration monthly averages during selected months after July 1993 are also listed in Table 4-8. The complete database of 241-SY-101 gas data is archived regularly. See Section 4.6.4 for ammonia concentrations from the SY Farm exhaust vent.

Table 4-7. Maximum SHMS Readings

Tank	SHMS Type	Date Installed	Maximum H ₂ Reading (ppm)	Date of Maximum Reading
241-SY-101 ¹	SHMS (3 units)	March 1992	5.0E+4	9/3/92
241-SY-103	SHMS-B	May 1992	5110	12/20/96
241-AW-101 ²	SHMS-B	September 1994	8800	10/4/94
AW Farm exhaust vent	SHMS-D	June 1996	110	3/5/97
241-AN-103	SHMS-B	September 1994	3000	8/22/95
241-AN-104	SHMS-C	September 1994	5900	5/3/96
241-AN-105 ²	SHMS-B	September 1994	1.7E+4	8/21/95
AN Farm exhaust vent	SHMS-D	June 1996	0	
241-A-101	SHMS-B	March 1995	SHMS O/S	
241-AX-101	SHMS-B	March 1995	540	12/10/96
241-AX-103	SHMS-B	March 1995	380	11/22/96
241-S-102	SHMS-B	March 1995	3780	5/20/96
241-S-111	SHMS-B	March 1995	1270	12/14/95
241-S-112	SHMS-B	March 1995	490	8/22/95
241-SX-101	SHMS-B	March 1995	400	8/22/95
241-SX-102	SHMS-B	March 1995	740	11/12/96
241-SX-103	SHMS-B	March 1995	640	12/12/95
241-SX-104	SHMS-B	March 1995	580	8/22/95
241-SX-105	SHMS-B	March 1995	710	12/28/96
241-SX-106	SHMS-B	March 1995	330	12/12/95
241-SX-109	SHMS-B	March 1995	310	4/21/97
241-T-110	SHMS-B	March 1995	200	3/16/96
241-U-103	SHMS-B	March 1995	1230	7/6/97
241-U-105	SHMS-B	March 1995	3680	10/24/96
241-U-107	SHMS-B	March 1995	1900	12/28/96
241-U-108	SHMS-B	March 1995	3280	2/25/96
241-U-109	SHMS-B	March 1995	2190	12/13/95
241-BY-103	SHMS-B	July 1995	770	11/27/96
241-BY-106	SHMS-B	July 1995	880	1/5/96
241-BY-109	SHMS-B	July 1995	650	12/5/95
241-AY-102	SHMS-C	March 1997	3	5/24/97
241-C-106	SHMS-C	March 1997	756	5/16/97

1: GMS-1 and GMS-2 also installed (November 1992)
 2: GCS installed (April 1996)

Table 4-8. 241-SY-101 Gas Monitoring

	Date	H ₂ , ppm	N ₂ O, ppm	NH ₃ , ppm
Steady-state	2/93	26	28	34
Steady-state	3/93	16	15	34
Steady-state	4/93	20	22	36
Steady-state	5/93	21	24	49
Steady-state	6/93	16	17	64
GRE	6/26/93	31200	32500	13000
Steady-state	7/93	24	27	68
Steady-state	1/94	30	31	38
Steady-state	1/95	36	52	32
Steady-state	1/96	35	46	28
Steady-state	9/96	40	49	39
Steady-state	1/97	34	44	28
Steady-state	5/97	42	38	30

4.6.2 Gas Characterization System

Gas characterization systems (GCS) are installed and operating on tanks 241-AW-101 and 241-AN-105 in addition to SHMS. The dome spaces of these tanks have had hydrogen concentrations greater than 6250 ppm, the action level for hydrogen. These high hydrogen concentrations have occurred during gas release events. To learn more about the gases emitted from these tanks, GCSs were installed and they began recording data in April 1996. A GCS has a GC for hydrogen measurements, another GC for nitrous oxide and methane measurements, and an FTIR for ammonia measurements. Table 4-9 lists the steady-state gas measurements from the system. The GCS readings are consistent with the results of the grab samples. The difference between continuous hydrogen measurements measured with a SHMS and the GCS is less than 150 ppm.

Table 4-9. Gas Characterization System Results (ppm)

Tank	Hydrogen		Nitrous Oxide		Methane		Ammonia	
	Average	Range	Average	Range	Average	Range	Average	Range
241-AN-105	30	0 - 300	9	0 - 60	0	0 - 1.1	20	0 - 200
241-AW-101	39	0 - 100	2	0 - 30	0	0 - 3	7	0 - 11

Table 4-10 lists the peak concentrations measured with the GCS during the GRES that have occurred since the systems were installed on the tanks. Hydrogen, nitrous oxide, and methane tend to peak together, but ammonia tends to peak about three hours later.

Table 4-10. GCS Results during GRES (ppm)

Tank	GRE Date	Peak Hydrogen	Peak Nitrous Oxide	Peak Methane	Peak Ammonia
241-AN-105	5/30/96	14,500	2850	150	610
241-AN-105	4/5/97	5751	1496	83	119
241-AW-101	5/14/96	1455	33	0	15
241-AW-101	6/4/96	2500	86	2	19

4.6.3 Gas Chromatograph Results

Tank 241-AN-104 has a SHMS-C installed. The GC has a much higher sensitivity and accuracy than the SHMS at low hydrogen concentrations. Steady-state hydrogen measurements have an average of 34 ppm and have ranged from below 10 to 300 ppm. The system has been very reliable.

During GRES, the difference between GC and Whittaker™ measurements has been less than 1000 ppm during the peak H₂ concentrations. During steady-state, the GC and vapor grab sample (mass spectroscopy) measurements are within 20 ppm.

Gas chromatographs were installed on tanks 241-AY-102 and 241-C-106 in 1997. Tank 241-C-106 has an average hydrogen measurement of 3 ppm with a range of 0 - 27 ppm. These measurements are steady-state. They do not include concentrations during a test during which the active ventilation through the tank was halted. The maximum concentration seen during the period of no ventilation was 140 ppm. Tank 241-AY-102 has an average of 15 ppm with a range of 8 - 28 ppm.

4.6.4 Ammonia and Hydrogen Monitoring of Tank Farm Exhaust Vents

Ammonia and hydrogen are monitored at the exhaust vents of AW and AN farms with a SHMS-D. Ammonia is monitored at SY farm with a photo-acoustic infrared multi-gas monitor. The averages and ranges are listed in Table 4-11.

Table 4-11. Stack Gases (ppm)

Farm	Ammonia		Hydrogen	
	Average	Range	Average	Range
241-AN	63	0 - 183	0	0
241-AW	47	1 - 91	0	0 - 80
241-SY (1/95 - 11/96)	36	25 - 90	not measured	not measured
241-SY (12/96 - 7/97)	26	0 - 100	not measured	not measured

5.0 Determination of In-Tank Gas Composition

The composition of gas stored in the waste needs to be known. This gas composition, when coupled with the volume of gas which can potentially be released and ignited, is used to calculate the consequences of a burn in the dome space. Without the specific composition of the gas a conservative assumption must be applied. The composition of the gas within the waste is also needed to assess the potential for ignition of the gas below the waste surface.

Due to the large size of gas releases in 241-SY-101 it is possible to estimate the gas composition stored in the waste from analysis of the headspace gas. For all other tanks this has not been possible and alternate methods such as the Retained Gas Sampler have been developed.

5.1 Composition of 241-SY-101 Waste Gas

Pasamehmetoglu (1994) analyzed a large body of gas composition data and provided estimates for the composition of gases released during a gas release event. The results are shown in Table 5-1. Hydrogen is less than one-third the total gas volume for tank 241-SY-101. The concentrations of nitrogen and nitrous oxide are similar, and ammonia is a principal component.

The data used in the estimate of the 241-SY-101 waste gas composition are from several sources. The hydrogen and nitrous oxide data are from grab sampling taken during large gas release events. The ammonia and methane data are taken

from the FTIR data recorded by GMS-2. The water vapor is calculated from vapor pressure data. The "other" is assumed to be carbon monoxide for the purpose of the burn energy calculation, although it likely consists of organic compounds as well.

The biggest problem in determining the composition is measurement of the amount of nitrogen. Nitrogen is the major constituent of the air and is also a significant constituent of the waste gas. The nitrogen is calculated using argon as an indicator gas with the assumption that all the argon is from air dilution of the headspace and that no argon is produced by the waste or contained in the waste gas. For the large releases in 241-SY-101 the waste gas comprised a significant percentage of the gas present in the headspace. This caused the argon concentration to be depressed a measurable amount. By knowing the ratio of argon to nitrogen for both the headspace gas and for "normal" air, the quantity of the nitrogen contributed by the waste can be calculated (Burke 1991).

Table 5-1. Estimated Composition of Gases at 46°C
in Tank 241-SY-101 (Pasamehmetoglu 1994)

Component	Estimated Composition, Mol. %
Hydrogen	29
Nitrous Oxide	24
Ammonia	11
Nitrogen	33
Methane	0.4
Other	0.3
Water	2.4

5.2 Waste Gas Composition for Other Tanks

Gas composition data were collected by mass spectrometry analysis of grab samples taken from the head space of various Hanford tanks (Tables 4-1 to 4-6). Some of these grab samples were collected during gas release events, but none of them were of sufficient volume to allow the application of the argon indicator method used for 241-SY-101 analysis. In order to determine the waste gas composition the retained gas sampler (RGS) was developed.

The RGS enables the composition of gases trapped in Hanford wastes to be determined by directly sampling the waste. Samples of trapped gas from tanks 241-AW-101, 241-A-101, 241-AN-103, 241-AN-104, and 241-AN-105 have been analyzed using the RGS. The results are discussed in Shekarritz, et al. (1997). Preliminary results from measurements of tank 241-U-103 are discussed in Mahoney, et al. (1997). The results from these tanks as well as preliminary results from tank 241-U-103 are presented in Table 5-2.

Table 5-2. Retained Gas Sampler Results

Tank	Gas Concentration (mol %)		
	Nitrogen	Hydrogen	Nitrous Oxide
241-AW-101	60	31	5.7
241-A-101	18	72	5.6
241-AN-105	27	60	11
241-AN-104	33	46	19
241-AN-103	35	60	6.7
241-U-103	31-36	14-26	27-32

Only nitrogen, hydrogen, and nitrous oxide are listed in Table 5-2; the remainder of the gas content is ammonia and hydrocarbons.

An alternate method being considered to measure gas concentration at depth in the waste is to collect a vapor grab sample from a conduit which has been inserted into the waste and held for a period of time long enough for a significant quantity of waste gas to accumulate in the vapor space inside the conduit. The conduit may either be open to the waste on the end (such as a core sampling drill string) or permeable to the gas of interest. Waste gases are known to accumulate in the core sampling drill string cover gas if left stagnant for a period of time. By purging the conduit with an inert gas such as argon prior to the hold period, or by applying a method similar to that used for estimation of the 241-SY-101 composition, the gas composition can be estimated. This method could be used to obtain waste gas composition information on tanks that cannot be sampled using the RGS. This method probably would not be capable of measuring the retained gas volume or distribution of the retained gas.

Table 5-3 lists waste gas concentrations measured from drill string grab samples taken during core sampling of several tanks. The ammonia values may be low due to gas adsorbing on the walls of the sampling equipment, or for AN-103 and AN-104, due to absorption in the water used as hydrostatic head fluid in the drill string.

Table 5-3. Waste Gas Sample Results from Drill String Grab Samples (ppm)^a

Tank	Date	Hydrogen	Nitrous Oxide	Methane	Ammonia
241-AN-103	9/16/96	96,000	10,400	410	<10
241-AN-104	9/11/96	68,000	22,900	1830	<10
241-AW-101	2/28/96	29,600	2360	<10	not reported
241-B-203	11/17/95	3150	<100	2	<10
241-BY-109	6/17/97	29,500	8800	520	not reported
241-BY-110	10/26/95	240,000	149,000	8330	2800
241-S-102	1/12/96	26,900	16,100	210	<10
241-S-102	2/14/96	21,400	1740	<10	not reported
241-S-106	2/25/97	63,100	15,700	<10	<1000
241-S-107	9/26/95	6800	900	110	not reported
241-SX-104 (LOW)	7/20/95	24,000	6400	200	450
241-U-109	12/28/95	14,400	2800	60	not reported
241-U-109	1/4/96	62,000	53,000	800	<100
241-U-109 (Quill Rod)	1/18/96	6500	4230	110	not reported

^a Schofield 1997

6.0 Hydrogen Generation Rates

Hydrogen generation and release rates were calculated for the double-shell tanks and the single-shell tanks.

6.1 Double-Shell Tanks

A hydrogen generation rate was estimated for each double-shell tank. Hydrogen generated by the waste is either retained (accumulated) by the waste or released to the head space (steady-state release). By measurement of these two rates, the generation rate can be estimated.

Accumulation rate

The amount of hydrogen accumulating in the waste was estimated by

$$(1) \quad R_A = C_S * S * V_2$$

R_A = rate of gas accumulation [m^3/day]

C_S = hydrogen vapor fraction in the slurry gas

S = rate of slurry growth [cm/day]

V_2 = gas volume per cm of slurry growth [$m^3/tank\ cm$]

This accumulation rate does not account for any crust formation or the accumulation of any gas in the crust. Neglecting the gas in the crust may cause an overestimation of the overall accumulation rate. Hydrogen is also assumed to be negligibly soluble in the waste.

The volume of slurry gas per tank inch of slurry growth (V_2) was calculated as follows: The waste in these tanks show cycles of waste height growth and drops. The drops can be correlated to gas release events. In double-shell tanks, one vertical inch (2.54 cm) is equal to 2750 gallons (10.4 m^3). Converting this to cubic feet (and cubic meters):

$$\begin{aligned} 1 \text{ inch} &= 367.7 \text{ ft}^3 \\ 1 \text{ cm} &= 4.1 \text{ m}^3 \end{aligned}$$

This would be the gas volume per unit length if the gas was not under pressure. However, it is believed that the gas is trapped in the waste sludges in the lower parts of the tanks. The waste places hydrostatic pressure on the gas. This pressure can be calculated by:

$$(2) \quad P_h = D * H * G$$

P_h = hydrostatic pressure

D = density of the waste

H = height of waste above the gas

G = acceleration of gravity

The total pressure on the gas is the sum of the hydrostatic pressure and the atmospheric pressure.

$$(3) \quad P_{\text{total}} = P_h + P_{\text{atm}}$$

The gas is assumed to behave as an ideal gas, which is valid for pressures below 3 atm. The volume of an ideal gas can be calculated at different pressures by

$$(4) \quad (P_1 * V_1)/T_1 = (P_2 * V_2)/T_2 \quad \text{or} \quad V_2 = V_1 * (P_1/P_2) * (T_2/T_1)$$

where P_1 = total pressure on the stored gas
 V_1 = gas volume under pressure P_1
 T_1 = waste temperature
 P_2 = pressure at standard condition (1 atm)
 V_2 = gas volume at standard temperature and pressure
 T_2 = temperature at standard conditions (288.15 K).

Assuming waste growth occurs where the gas accumulates, V_2 represents the volume of gas (at standard temperature and pressure) that is displacing the waste.

The waste density in the tank sludges has been estimated using a ball rheometer (Stewart et al. 1996a). (A ball rheometer is a 71-N (16 lb.) tungsten alloy ball tethered to a cable. As the ball is lowered into the waste, the tension on the cable is measured. The rheology and density of the waste can be estimated from the drag force on the ball.) These densities were used to calculate an average pressure at the sludge layers. These pressures were corrected to standard temperature and pressure as an effective pressure ratio:

$$(5) \quad P = (P_1/P_2) * (T_2/T_1)$$

Substituting P into (4) gives:

$$(6) \quad V_2 = V_1 * P$$

V_2 is used in equation (1).

The rate of slurry growth, S, was estimated using waste level measurements since January 1997. S is used in equation (1).

The amount of hydrogen in the slurry gas, C_s , was based on retained gas sampler (RGS) measurements (Shekarriz et al., 1997), except for 103-SY. The amount of hydrogen in the slurry gas for 103-SY was estimated based on past GRE peak concentrations and the amount of total gas released based on the level drop following the GRE.

Release rate

The amount of hydrogen released during steady-state was estimated using the tank ventilation rate and the steady-state hydrogen concentration.

$$(7) \quad R_{ss} [\text{m}^3/\text{day}] = Q [\text{m}^3/\text{min}] * 1440 \text{ min/day} * C_{ss}$$

R_{ss} = rate of hydrogen released at steady-state

Q = tank ventilation rate

C_{ss} = steady-state hydrogen vapor fraction

The steady-state hydrogen concentration was calculated from the average of the vapor grab sample concentrations (see section 4.3) with the exception of tanks 241-AN-104 and 241-AN-105. The average hydrogen measurements measured with the gas chromatographs since March 1997 were used for these tanks. The vent flow through these tanks was increased in February 1997. Results from these calculations are listed in Table 6-1. The total hydrogen generation rate is the sum of the accumulation rate and the steady-state release rate.

Table 6-1. Hydrogen Generation Rates (DSTs)

Tank	m^3 gas per tank cm	H_2 accumulation (m^3/day)	H_2 release (m^3/day)	H_2 generation (m^3/day)
241-SY-101 (pre-mixer pump)	8.9 ⁽¹⁾	0.54	0.45	0.99
241-SY-103	7.0	0.05	0.09	0.14
241-AW-101	8.7	0.03	0.17	0.20
241-AN-103	7.9	0.08	0.10	0.18
241-AN-104	8.2	0	0.21	0.21
241-AN-105	8.5	0.03	0.12	0.15

- (1) The amount of gas per inch of slurry growth for tank 101-SY is from an internal memo by D. A. Reynolds which is included in the Appendix of Erhart (1991).

An estimate of the hydrogen generation rate in tank 241-SY-103 has also been made based on a laboratory test of tank waste samples taken in 1994 from the convective layer. The result was 8.7 mol/day for the entire tank (King 1997). Assuming the hydrogen is at 15°C and 1 atm, 0.14 m^3/day , converts to 5.9 mol/day. The two values are in reasonable agreement when the uncertainties in the measurements are considered.

Generation rates for other gases were also calculated in a manner similar to the hydrogen generation calculation and are listed in Table 6-2. RGS measurements were used as estimates of the amounts of nitrous oxide and methane in the waste gas. Tanks 241-SY-101 and 241-SY-103 have not had RGS

measurements performed and are not included. Vapor grab samples and gas chromatograph or FTIR measurements (where available) were used to estimate the amount of nitrous oxide and in the tank exhaust. The nitrous oxide rate is based on the sum of nitrous oxide accumulating in the waste and the amount leaving the tank in the exhaust. The methane rate is based on the amount accumulating in the waste only; methane concentrations have been less than detectable in the vapor grab samples and steady-state measurements with the gas chromatographs have been near zero.

Table 6-2. Other Gas Generation Rates

Tank	Nitrous Oxide (m ³ /day)	Methane (m ³ /day)
241-AW-101	0.02	0.001
241-AN-103	0.09	0.0008
241-AN-104	0.05	0
241-AN-105	0.04	0.006

6.2 Single-Shell Tanks

The steady-state hydrogen generation rate was calculated based on the steady-state hydrogen concentration and the tank ventilation rate using equation (7). The steady-state hydrogen concentration was estimated from the vapor grab samples (see Table 4-6). The ventilation rates are estimated in section 7.0. The rates listed here (except 241-S-102) are the averages of the rates listed in the third column of Table 7-1 for each tank. For tank 241-S-102, the result of the tracer gas test listed in column 4 was used.

Five tanks (241-S-102, 241-U-103, 241-U-105, 241-U-107, and 241-U-108) show waste level growth which may indicate gas retention. The amount of hydrogen accumulating in the waste was estimated using equation (1). The amount of hydrogen in the slurry gas, C_s , for tank 241-U-103 was based on preliminary retained gas sampler measurements (see Table 5-2). The amount of hydrogen in the slurry gas for the other tanks was assumed to be 50 vol%. The volume of gas per cm of slurry growth (V_2) was calculated as shown in section 6.1. The center of the trapped gas was assumed to be at a fraction of 0.43 of the nonconvective layer height measured from the tank bottom. This estimate is based on a probability distribution curve included in Barker 1997.

The total generation rate is the sum of the steady-state release rate and the accumulation rate.

Table 6-3. Hydrogen Generation Rates (Single-Shell Tanks)

Tank	Steady-state H ₂ (ppm)	Ventilation rate (m ³ /min)	Steady-state Release Rate (m ³ /day)	Accumulation Rate (m ³ /day)	Total Generation (m ³ /day)
241-S-102	617	0.06 (tracer test)	0.053	0.013	0.066
241-S-111	72	0.084	0.009		0.009
241-S-112	27	0.11	0.004		0.004
241-SX-103	30	1.2	0.052		0.052
241-SX-104	10	0.71	0.010		0.010
241-SX-105	13	1.5	0.028		0.028
241-SX-106	35	1.0	0.050		0.050
241-SX-109	9	0.85	0.011		0.011
241-U-103	614	0.13	0.115	0.003	0.118
241-U-105	587	0.19	0.168	0.010	0.178
241-U-107	352	0.09	0.046	0.006	0.052
241-U-108	429	0.09	0.056	0.012	0.068
241-U-109	324	0.09	0.042		0.042

This revision reports new generation rates. Additional ventilation rates from calculations based on recent gas release events are included in the averages in Table 6-3. Also, the accumulation terms listed here were not calculated in the previous report.

An estimate of the hydrogen generation rate in tank 241-S-102 has also been made based on a laboratory test of tank waste samples. The result of this test was 1.0 mol/day for the entire tank (King 1997). Assuming the hydrogen is at 15°C and 1 atm, 0.066 m³/day, converts to 2.8 mol/day.

The range in hydrogen generation rate reported for the laboratory test based on experimental uncertainties is 0.8 to 1.2 mol/day. It should be noted that this range only includes the experimental uncertainties and does not include the effects of extrapolating measurements from a core sample in a discrete location to the whole tank. In other words, the uncertainty in the generation rate extrapolated to the whole tank is certainly greater than just the experimental uncertainty.

The range in hydrogen generation rate estimated using equation (7) is 1.1 to 4.1 mol/day. This range is calculated using the minimum and maximum hydrogen

concentrations measured in the dome space by grab sampling (Table 9 of Appendix B) and the 95% confidence limits in the ventilation rate as measured in the tracer gas study of this tank. Although the nominal values differ by a factor of 3, when the range of uncertainty in the estimates is considered, the two methods are in agreement.

The hydrogen generation rate is important in the safe operation of the tanks from the standpoint of setting controls for ventilation rates and maximum time allowed without ventilation. Assuming the nominal hydrogen generation rate as estimated by equation (7), it is not possible for the headspace concentration to reach 25% of the lower flammability limit (LFL) (Stauffer 1997).

7.0 Tank Ventilation Rates

The proposed Data Quality Objective (DQO) for the flammable gas safety issue (Jackson 1997) identifies the need for suitable algorithms or models to predict short and long term Gas Release Events (GRE) and steady state flammable gas concentrations. The Standard Hydrogen Monitoring Systems (SHMS) are intended to provide much of the data needed to develop and benchmark the needed algorithms. An evaluation was performed for the SST SHMS data to assess flammable gas GRE and steady state behavior. A significant parameter for the steady state algorithm is ventilation flow. For double-shell tanks and actively ventilated single-shell tanks, nominal breathing rates are established. However, for passively ventilated SSTs, breathing rates are unknown. An evaluation of the ventilation rate based upon the SHMS data was also performed. This work is in progress and as such the results presented in sections 7.1 and 7.2 should be considered preliminary until the work is complete. An attempt to measure passive ventilation rates was made using tracer gases in some tanks, and the results are presented in section 7.4.

7.1 GRE Behavior

The SHMS data for Tank 241-U-103 and 241-SX-106 are shown in Figures 7-1 and 7-2. These represent typical data for passively and actively ventilated single-shell tanks, respectively. The barometric pressure is also plotted. Two GREs are clearly seen for both tanks. These occurred in December 1995 and February 1996. The hydrogen concentration rises rapidly followed by a long period of decreasing concentration. The period of decreasing concentration appears to follow an exponential decay. Both GREs occurred during a significant weather disturbance resulting in a decrease in barometric pressure.

Because of the sensitivity of the SHMS instruments, the steady state and GRE concentrations are too small to provide reliable estimates of their absolute magnitude. However, the relative change in concentrations should be reliable.

7.2 GRE Model

If the dome space is well mixed following a GRE and the steady state release rate is small compared with the ventilation flow rate, then the dome space hydrogen concentration is given by the following expression:

$$C_h/C_{ho} = e^{-Q \cdot t/V}$$

where

C_h = time dependent dome space hydrogen concentration

C_{ho} = initial dome space hydrogen concentration

Q = ventilation rate

V = dome space volume

t = time after the GRE

Given the relative hydrogen concentration, the tank ventilation flow rate can be obtained. The simple GRE model was applied to the December 1995 GRE for tank 241-U-103 (Figure 7-1) and is shown in Figure 7-3. The model fits the data well with a ventilation flow rate of 0.057 m³/min (2 cfm). The model was applied similarly to all the distinguishable GREs from the SHMS data available.

Figure 7-1 Tank 241-U-103 SHMS Data.

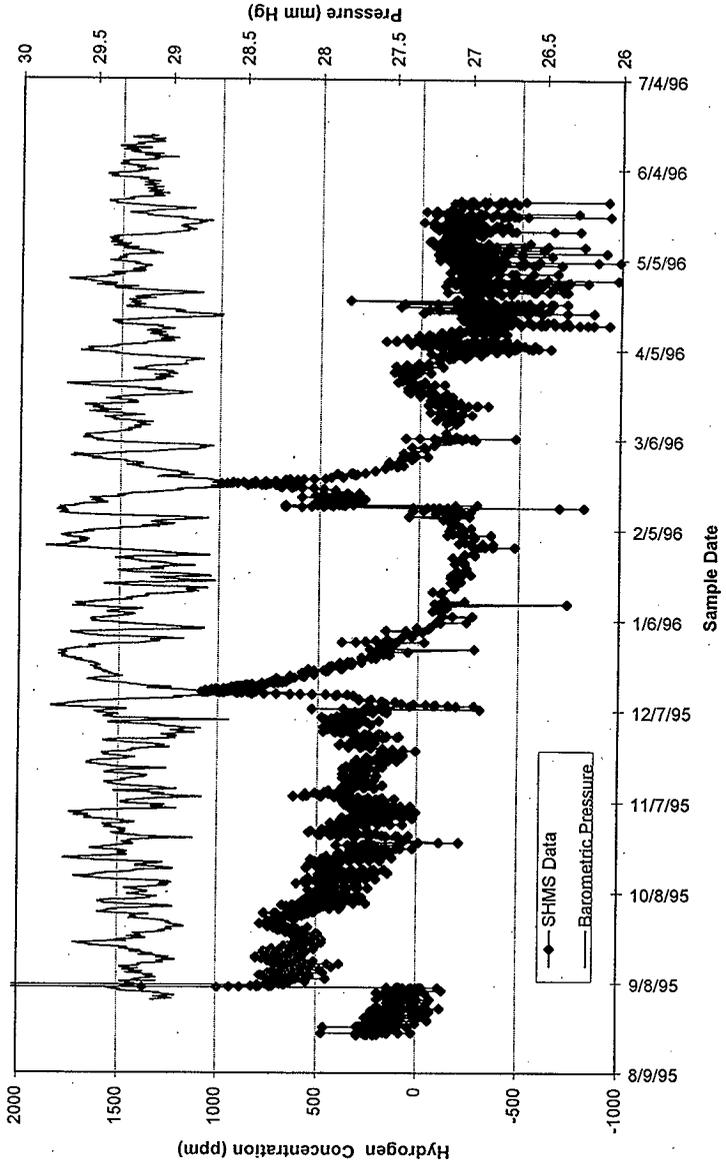


Figure 7-2 Tank 241-SX-106 SHMS Data

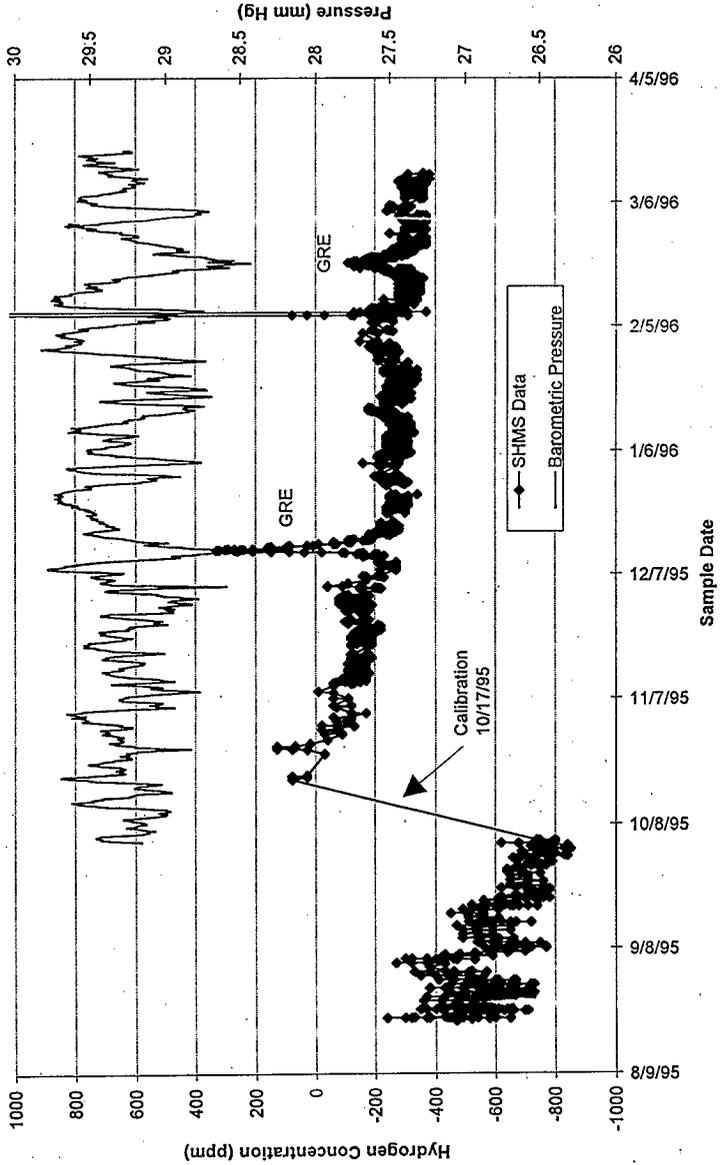
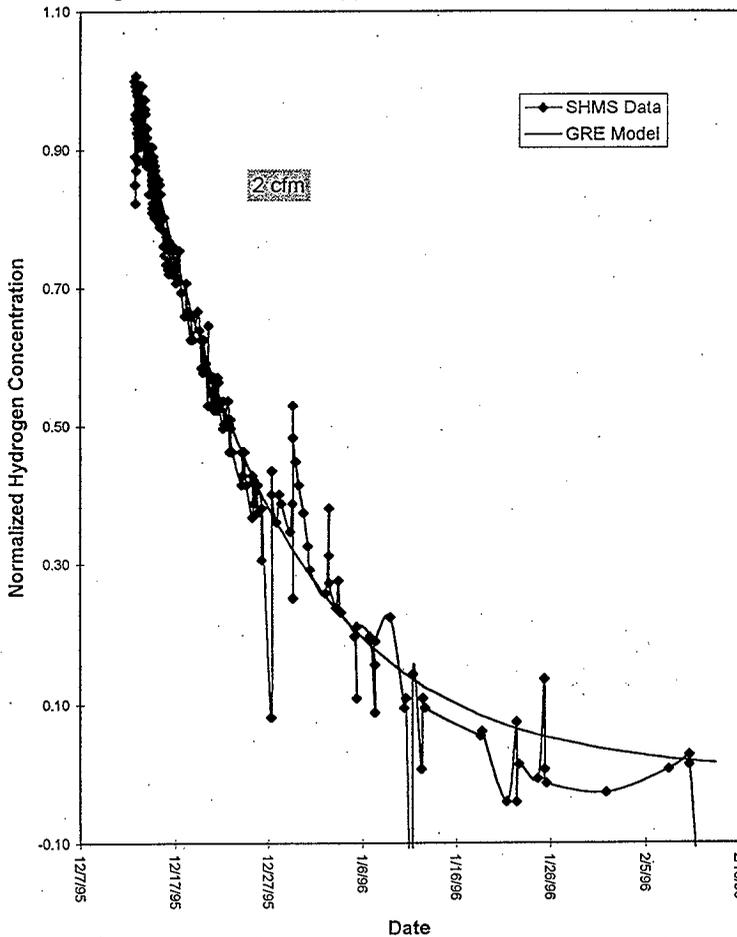


Figure 7_3 GRE model applied to tank 241-U-103 GRE.



7.3 GRE Data Evaluation

A summary of the application of the GRE model to the SHMS data is shown in Table 7-1. These results should be considered preliminary until the evaluation is complete.

Table 7-1. Summary of GRE evaluation (preliminary)

Tank Description	SHMS Data		Other Data/Analyses		Barometric Breathing (m ³ /min)
	Date	Ventilation Flow (m ³ /min)	Ventilation Rate (m ³ /min)	Comment	
241-S-102			0.06 ^a	Tracer test	0.0057 ^a
241-S-111	Nov-95	0.06			0.0057 ^a
	Dec-95	0.11			
	Dec-95	0.11			
	Feb-96	0.11			
	Nov-96	0.06			
	Dec-96	0.06			
	Jan-97	0.08			
241-S-112	Jan-96	0.11			0.0057 ^a
241-SX-103	Dec-95	1.4	0.82 ^b	Gothic analyses	
	Dec-96	1.13			
	Dec-96	1.13			
	Jan-97	1.13			
241-SX-104	Dec-95	0.85	1.0 _c	Gothic analyses	
	Feb-96	0.57			
241-SX-105	Dec-95	2.8	0.62 ^b	Gothic analyses	
	Feb-96	1.1			
	Dec-96	0.67			
241-SX-106	Oct-95	0.85	0.82 ^b	Gothic analyses	
	Dec-95	1.4			
	Feb-96	0.99			
	Dec-96	0.85			
241-SX-109	Dec-95	0.85	0.62 ^b	Gothic analyses	
	Nov-96	0.85			
	Nov-96	0.85			
241-U-103	Sep-95	0.07	0.04 ^a	Tracer test	0.0028 ^a
	Oct-95	0.20			
	Dec-95	0.06			
241-U-105	Feb-96	0.20			
	Dec-95	0.25	0.14 ^a	Tracer test	0.0057 ^a
	Feb-96	0.14			
	Nov-96	0.11			
241-U-107	Dec-96	0.25			
	Dec-95	0.13			0.0057 ^a
	Feb-96	0.085			
	Sep-96	0.08			
241-U-108	Jan-97	0.06			
	Oct-95	0.085			0.0028 ^a
	Nov-95	0.11			
	Dec-95	0.085			
241-U-109	Sep-95	0.11			0.0028 ^a
	Oct-95	0.14			
	Dec-95	0.03			
	Oct-96	0.06			
	Dec-96	0.06			
	Dec-96	0.06			
	Dec-96	0.06			

a - See Section 7.4, b - McLaren 1995, c - Hodgson et al. 1996

The magnitude of the GREs seem to be small relative to the Lower Flammability Limit (LFL); however, nearly thirteen of nineteen tanks demonstrated some GRE behavior. There seems to be a correlation between weather disturbances and SST GREs. Nearly all the tanks listed in Table 7-1 had a GRE during the December 1995 weather disturbance and the GREs distinguishable by the SHMS data occur during the winter months when the barometric pressure disturbances are largest.

The ventilation rates derived from the SHMS data and the simple GRE model are also shown in Table 7-1. The ventilation rates for passively ventilated tanks range from 0.03 m³/min (1 cfm) to 0.25 m³/min (9 cfm). These rates are an order of magnitude larger than barometric breathing rates (0.45 % of the dome tank free volume per day [Hodgson 1996]) shown in the table. The ventilation rate for the actively ventilated tanks of the SX farm are much larger than the passive rates as expected. They range from 0.57 to 1.4 m³/min (20 to 50 cfm). Estimates of the SX farm ventilation rates based on thermal hydraulic analyses using tank temperature data (McLaren 1995) are shown in Table 7-1. There is reasonable agreement with the ventilation rates derived from the SHMS data.

7.4 Tracer Gas Tests

Ventilation measurements were made for several passively ventilated tanks using tracer gases (helium and sulfur hexafluoride). Small quantities of tracer gases were injected into the headspaces. Concentrations were determined and monitored as a function of time to determine the rates at which the gases were removed by ventilation. Concentrations were monitored by collecting and analyzing headspace air samples at various times after the gases were injected.

Three assumptions were made: the tracer gases are inert, the tank headspace is well-mixed, and the amount of air exchanged with connected tanks was small compared with the amount of air exchanged with the atmosphere. The tank ventilation rate was calculated with the following equation:

$$Q = \frac{V}{(t_j - t_i)} \ln \left(\frac{C_j}{C_i} \right)$$

where Q is the volumetric ventilation rate, V is the headspace volume, and C_i and C_j are the concentrations of the tracer gas at times t_i and t_j.

Observations were made that in some tanks the ventilation rates calculated using sulfur hexafluoride as a tracer gas can be more than two times higher than those calculated using helium as a tracer gas. The cause of this effect has not been pinpointed, however it is postulated that mechanisms such as radiolysis or adsorption/absorption are causing the sulfur hexafluoride to disappear from the system at the accelerated rate. Because of this unexpected behavior, sulfur hexafluoride has been dropped as a tracer gas. The breathing rate tests are proceeding with helium as the sole tracer gas.

Table 7-2. Ventilation rates from tracer gas tests^a

Tank	Period of study	Ventilation rate (m ³ /min)
241-A-101	7/9/97 - 7/15/97	0.285
241-AX-103	2/25/97 - 3/3/97	0.695
241-BY-105	4/17/97 - 5/8/97	0.44
241-C-107	2/21/97 - 3/21/97	0.04
241-S-102	9/24/96 - 2/11/97	0.06
241-U-103	2/27/97 - 7/22/97	0.04
241-U-105	7/18/97 - 7/24/97	0.14

^aHuckaby 1997

8.0 Flammable Gas Action Levels for Hanford Waste Tanks

The following sections define the flammable gas action level for Hanford waste tanks, the planned response should the action level be exceeded, and a summary of the occurrences in which the action level has been exceeded.

8.1 Description of Action Level

The Tank Farm Operations organization is required by DOE Order 5480.4 to follow the guidelines provided within the National Fire Protection Association NFPA 69. This guideline requires systems which contain flammable gas and have the potential for an ignition source to be maintained at a concentration below 25% of the lower flammability limit (LFL) of the gas or gas mixture.

Each of the Hanford tanks generates a different composition of flammable gas. The fuel gases produced by the tanks are composed primarily of hydrogen, but also can contain significant quantities of ammonia and methane. In addition to the fuel gases, the tanks can also produce nitrous oxide, which under certain conditions can enhance the flammability of the mixture. It is cumbersome and expensive to monitor for all the gases which can contribute to the flammable gas issue. For this reason hydrogen, being by far the dominant flammable gas of concern, was selected as the gas species to be monitored as the indicator when additional action is required.

To account for the effect of the other gases which may be present, the hydrogen concentration at which action is taken is adjusted (Sherwood 1995). The action level is set at 6250 ppm of hydrogen. This concentration of hydrogen is equivalent to 25% of the LFL for the expected worst case gas mixture from a Hanford tank. This is the level at which additional characterization of the headspace gas and other mitigation measures would be considered.

8.2 Action Level Response

In the event a hydrogen vapor reading in a tank headspace exceeds 6250 ppm, an engineering evaluation is to be performed (Sherwood 1995).

The purpose of this evaluation is to determine whether or not the tank presents a serious safety issue and if mitigation of the tank is necessary. This approach in deciding the need for mitigation is used because of the high cost of implementing the mitigation methods, such as installation and operation of a mixer pump, and also the substantial safety risk to the tank farm workers in installing this type of equipment.

The following is a typical example of the recommendations resulting from the engineering evaluation of a gas release event in waste tank 241-AN-105 (Minteer 1996). It should be noted that this action plan is for an actively ventilated double-shell tank and portions of this plan would likely be different for a passively ventilated single-shell tank:

- a) Improve tank monitoring and characterization capabilities in order to obtain the data necessary to lower uncertainties in the gas composition, gas release volume, and waste gas inventory determinations.
 - install gas characterization system
 - install hydrogen/ammonia monitor in ventilation system
 - obtain characterization data from void fraction meter, viscometer, and retained gas sampler tests
 - install air flow meter
 - increase frequency of tank waste level measurements

- b) Optimize tank ventilation flows to ensure that dilution air flow is adequate to minimize the time required to reduce the flammable gas concentration following a release.
 - determine optimum tank air flow balance, considering any necessary dilution at existing fan
 - provide air flow control capability for every tank in the farm and set flow rates to the optimum values
 - for the interim, ensure flammable gas watch list tank air flows are maintained at above 2.8 m³/min (100 cfm) (based on engineering judgement)

- c) Assure low risk of igniting a flammable gas mixture to prevent ignition of the released gas in the event the LFL is exceeded.
 - evaluate need to de-energize or replace ventilation system heaters, and other options
 - evaluate need to replace ventilation fan with "spark less" model, and other options
 - evaluate need to de-energize or replace any other potential ignition sources

- d) Determine the need for additional actions after subsequent gas release event data are obtained and evaluated.

8.3 Summary of Gas Release Events Exceeding the Action Level

Other than the major gas release events recorded in waste tank 241-SY-101, three events have been observed since the installation of SHMS units in which the tank headspace flammable gas concentration exceeded the action level. Two of these events were observed in tank 241-AN-105 (both exceeded 14,000 ppm H₂) and one in 241-AW-101 (approximately 8800 ppm). The flammable gas headspace concentration has not exceeded the action level in tank 241-SY-101 since installation of the mixer pump in July 1993.

Tanks 241-AN-105 and 241-AW-101 have undergone additional characterization as a result of these events. This characterization includes installation of gas characterization systems (GCS), sampling with the retained gas sampler, and measurements with the void fraction instrument and ball rheometer. Ventilation system upgrades are in progress for these tanks. Inlet flow

controllers and exhaust port flowmeters have been installed, and installations of intrinsically safe fans and duct heaters are planned.

9.0 Action Plans for Continued Monitoring

Continued monitoring of the Watch List tanks and other tanks with a serious potential to exceed 25% of the LFL in the headspace will be accomplished using either the currently installed SHMS units, the gas characterization systems, or new systems which will be installed. Improvements to the existing systems are planned to correct operational problems encountered to date.

9.1 Current System Issues and Corrective Actions Planned

Issues affecting the operations of the SHMS units and the quality of the data obtained include plugging of the sample line filter with condensed water, failure of the system to record data, and plugging of the sample line with ammonium nitrate.

Plugging of sample line filter with condensed water - The waste tank headspace temperature is typically warmer than the ambient temperature. Since one of the major components of the waste is water it is expected that the moisture content in the dome space will be above the saturation level for the ambient conditions. Moisture becomes an issue in the system when the volume of collected water becomes so great that the sample line filter becomes plugged. Provisions are included in the design of the SHMS to minimize the effects of the moisture by heat tracing the sample lines and controlling the temperature of the instrumentation cabinet in an attempt to prevent the moisture from condensing in the sample piping. In the majority of the systems these provisions have worked well, however for tanks 241-A-101, 241-AX-101, 241-S-102, and 241-SX-102 the moisture accumulation problem is so severe that a permanent engineering solution is needed. The moisture accumulation does not affect the quality of the data, but it does affect the quantity of data. Plugging of the sample line prevents any gas from moving through the Whittaker™ cell.

Data Recording - One of the main purposes of the SHMS is to record the history of hydrogen concentrations. This is accommodated in the system design by an output channel for connection to the Tank Monitoring and Control System (TMACS) and an internal chart recorder. The chart recorder system was included as a temporary data recorder for use in the short term until TMACS was connected to the system and also to act as a back-up data logger. Unfortunately, the TMACS connection for many of the systems has been delayed and the chart recorders have experienced many of the typical problems for these components, such as jammed paper, running out of paper, running out of ink, not turned back on after servicing, etc., which has resulted in loss of some data. In addition the data from the charts themselves are very cumbersome to analyze.

Plugging of sample lines with ammonium nitrate - This problem has only been encountered with the system installed on waste tank 241-AX-103. In this case the sample line does not plug with water but with a substance that is composed of ammonium nitrate contaminated with PUREX solvent and solvent degradation products (see Appendix A). This material is known to have been the culprit in plugging of ventilation systems previously in Hanford waste tanks (Borsheim 1991). Proper precautions must be implemented when performing work on the portions of the system which may contain this material.

False hydrogen readings - On four occasions, one Whittaker™ cell has appeared to detect high hydrogen concentrations, and the other cell shows only steady-state concentrations. The SHMS on the following tanks have shown this phenomenon: 241-S-102, 241-BY-103, 241-U-107, and 241-AY-102. The cells respond normally when calibrated. The high hydrogen concentrations are not considered to be real (see section 2.3). The behavior may be due to electrolyte leakage from the Whittaker cells. In the case of AY-102, the problem may be due to a main circuit board production problem. The Whittaker™ readout voltmeter has been replaced.

Hydrogen concentration diurnal variation - During the summer months, the Whittaker™ cell will record a dip in hydrogen concentration followed by a sharp rise. The difference between valley and peak can be as much as 400 ppm. The concentration will stabilize at the prior baseline within fifteen minutes. This phenomenon occurs in most of the SHMS and happens at the same hour every morning. It may be caused by sunlight shining directly through the SHMS viewing windows, which face east. The sunlight may be briefly heating the Whittaker™ cells. A film which reflects ultraviolet and infrared radiation was placed on the 241-U-107 SHMS viewing window. The film has dampened the effect but has not eliminated it. The daily variation has decreased from 200 ppm to 50 ppm.

Long term solutions for some of these issues have been developed and are being implemented as described in section 9.1.1.

9.1.1 Issue Resolution

Plugging of sample line filters with condensed water - For SHMS on tanks with a history or potential of high vapor space moisture, gas sample conditioners (GSCs) have been or are being installed. These systems consist of a condenser coil that separates moisture from the sample stream. These systems are intended to prevent moisture clogging of the SHMS sample lines. These systems have been installed on waste tanks 241-A-101 and 241-C-106. Tanks 241-AY-102, 241-AX-101, 241-AZ-101, 241-AZ-102, 241-S-102, and 241-SX-102 will have GSCs installed in the future. Any portable SHMS used in the tank farms will also have GSCs.

Data Recording - There are two approaches being pursued. The first is to connect as many of the systems as practical to TMACS. This was accomplished for all the SHMS units other than those in AX, AW, AY, BY, and C farms. For AX and AW farms, as well as any new systems for which TMACS is not available, a separate data acquisition system is being installed in each unit. This system will digitally record the data. These systems have already been

installed in the SHMS units for 241-AY-102 and 241-C-106. For the SHMS-E+ units the data will also be accessible over the Hanford Local Area Network (HLAN) similar to the system used for the gas characterization systems (GCS).

Plugging of sample lines with ammonium nitrate - A final solution to this issue has not been determined. The current method of flushing the system and allowing the material to reform is not acceptable in the long run. The solution applied to solve a similar problem installed a "scrubber" in the sample line. The "scrubber" is simply a water bath that the gas is bubbled through, which causes the water to absorb the material (ammonia and ammonium nitrate). This method should work but has the disadvantage of adding moisture (already a problem in some tanks) and it removes ammonia from the sample stream. Removal of ammonia is only an issue if it is identified as a gas which must be measured.

9.2 Application of New Systems

An assessment of the flammable gas monitoring needs was conducted in late Fiscal Year 1996 to determine equipment requirements and priorities so that the various project needs could be addressed and available resources used effectively. The results of that assessment have been reported in Revision 1 of this document as well as the Flammable Gas Topical Report (Johnson 1997).

A total of thirteen new gas monitoring systems were installed in Fiscal Year 1997. These systems are listed in Table 9-1. Plans for Fiscal Year 1998 call for installation of four new systems and one cart-mounted SHMS-E+ monitor. These systems are listed in Table 9-2. Plans for Fiscal Year 1998 also call for installation of gas sampling probes in nine double-shell tanks. This work will complete installation of probes in all double-shell tanks which will facilitate characterization of tank vapor spaces using either the cart-mounted SHMS-E+ monitor or grab sampling.

Table 9-1. New SHMS Installations in Fiscal Year 1997

Tank	SHMS Type	Project
241-A-101	SHMS-E+ with GSC	Flammable Gas Upgrade
241-BY-105	SHMS-E+	Flammable Gas
241-SY-102	SHMS-E+	Salt Well Pumping Receiver Tank
241-S-107	SHMS-B	Flammable Gas
241-C-106	SHMS-C with GSC	W-320 Sluicing
241-AY-102	SHMS-C with GSC	W-320 Sluicing
241-AN-101	SHMS-E+	Salt Well Pumping Receiver Tank
241-AN-107	SHMS-B	Flammable Gas
241-AZ-101	SHMS-E with GSC	Aging Waste
241-AZ-102	SHMS-E with GSC	Aging Waste
241-S-101	SHMS-E	Flammable Gas
241-S-106	SHMS-E+	Flammable Gas
241-S-109	SHMS-E+	Flammable Gas

Table 9-2. New SHMS Installations Planned for Fiscal Year 1998

Tank	SHMS Type	Project
241-SX-103	SHMS-E+	Flammable Gas Upgrade
241-U-102	SHMS-E	Flammable Gas
241-U-105	SHMS-E+	Flammable Gas
241-AP-104	SHMS-E+	Salt Well Pumping Receiver Tank
241-AW-104	Cart-Mounted SHMS-E+	Flammable Gas

10.0 Conclusions

SHMS units have been designed, procured, fabricated, and installed on all 25 Flammable Gas Watch List tanks. Vapor space grab samples have been obtained and analyzed for all 25 tanks. Additional SHMS units are being installed on high priority tanks. The background gas compositions for the tanks have been measured and are reported here. The vapor spaces of the tanks have been observed for a significant period of time. The length of time has been sufficient to demonstrate that steady state release of gas into the tank headspace of passively ventilated and actively ventilated tanks does not result in gas concentrations exceeding the action level.

Monitoring to date has shown that:

1. Single-shell tanks do not appear to be subject to large rapid gas releases. The peak hydrogen concentrations during GREs in the single-shell tanks have been below 25% of the LFL. GREs in the single-shell tanks require days to increase from steady-state concentrations to the peak concentration.
2. SHMS reliably detect GRE's. The detection of hydrogen increases using the Whittaker™ cells has been confirmed with data from vapor grab samples and gas chromatographs.
3. The composition of gas retained in the waste appears to vary widely between tanks. In the double-shell tanks, data from vapor grab samples show H₂/N₂O ratios of about 1 for tank 241-SY-103 and near 60 for tank 241-AW-101. These ratios tend to be below 10 in the single-shell tanks.

Plans currently call for monitoring of the existing FGWL tanks to continue through September 2000 and for monitoring of additional high priority tanks using improved SHMS units.

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Appendix A

Internal Memo, N. W. Kirch to W. E. Ross, "Potential Hazard Due to Plugging of 241-AX-103 Sample Line," dated June 28, 1996.

**Westinghouse
Hanford Company**
**Internal
Memo**

From: Process Control
 Phone: 373-2380 R2-11
 Date: June 28, 1996
 Subject: POTENTIAL HAZARD DUE TO PLUGGING OF 241-AX-103 VAPOR SAMPLE LINE

74A30-96-029

To: W. E. Ross S5-07

cc: H. Babad	S7-14	J. J. Klos	R2-54
W. B. Barton	R2-11	D. C. Larsen	T4-08
R. E. Bauer	S7-14	J. W. Lentsch	S7-14
L. M. Calderon	R3-08	D. P. Reber	T4-07
K. G. Carothers	R1-51	D. A. Reynolds	R2-11
R. A. Dodd	S5-07	T. C. Schneider	L6-37
G. L. Dunford	A2-34	O. M. Serrano	R2-54
J. E. Geary	S5-07	J. P. Sloughter	R2-54
J. W. Hagan	R3-01	A. M. Umek	H6-35
G. N. Hanson	S5-05	NWK File/LB	
G. D. Johnson	S7-14		

Reference: WHC-EP-0347, "Summary of Single-Shell Tank Waste Stability," dated March 1991.

The standard hydrogen monitoring system (SHMS) on tank 241-AX-103 experienced sample line plugging after only a short period of operation. The material plugging the line, which was described as "green goo," was sampled and analyzed. The sample analysis indicated approximately 50 weight % nitrate, with no commensurate amount of cation identified, and approximately 9.1 weight % organic carbon. A differential scanning calorimeter (DSC) analysis indicated 760 joules per gram.

Based on previous tank farm and process plant experience at Hanford, it is very likely that this material is ammonium nitrate, contaminated with PUREX solvent and solvent degradation products. A summary of ammonium nitrate issues in the Hanford tank farms is provided in Reference 1; which discusses previous incidents of tank ventilation system plugging with ammonium nitrate.

Ammonium nitrate is an important industrial chemical in agricultural fertilizers and explosives. As an explosive ingredient or as an explosive material, it is exceedingly stable. However, a number of experiments have indicated that confined ammonium nitrate (as in a closed pipe) will detonate a short time after being heated to the point where a decomposition reaction begins (approximately 410 °F). It was concluded in Reference 1 that:

". . . ammonium nitrate cannot exist in the liquid SST waste and the formation of ammonium nitrate in the tank vapor space and tank ventilation systems should not be considered a hazard unless high temperatures are experienced, the system is confined under pressure or contamination of the ammonium nitrate with organic

W. E. Ross
Page 2
June 28, 1996

74A30-96-029

material is experienced. These conditions are not present during interim storage in the tank farms."

A recognition that ammonium nitrate may exist in tank ventilation or vapor sampling systems important to the safety of the workers.

The presence of ammonium nitrate in a vapor sample line presents an industrial safety hazard should any hotwork (ie. work that creates intense heat or sparks) be performed on the line. The Tank Farm Health and Safety Plan, WHC-SD-WM-HSP-002 refers to "Controlling Hotwork," WHC-CM-4-41, Section 5.3 for the requirements and responsibilities to control hazards associated with these activities. This section states that:

"If the hotwork is to be performed on pipes or other metal, then verify that combustibles in contact with the metal are protected from ignition caused by heat conduction through the metal or are too far from the heat source to be at risk."

It also states:

"Before starting hotwork on items too small or constricted to enter (such as small tanks, pipes, vessels, or containers), ensure the interior of the item is cleaned and purged according to the job hazard analysis or work package until it contains no flammable materials or other materials that might create flammable or toxic vapors if heated."

Tank 241-AX-103 is a Flammable Gas Watch List tank. Although it is not anticipated that hotwork would be performed on this sample line, the requirements for hotwork can be met by flushing the line with water to remove highly soluble ammonium nitrate. Awareness that the potential for ammonium nitrate to exist in these systems is important to ensuring the proper precautions are implemented.

If you have any questions, please contact me at 373-2380.

N. W. Kirch
N. W. Kirch, Manager
Process Control

mjg

Appendix B
Vapor Grab Sample Results

The following tables contain vapor grab sample results from the single-shell tanks.

Table 1. A-101 Vapor Grab Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
5-18-95	1260	7	220
6-8-95	743	<12	217
6-8-95	746	<12	219
6-8-95	786	<12	218
7-25-95	1180	8	210
7-27-95	1460	8	210
8-3-95	360	6	55
8-4-95	390	5	53
8-7-95	1540	14	250
8-8-95	1370	13	220
8-10-95	1350	13	230
8-11-95	1420	12	230
8-15-95	950	10	160
[H ₂] _{Range}		360 - 1540 ppm	
[H ₂] _{Average}		1,043 ppm	
[H ₂]/[N ₂ O] _{Range}		3 - 7 ppm	

HNF-SD-WM-TI-797, Rev. 2

Six samples were taken on July 29, 1997, during ventilation rate measurements using helium as a tracer gas (see Section 7.4 for a test description). The valves on canisters 011 and 069 were found to be leaking slightly.

Table 2. A-101 SUMMA™ Canister Samples

Sample Identification	Hydrogen (ppm)	Methane (ppm)	Nitrous Oxide (ppm)	Helium (ppm)
V0001-A01.011	170	3	69	4
V0001-A02.057	170	3	66	4
V0001-B01.149	190	3	64	580
V0001-B02.223	190	3	74	580
V0001-C01.069	160	2	74	72
V0001-C02.071	180	<2	73	79

Table 3. AX-101 Vapor Grab Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-15-95	103	< 12	< 13
6-15-95	102	< 12	< 13
7-25-95	59	2	6
7-27-95	67	2	8
7-28-95	50	1	5
7-31-95	43	2	5
8-3-95	57	2	6
8-7-95	17	2	13
8-8-95	56	2	5
8-9-95	44	2	5
8-10-95	100	3	9
8-11-95	62	3	8
8-15-95	78	2	7
10-3-96	65	<10	<10
10-3-96	63	<10	<10
12/19/96	28	<10	<10
12/19/96	40	<10	<10
1/29/97	18	<10	<10
3/12/97	26	<10	<10
3/12/97	18	<10	<10
[H ₂] Range 17 - 103 ppm			
[H ₂] Average 55 ppm			
[H ₂]/[N ₂ O] Range 1 - 11			

HNF-SD-WM-TI-797, Rev. 2

Table 4. AX-103 Vapor Grab Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-21-95	<98	<12	24
6-21-95	<98	<12	24
6-21-95	<98	<12	23
7-25-95	27	2	21
7-27-95	33	2	24
7-28-95	28	1	24
7-31-95	27	2	22
8-3-95	24	2	24
8-4-95	26	3	25
8-7-95	17	2	13
10-3-96	36	<10	40
10-3-96	20	<10	20
[H ₂] _{Range}		17 - < 98 ppm	
[H ₂] _{Average}		26 ppm	
[H ₂]/[N ₂ O] _{Range}		0.9 - 1.4	

Table 5. BY-103 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
5/5/94	21	NR	49
5/5/94	22	NR	49
5/5/94	21	NR	49
9/22/95	230	4	70
10/2/95	130	3	22
10/9/95	200	3	25
10/13/95	150	2	19
3/27/96	66	<10	20
3/27/96	69	<10	20
$[H_2]_{Range}$		21 - 230 ppm	
$[H_2]_{Average}$		101 ppm	
$[H_2]/[N_2O]_{Range}$		0.43 - 8	

NR - Not Reported

Table 6. BY-106 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
5/4/94	48	< 61	92
5/4/94	43	< 61	91
5/4/94	46	< 61	96
7/8/94	104	3.6	70
7/8/94	47	4	71
7/8/94	40	4	71
9/22/95	1,110	20	1,140
10/2/95	520	12	410
10/9/95	210	5	17
10/13/95	140	2	45
3/27/96	51	<10	41
3/27/96	50	<10	34
[H ₂] _{Range} 40 - 1,110 ppm			
[H ₂] _{Average} 201 ppm			
[H ₂]/[N ₂ O] _{Range} 0.46 - 12			

HNF-SD-WM-TI-797, Rev. 2

Table 7. BY-109 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
9/22/95	154	2	40
10/2/95	90	4	9
10/9/95	100	4	7
10/13/95	80	2	6
3/27/96	10	<10	<5
3/27/96	15	<10	<5
[H ₂] _{Range}		10 - 154 ppm	
[H ₂] _{Average}		75 ppm	
[H ₂]/[N ₂ O] _{Range}		2 - 14	

HNF-SD-WM-TI-797, Rev. 2

Table 8. C-106 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
3/17/97	4	4	<10
3/17/97	4.4	5	<10
3/18/97	5	4	<10
3/18/97	4.2	4	<10
3/19/97	5	5	<10
3/19/97	4.4	5	<10
3/20/97	6.5	4	<10
3/20/97	1.8	5	<10
3/21/97	8.7	5	<10
3/21/97	6.6	4	<10
3/27/97	5.8	3	<10
3/27/97	4.5	4	<10
6/4/97 (1445)	4.2	2	<10
6/4/97 (1445)	4.3	2	<10
6/4/97 (2146)	22	1	11
6/4/97 (2146)	20	1	11
6/5/97 (0509)	38	1	18
6/5/97 (0509)	38	2	20
6/5/97 (1440)	69	2	32
6/5/97 (1440)	67	2	31
6/5/97 (2152)	68	2	32
6/5/97 (2152)	14	2	8
6/6/97 (0530)	100	2	55
6/6/97 (0530)	49	2	25
[H ₂] _{avg}		1.8 - 100 ppm	
[H ₂] _{max}		23 ppm	
[H ₂]/[N ₂ O] _{avg}		1.8 - 2.2	

Table 9. S-102 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
3-14-95	669	< 12	491
3-14-95	670	< 12	550
3-14-95	668	< 12	487
5-5-95	300	4	210
8-4-95	600	4	410
8-7-95	280	4	210
8-7-95	410	5	280
8-8-95	750	7	560
8-8-95	720	8	510
8-9-95	700	9	490
8-10-95	750	10	530
8-10-95	760	9	540
8-11-95	750	10	530
[H ₂] _{Range}		280 - 760 ppm	
[H ₂] _{Average}		617 ppm	
[H ₂]/[N ₂ O] _{Range}		1.2 - 1.5	

Table 10. S-111 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
7-11-95	53	< 5	< 10
7-14-95	16	< 5	< 10
7-17-95	< 5	< 5	< 10
8-3-95	77	2	17
8-4-95	5	2	< 5
8-7-95	210	3	38
$[H_2]_{Range}$ < 5 - 210 ppm			
$[H_2]_{Average}$ 72 ppm			
$[H_2]/[N_2O]_{Range}$ 0.5 - 5			

Table 11. S-112 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
5-3-95	27	< 5	< 10
7-11-95	33	< 5	< 10
7-14-95	24	< 5	< 10
7-17-95	32	< 5	< 10
8-3-95	28	2	7
8-4-95	16	2	< 5
8-7-95	27	2	9
$[H_2]_{Range}$ 16 - 33 ppm			
$[H_2]_{Average}$ 27 ppm			
$[H_2]/[N_2O]_{Range}$ 3 - 4			

Table 12. SX-101 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
6-2-95	8	2	< 5
6-6-95	5	< 5	< 5
6-9-95	< 5	2	< 5
6-22-95	7	< 5	< 5
6-27-95	< 5	< 5	< 5
6-30-95	< 5	< 10	< 5
7-7-95	< 5	< 10	< 5
9-11-95	< 5	2	< 5
9-15-95	NR	NR	NR
9-19-95	NR	2	NR
9-25-95	10	2	NR
10-4-95	NR	4	NR
3-20-96	NR	NR	NR
3-20-96	NR	NR	NR
[H ₂] _{Range}		< 5 - 10 ppm	
[H ₂] _{Average}		7.5 ppm	

N/R - Not reported

Table 13. SX-102 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-2-95	35	2	6
6-6-95	16	< 5	5
6-9-95	12	2	5
6-12-95	14	1	5
6-22-95	16	< 5	30
6-27-95	26	< 5	< 5
7-7-95	13	< 10	< 5
8-18-95	< 5	3	< 5
8-25-95	5	2	< 5
9-1-95	42	2	8
9-11-95	< 5	2	<5
9-15-95	20	2	NR
9-19-95	7	2	NR
9-25-95	15	2	NR
10-4-95	8	2	NR
[H ₂] _{Range}		< 5 - 42 ppm	
[H ₂] _{Average}		18 ppm	
[H ₂]/[N ₂ O] _{Range}		0.5 - 6	

NR - Not reported

Table 14. SX-103 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-2-95	66	2	15
6-6-95	32	2	8
6-9-95	24	2	8
6-12-95	28	2	9
6-22-95	31	< 5	7
6-27-95	47	< 5	8
6-30-95	40	10	8
7-7-95	19	< 10	< 5
8-18-95	19	2	< 5
8-25-95	16	3	5
9-1-95	63	< 3	13
9-11-95	15	2	<5
9-15-95	45	2	8
9-19-95	16	2	NR
9-25-95	37	2	NR
10-4-95	23	3	NR
3-20-96	6	NR	NR
3-20-96	10	NR	< 5
[H ₂] _{Range}		6 - 66 ppm	
[H ₂] _{Average}		29.8 ppm	
[H ₂]/[N ₂ O] _{Range}		2 - 6	

NR - Not reported

Table 15. SX-104 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
6-2-95	9	< 5	< 5
6-6-95	< 5	< 5	< 5
6-9-95	2	2	< 5
6-12-95	5	2	< 5
6-22-95	< 5	< 5	< 5
6-27-95	< 5	< 5	< 5
6-30-95	< 5	< 10	< 5
7-7-95	7	< 10	< 5
8-18-95	< 5	3	< 5
8-25-95	< 5	2	< 5
9-1-95	14	2	< 5
9-11-95	< 5	2	< 5
9-15-95	NR	2	NR
9-19-95	7	1	NR
9-25-95	28	2	NR
10-4-95	5	1	NR
[H ₂] _{Range}		2 - 28 ppm	
[H ₂] _{Average}		10 ppm	

NR - Not reported

Table 16. SX-105 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
6-2-95	16	< 5	< 5
6-6-95	5	< 5	< 5
6-9-95	5	2	< 5
6-12-95	5	2	< 5
6-22-95	< 5	< 5	< 5
6-27-95	6	< 10	< 5
6-30-95	8	< 10	< 5
7-7-95	10	< 10	< 5
8-18-95	12	2	< 5
8-25-95	< 5	2	< 5
9-1-95	54	2	10
9-11-95	< 5	2	< 5
9-15-95	12	2	NR
9-19-95	5	2	NR
9-25-95	21	2	NR
10-4-95	12	2	NR
3-20-96	NR	NR	NR
3-20-96	NR	NR	NR
[H ₂] _{Range}		< 5 - 54 ppm	
[H ₂] _{Average}		13 ppm	
[H ₂]/[N ₂ O] _{Range}		1 - 5	

NR - Not reported

Table 17. SX-106 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
6-2-95	48	2	25
6-6-95	12	2	10
6-9-95	12	2	9
6-12-95	13	2	12
8-18-95	15	2	< 5
8-25-95	18	3	< 5
9-1-95	89	3	7
9-11-95	27	2	6
9-15-95	66	2	22
9-19-95	27	3	6
9-25-95	70	2	16
10-4-95	42	3	8
3-20-96	20	NR	14
3-20-96	25	NR	14
[H ₂] _{Range}		12 - 89 ppm	
[H ₂] _{Average}		35 ppm	
[H ₂]/[N ₂ O] _{Range}		1 - 13	

NR - Not reported

Table 18. SX-109 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-2-95	15	2	5
6-6-95	7	2	< 5
6-9-95	6	2	< 5
6-12-95	8	< 5	3
8-25-95	< 5	1	< 5
9-1-95	17	< 5	< 5
3-20-96	5	NR	NR
3-20-96	6	NR	NR
[H ₂] Range < 5 - 17 ppm			
[H ₂] Average 9 ppm			
[H ₂]/[N ₂ O] Range 1 - 3			

NR - Not reported

Table 19. T-110 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-27-95	8	< 10	< 5
6-30-95	7	< 10	< 5
7-7-95	7	< 10	< 5
7-11-95	6	< 5	< 10
7-14-95	< 5	< 5	< 10
7-17-95	< 5	< 5	< 10
7-25-95	7	NR	NR
7-27-95	7	NR	NR
7-31-95	NR	2	NR
2-6-96	9	NR	NR
2-6-96	8	NR	NR
[H ₂] Range < 5 - 9 ppm			
[H ₂] Average 7 ppm			

NR - Not reported

Table 20. U-103 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
2-15-95	552	<61	875
2-15-95	557	<61	856
2-15-95	555	<61	904
5-3-95	780	21	910
6-27-95	740	21	750
6-30-95	780	19	790
7-7-95	840	20	880
7-11-95	830	16	1240
7-14-95	620	13	830
7-17-95	360	8	500
7-25-95	460	10	630
7-27-95	440	6	630
7-31-95	470	10	660
[H ₂] _{Range}		360 - 840 ppm	
[H ₂] _{Average}		614 ppm	
[H ₂]/[N ₂ O] _{Range}		0.62 - 1	

Table 21. U-105 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
7-7-95	660	24	1120
6-30-95	500	16	830
7-11-95	670	18	1660
7-14-95	670	17	1670
7-17-95	650	17	1620
2-7-96 (not included in average calculations)	26 (bad valve on grab sampler)	NR	390
2-7-96	460	NR	1260
5-9-96	500	20	1360
$[H_2]_{Range}$		460 - 670 ppm	
$[H_2]_{Average}$		587 ppm	
$[H_2]/[N_2O]_{Range}$		0.4 - 0.6	

NR - Not reported

Table 22. U-107 Vapor Sample Results

Sample Date	H2 (ppm)	CH4 (ppm)	N2O (ppm)
2-17-95	496	< 12	701
2-17-95	505	< 12	698
2-17-95	499	< 12	703
6-20-95	280	< 10	280
6-30-95	330	10	350
7-10-95	340	10	340
7-10-95	340	10	340
7-11-95	330	7	510
7-14-95	330	< 5	490
7-17-95	310	6	410
7-25-95	380	NR	580
7-27-95	430	NR	640
7-31-95	380	NR	520
2-7-96	260	NR	490
2-7-96	256	NR	490
5-9-96	260	< 10	430
5-9-96	260	< 10	430
[H ₂] _{Range}		256 - 505 ppm	
[H ₂] _{Average}		352 ppm	
[H ₂]/[N ₂ O] _{Range}		0.5 - 1	

NR - not reported

Table 23. U-108 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
6-27-95	430	11	330
6-30-95	410	8	310
7-7-95	500	10	360
7-11-95	470	10	530
7-14-95	450	8	510
7-17-95	430	18	450
9-11-95	490	7	530
9-11-95	480	8	550
9-18-95	NR	2	NR
9-18-95	8	1	NR
2-7-96	296	NR	370
2-7-96	145	NR	120
5-9-96	520	10	600
5-9-96	530	20	600
[H ₂] _{Range}		145 - 530 ppm	
[H ₂] _{Average}		429 ppm	
[H ₂]/[N ₂ O] _{Range}		0.8 - 1.4	

NR - Not reported

The samples taken on 9/18/95 were not included in the average calculation or range because the values are unusually low. A problem with the sample cylinder is suspected.

Table 24. U-109 Vapor Sample Results

Sample Date	H ₂ (ppm)	CH ₄ (ppm)	N ₂ O (ppm)
7-7-95	460	11	390
7-11-95	410	8	460
7-14-95	420	7	520
7-17-95	390	7	470
2-7-96	212	NR	273
2-7-96	215	NR	272
5-9-96	240	10	29
5-9-96	240	10	30
[H ₂] _{Range}		212 - 460 ppm	
[H ₂] _{Average}		324 ppm	
[H ₂]/[N ₂ O] _{Range}		.78 - 1.2	

NR - not reported

Appendix C

Attachment to Funderburke, W. M., October 24, 1996, *Transmittal of Defense Nuclear Facilities (DNFSB) Recommendation 93-5, Revision 1, Milestone 5.4.3.5.G "Letter Reporting Completion of Flammable Gas Safety Screening of Remaining Passively Ventilated Single Shell Tanks (SSTs) to Determine if Steady-State Vapors Are Less Than 25 Percent of the Lower Flammability Limit (LFL)"*, Letter from Duke Engineering and Services Hanford to S. Marchetti, Fluor Daniel Hanford, Richland, WA.

**RESULTS OF VAPOR PHASE SAMPLING OF THE HANFORD
PASSIVELY VENTILATED SINGLE-SHELL TANKS**

All 134 passively ventilated single-shell tanks have had their vapor phase sampled for flammable gas either by use of the vapor sampling system (VSS) truck (Reference 1) or by direct measurement on a stream extracted from the tank's dome space using a combustible gas meter (CGM, Reference 2). The results of this sampling for each tank are presented in the attached table. The table lists each tank, the date the tank was sampled, the type of sampling performed and the resulting percentage of the lower flammability limit obtained.

The tank which showed the highest percentage of the LFL is 241-C-103. The result reported for this tank is only 13% of the LFL, well below the action limit of 25% of the LFL. This tank has a floating organic layer on its surface and is expected to have relatively higher concentrations of both flammable organic vapors and hydrogen. The next highest tank was 241-S-101 at 7% of the LFL. Of the 134 tanks sampled only 27 showed flammable gas concentrations above 1% of the LFL.

The purpose of this sampling is to understand the steady state concentration of flammable gas in these tanks under normal operating conditions. There was no attempt made to sample during periods of restricted passive ventilation or gas release events. While these conditions may occur and would result in elevated flammable gas conditions in the tank, it is important to understand that the normal condition for the dome space is nonflammable even in tanks which only experience passive ventilation.

References:

1. Bratzel, D. R.; H. Babad; J. L. Huckaby, "Headspace Gas and Vapor Characterization Summary for 43 Vapor Program Suspect Tanks"; Section 3.2.1 pages 8-9, WHC-SD-WM-ER-514, September, 1995
2. Grigsby, J. M.; C. E. Leach, "Flammable Gas/Slurry Growth Unreviewed Safety Question: Justification for Continued Operation for the Tank Farms", Appendix A section A4.1 pages A12-A13, WHC-SD-WM-JCO-007 rev. 0A.

Tank #	Sample Date	Sample Type	Total LFL (%)
SST Passive			
A-101	04/09/95	VSS	2.5
A-102	11/10/95	VSS	0.93
A-103	11/09/95	VSS	1.38
A-104	01/14/96	CGM	0
A-105	01/19/96	CGM	0
A-106	08/12/96	CGM	2
AX-101	04/15/95	VSS	0.32
AX-102	06/28/95	VSS	0
AX-103	04/21/95	VSS	<0.31
AX-104	01/14/96	CGM	0
B-101	03/26/96	CGM	0
B-102	04/18/96	VSS	0
B-103	02/08/95	VSS	0
B-104	03/26/96	CGM	0
B-105	06/06/96	CGM	0
B-106	04/26/96	CGM	0
B-107	06/06/96	CGM	2
B-108	04/26/96	CGM	0
B-109	06/12/96	CGM	0
B-110	04/26/96	CGM	0
B-111	03/19/96	CGM	0
B-112	08/30/95	CGM	0
B-201	06/04/96	CGM	0
B-202	06/04/96	CGM	0
B-203	11/20/95	CGM	0
B-204	04/26/96	CGM	0

Tank #	Sample Date	Sample Type	Total LFL (%)
BX-101	04/24/96	CGM	0
BX-102	06/24/96	CGM	0
BX-103	03/26/96	CGM	0
BX-104	12/30/94	VSS	0.4
BX-105	04/24/96	VSS	0
BX-106	12/19/95	CGM	0
BX-107	11/17/95	VSS	0.1
BX-108	08/29/95	CGM	0
BX-109	04/24/96	CGM	0
BX-110	10/02/95	CGM	0
BX-111	04/24/96	CGM	0
BX-112	04/16/95	CGM	0
BY-101	08/08/96	CGM	0
BY-102	11/21/95	VSS	0.26
BY-103	11/01/94	VSS	0.1
BY-104	06/24/94	VSS	1
BY-105	07/07/94	VSS	0.3
BY-106	07/08/94	VSS	0.2
BY-107	10/26/94	VSS	2.3
BY-108	10/27/94	VSS	3.4
BY-109	08/08/96	CGM	0
BY-110	11/11/94	VSS	0.4
BY-111	11/16/94	VSS	0.2
BY-112	11/18/94	VSS	0.1
C-101	09/01/94	VSS	1.8
C-102	08/23/94	VSS	1.2
C-103	05/24/94	VSS	13

Tank #	Sample Date	Sample Type	Total LFL (%)
C-104	3/3/94	VSS	0.3
C-107	09/29/94	VSS	0.6
C-108	08/05/94	VSS	0
C-109	08/09/94	VSS	0.3
C-110	08/24/94	VSS	0.2
C-111	09/13/94	VSS	0.03
C-112	08/11/94	VSS	0.5
C-201	08/31/95	CGM	0
C-202	08/31/95	CGM	0
C-203	08/29/95	CGM	0
C-204	06/03/96	CGM	0
S-101	04/03/96	CGM	7
S-102	03/14/95	VSS	2
S-103	05/17/96	CGM	0
S-104	03/19/96	CGM	0
S-105	12/07/95	VSS	0.09
S-106	05/17/96	CGM	0
S-107	09/30/95	CGM	4
S-108	12/06/95	VSS	0.09
S-109	05/17/96	CGM	0
S-110	12/05/95	VSS	0.45
S-111	03/21/95	VSS	1.1
S-112	07/11/95	VSS	0.1
SX-113	08/18/95	CGM	0
SX-115	03/08/96	CGM	0
T-101	07/30/96	CGM	0
T-102	05/09/96	CGM	0

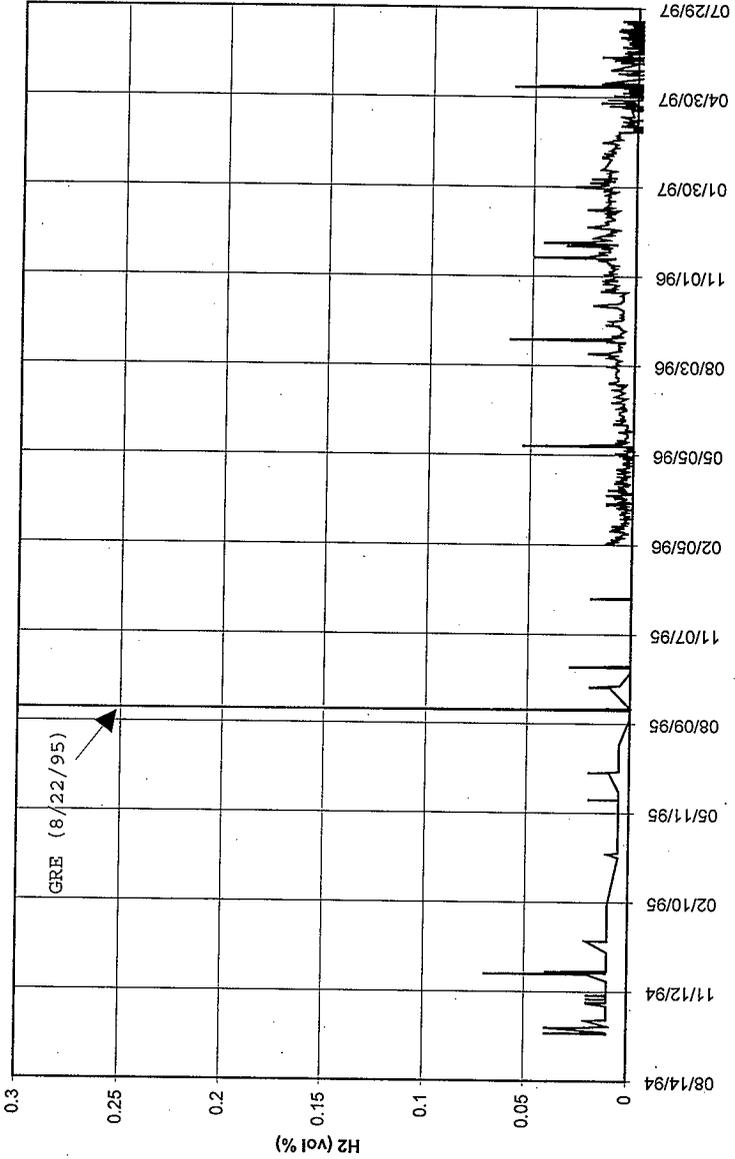
Tank #	Sample Date	Sample Type	Total LFL (%)
T-103	02/15/96	CGM	0
T-104	2/7/96	VSS	0
T-105	05/09/96	CGM	0
T-106	05/09/96	CGM	0
T-107	12/18/95	VSS	0.1
T-108	05/09/96	CGM	0
T-109	05/09/96	CGM	0
T-110	08/31/95	VSS	0.1
T-111	12/20/95	VSS	0.2
T-112	05/09/96	CGM	0
T-201	07/31/96	CGM	0
T-202	08/09/96	CGM	2
T-203	03/19/96	CGM	0
T-204	07/31/96	CGM	0
TX-101	06/14/96	CGM	0
TX-102	06/20/96	CGM	0
TX-103	06/17/96	CGM	0
TX-104	07/23/96	CGM	0
TX-105	12/21/94	VSS	0
TX-106	07/23/96	CGM	0
TX-107	01/17/96	CGM	0
TX-108	07/17/96	CGM	0
TX-109	07/17/96	CGM	1
TX-110	07/17/96	CGM	0
TX-111	10/12/95	VSS	0.78
TX-112	07/24/96	CGM	0
TX-113	06/18/96	CGM	0

Tank #	Sample Date	Sample Type	Total LFL (%)
TX-114	06/18/96	CGM	0
TX-115	08/01/96	CGM	0
TX-116	3/19/96	CGM	0
TX-117	03/19/96	CGM	0
TX-118	12/16/94	VSS	0.3
TY-101	04/06/95	VSS	0
TY-102	04/05/96	CGM	0
TY-103	04/11/95	VSS	0.2
TY-104	04/27/95	VSS	0
TY-105	08/06/96	CGM	2
TY-106	08/18/95	CGM	0
U-101	02/14/96	CGM	1
U-102	04/30/96	CGM	3
U-103	02/15/95	VSS	1.9
U-104	05/10/96	CGM	0
U-105	02/21/95	VSS	0.2
U-106	03/08/95	VSS	1.2
U-107	02/17/95	VSS	1.6
U-108	08/29/95	VSS	1.85
U-109	08/16/95	VSS	2.33
U-110	03/19/96	CGM	2
U-111	02/28/95	VSS	1.1
U-112	07/03/96	CGM	2
U-201	08/18/95	CGM	0
U-202	08/18/95	CGM	0
U-203	08/09/95	VSS	0
U-204	08/08/95	VSS	0

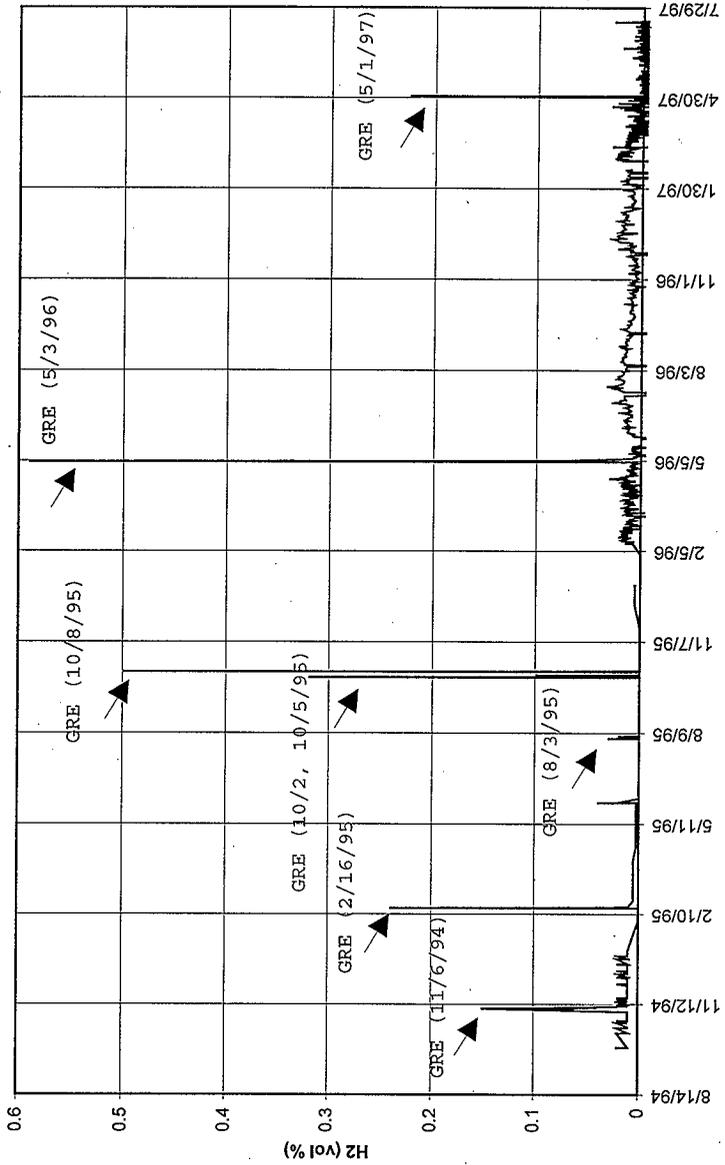
Appendix D

SHMS and Gas Characterization System Data Plots

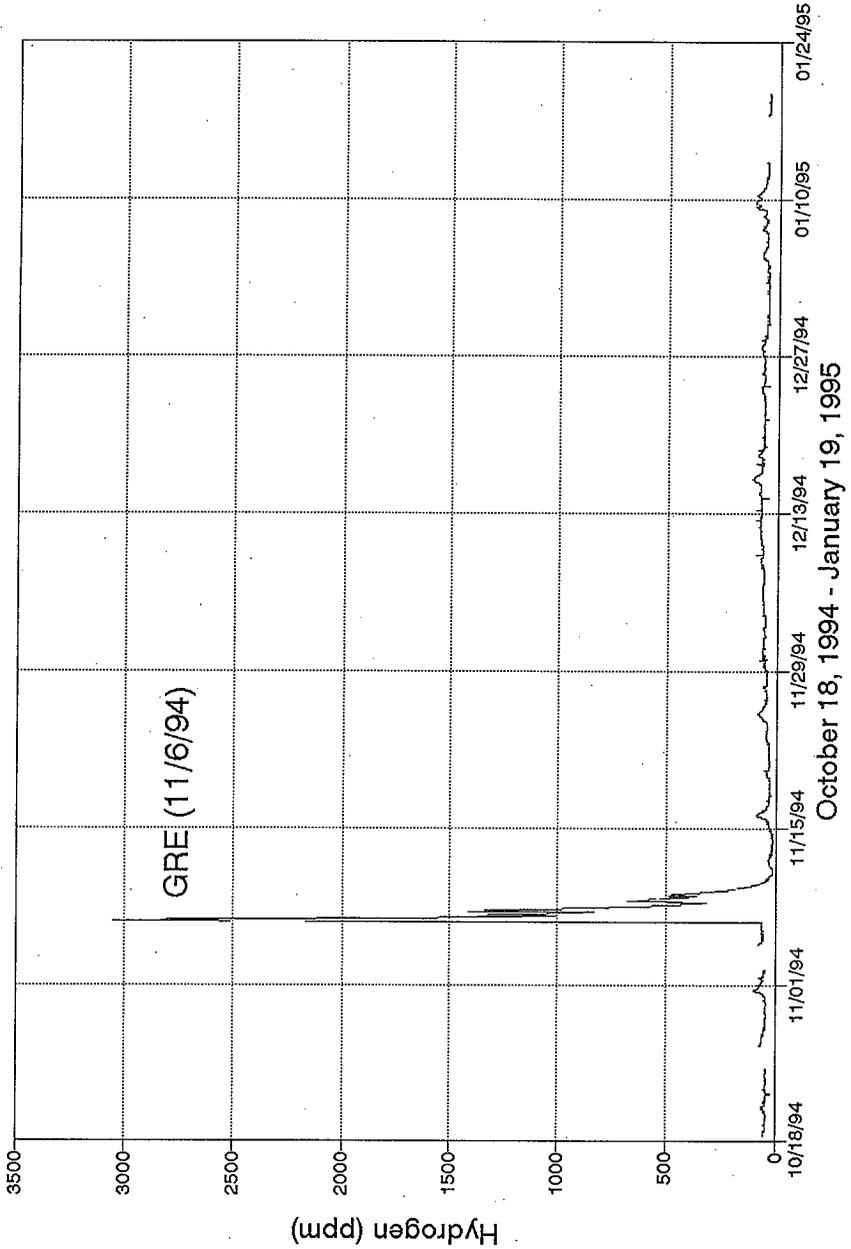
241-AN-103 SHIMS HYDROGEN (narrow range cell)



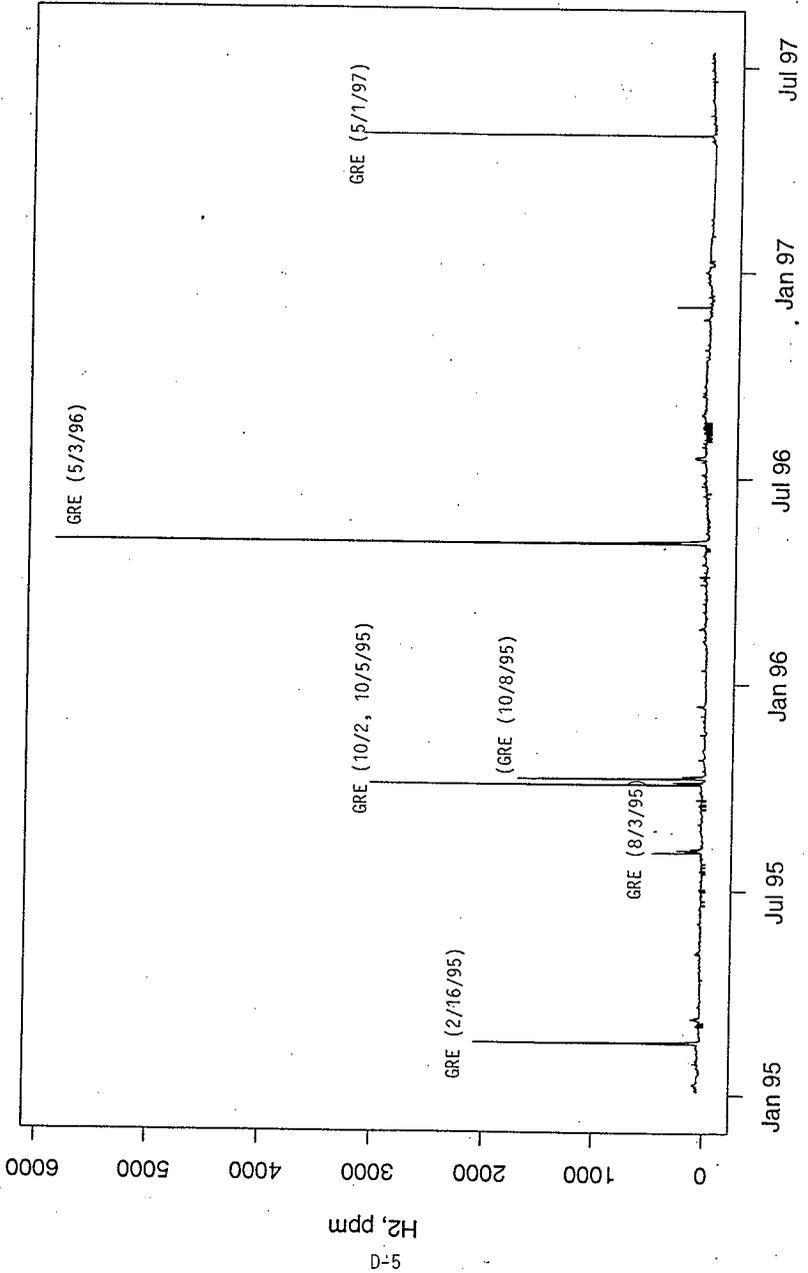
241-AN-104 SHIMS HYDROGEN (narrow range cell)



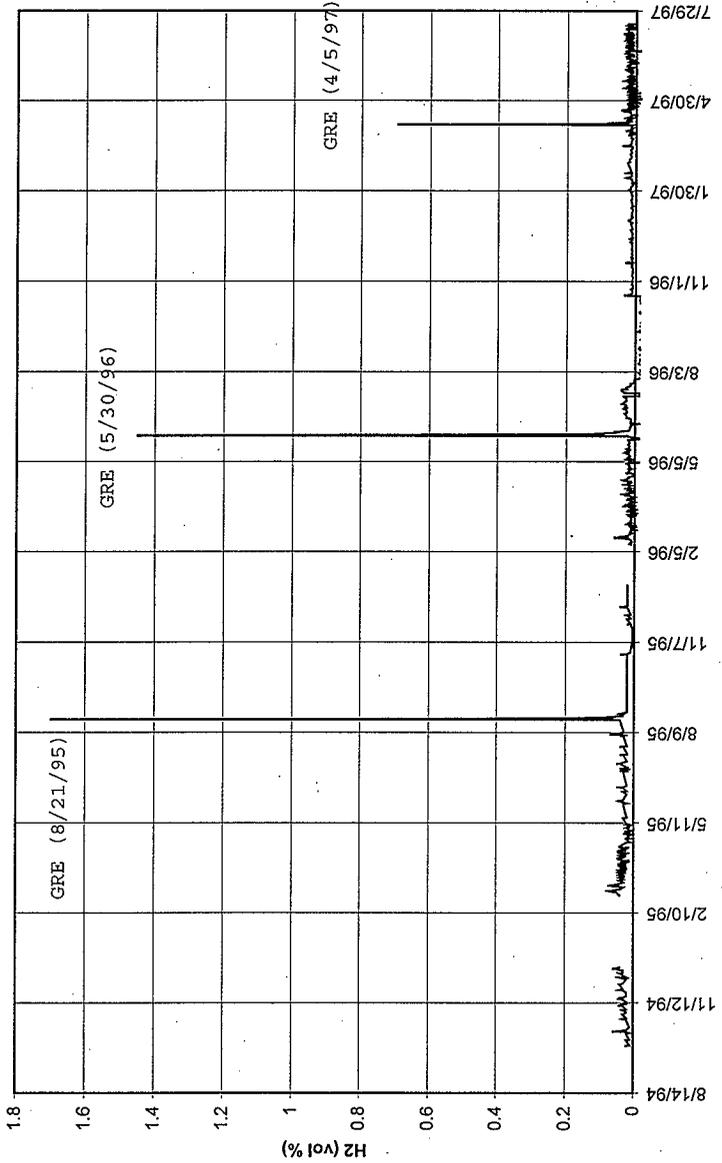
Tank 241-AN-104
Hydrogen Concentrations (GC)



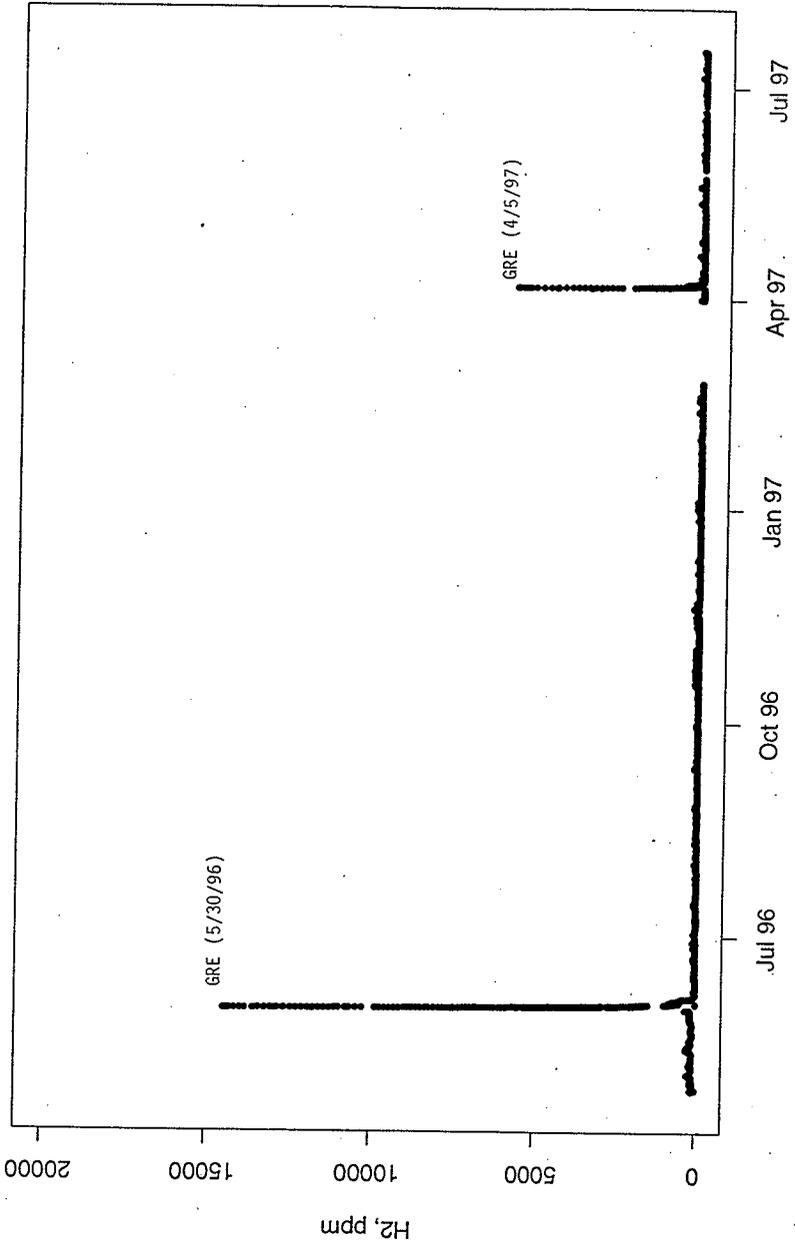
AN104 Hydrogen (GC)



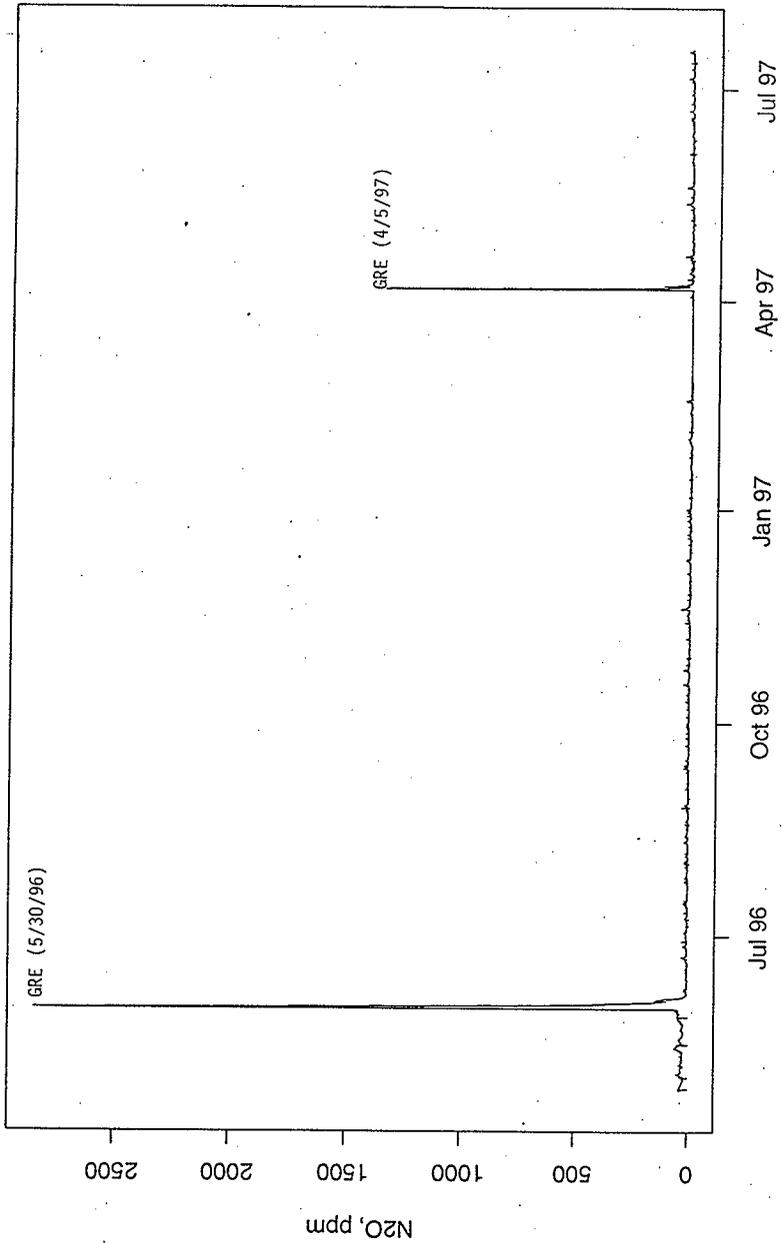
241-AN-105 SHIMS HYDROGEN (narrow range cell)



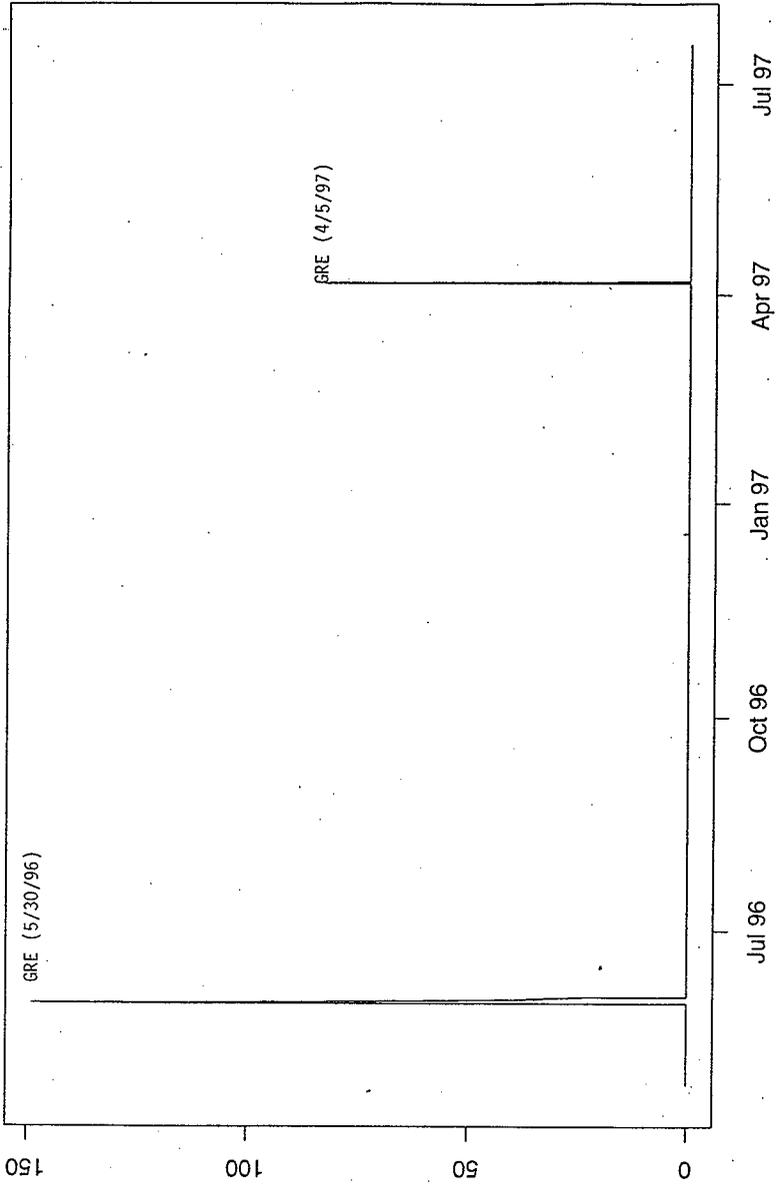
105-AN H2, High range GC



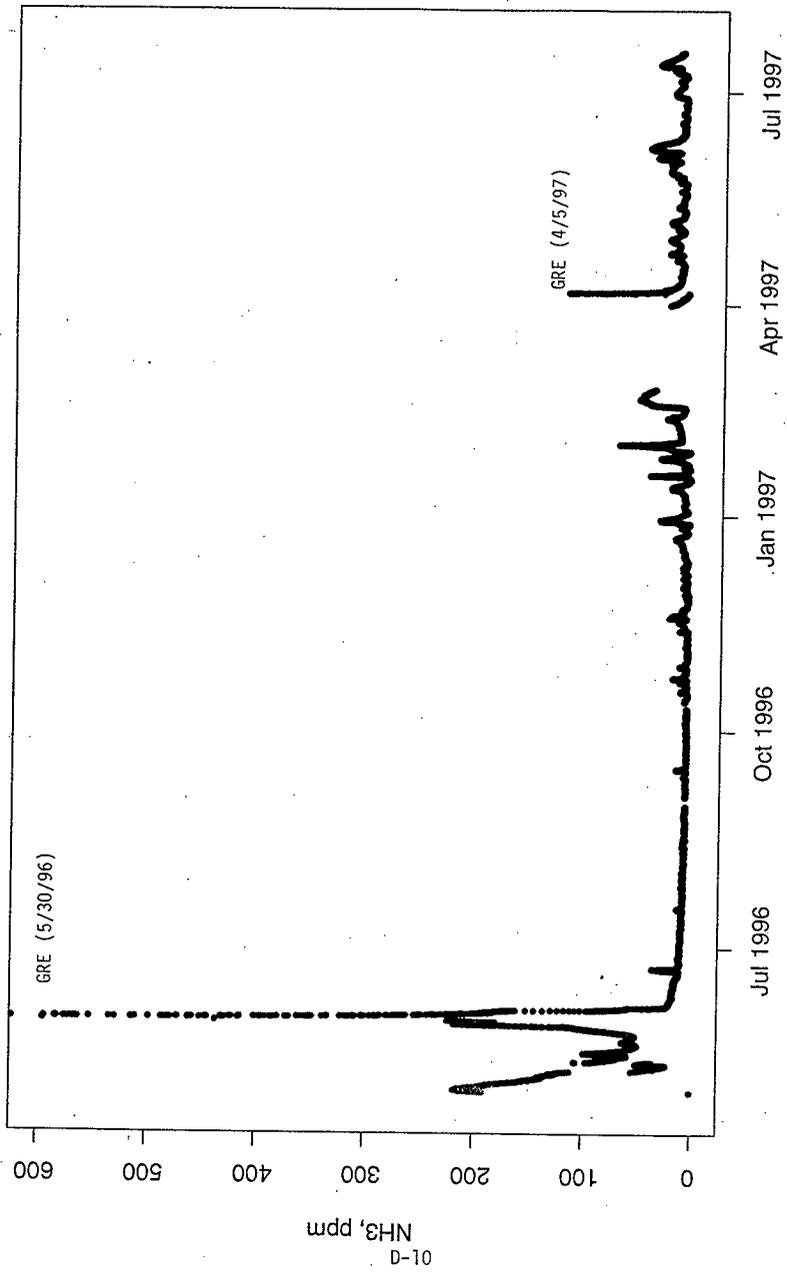
AN-105 N₂O, Low range GC



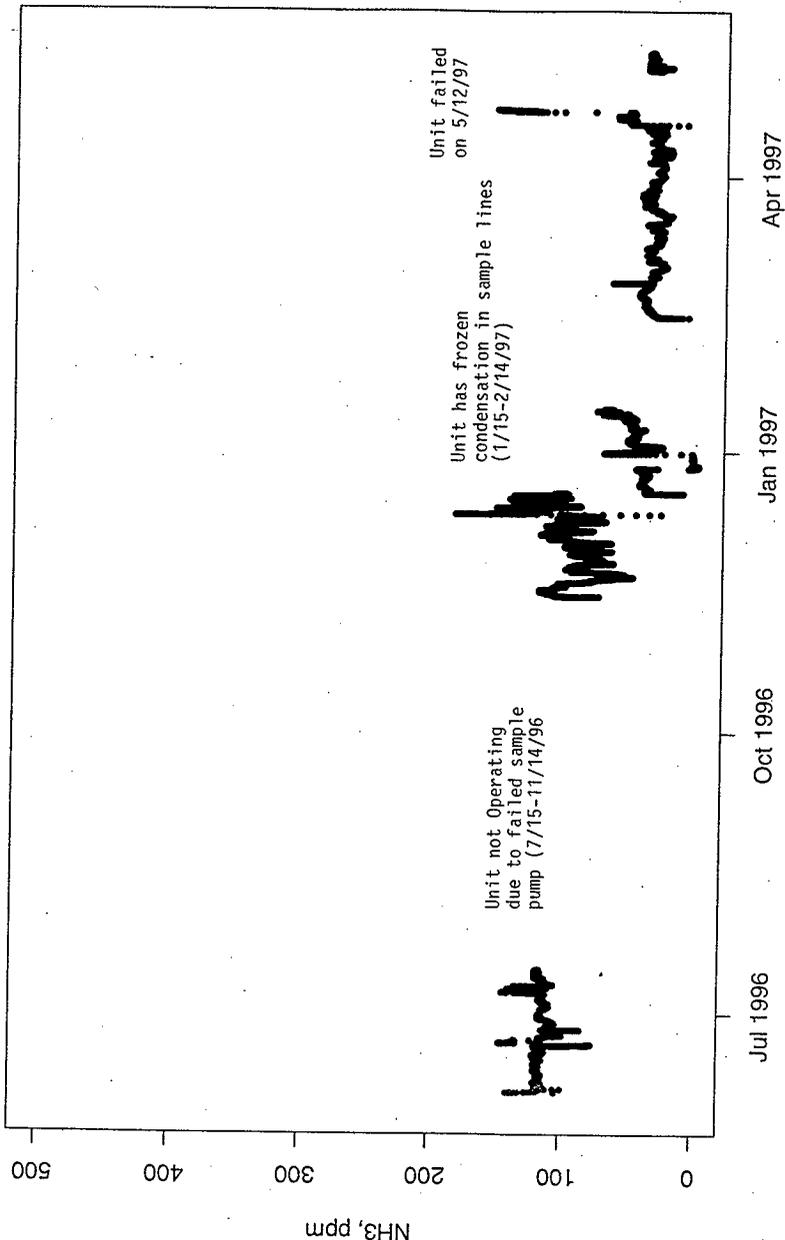
AN-105 CH4, Low range GC



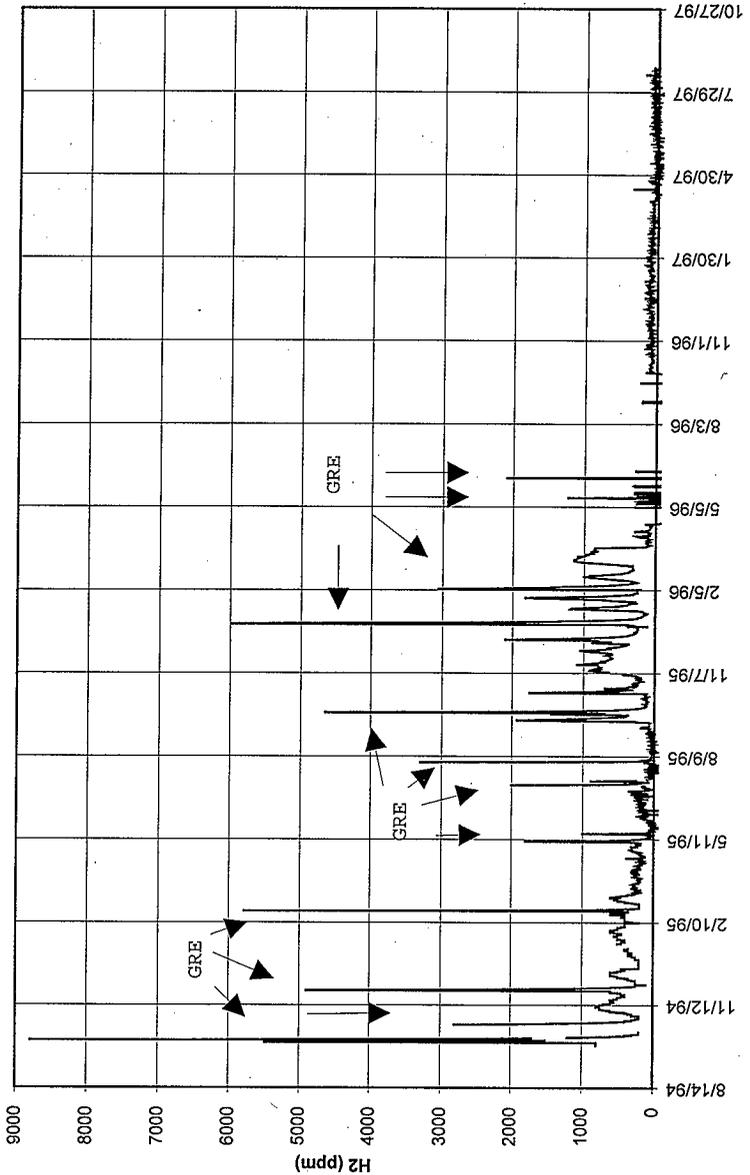
105-AN NH3, Low range FTIR



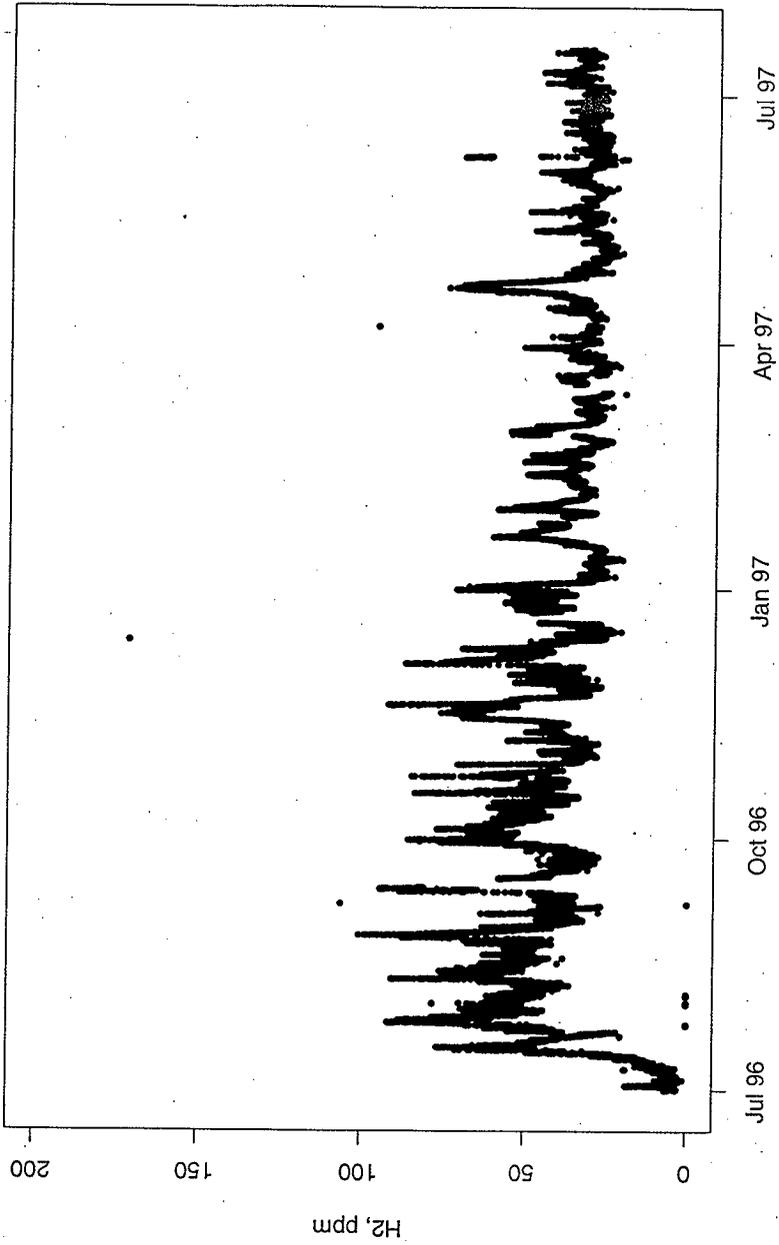
Ammonia from AN Stack



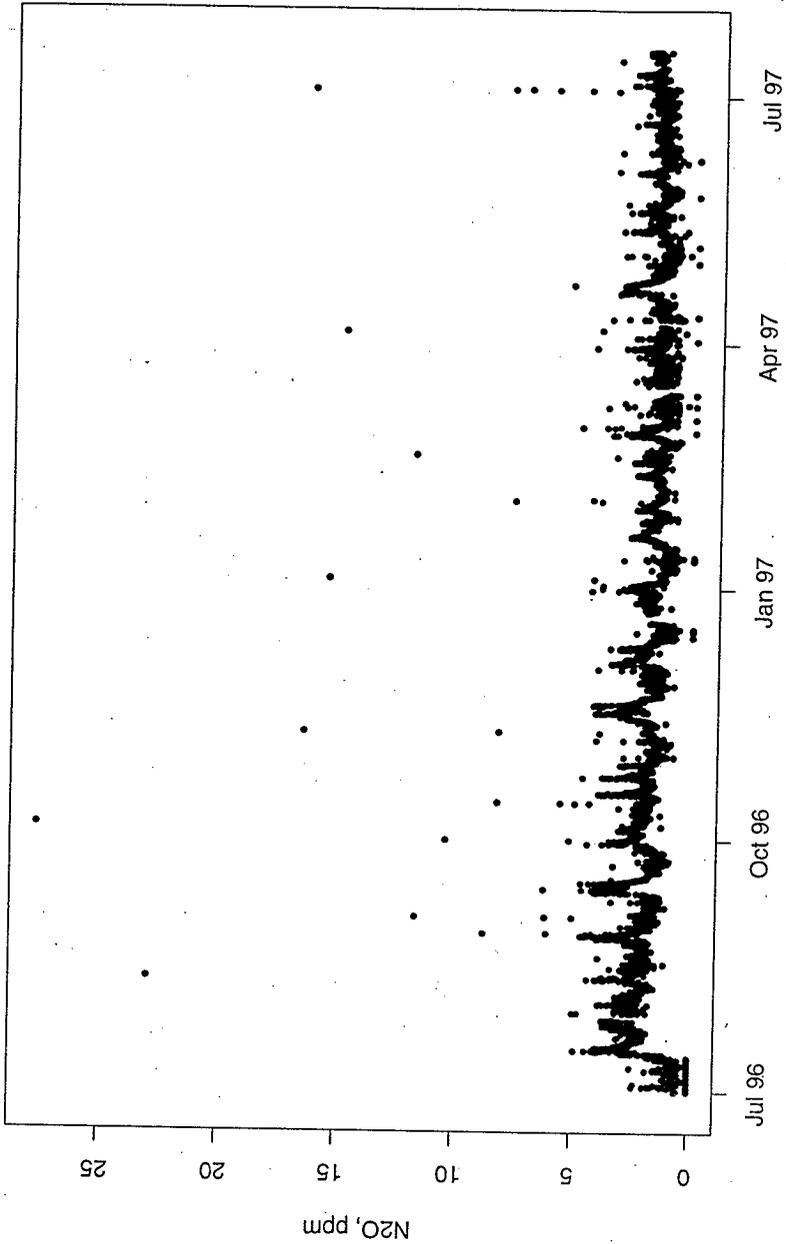
241-AW-101 SHIMS HYDROGEN (narrow range)



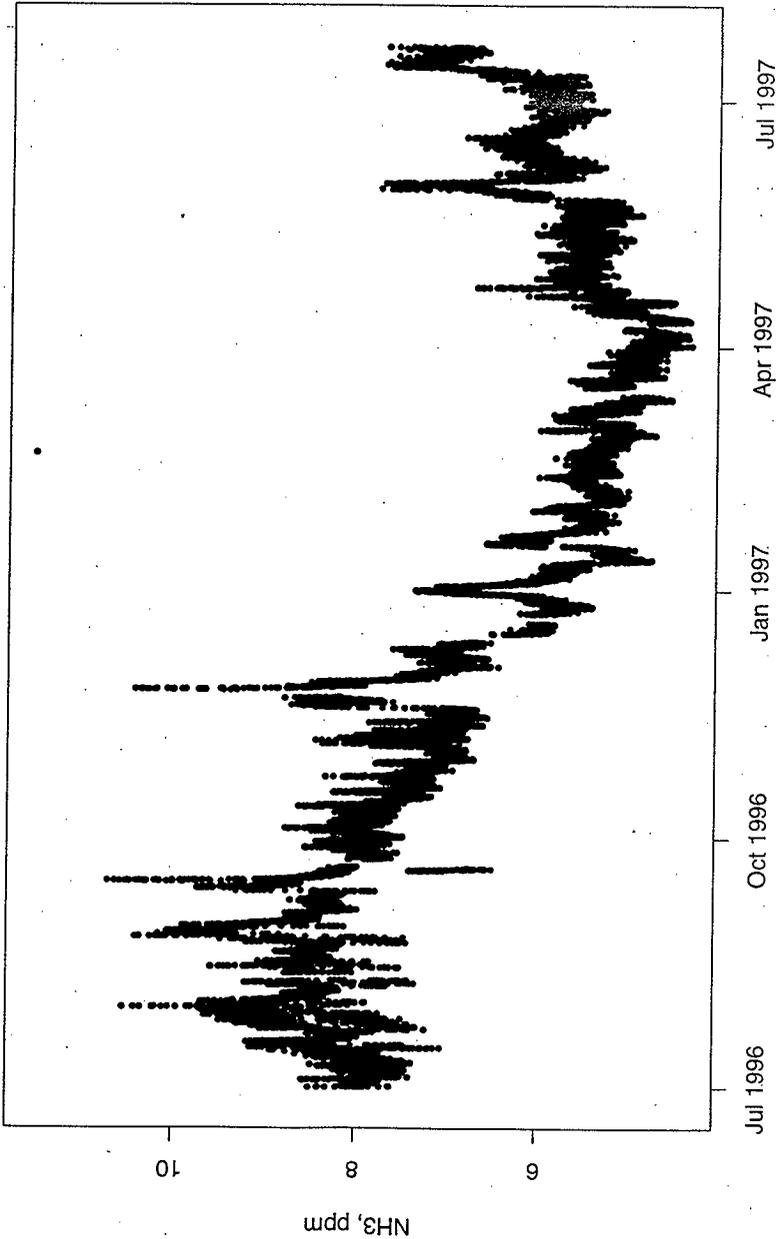
AW101 H2, Low range GC



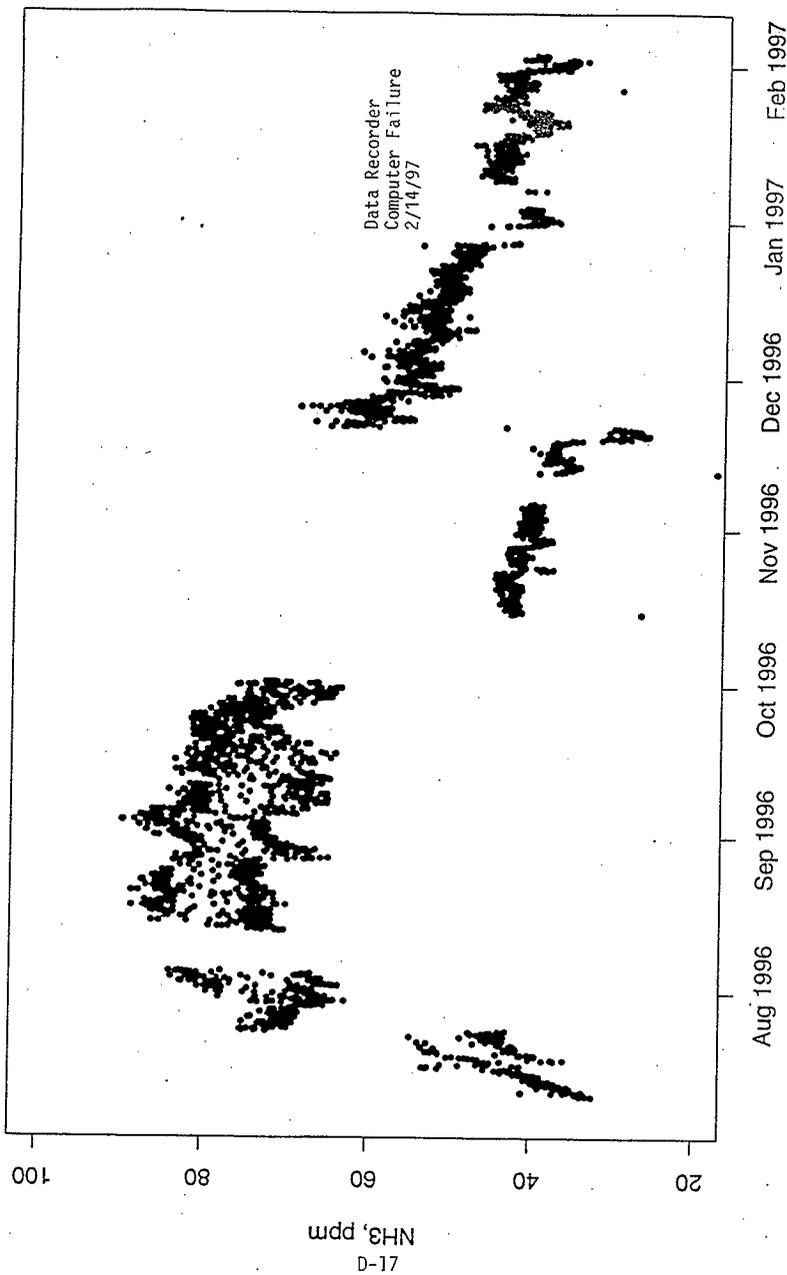
AW101 N2O, Low range GC



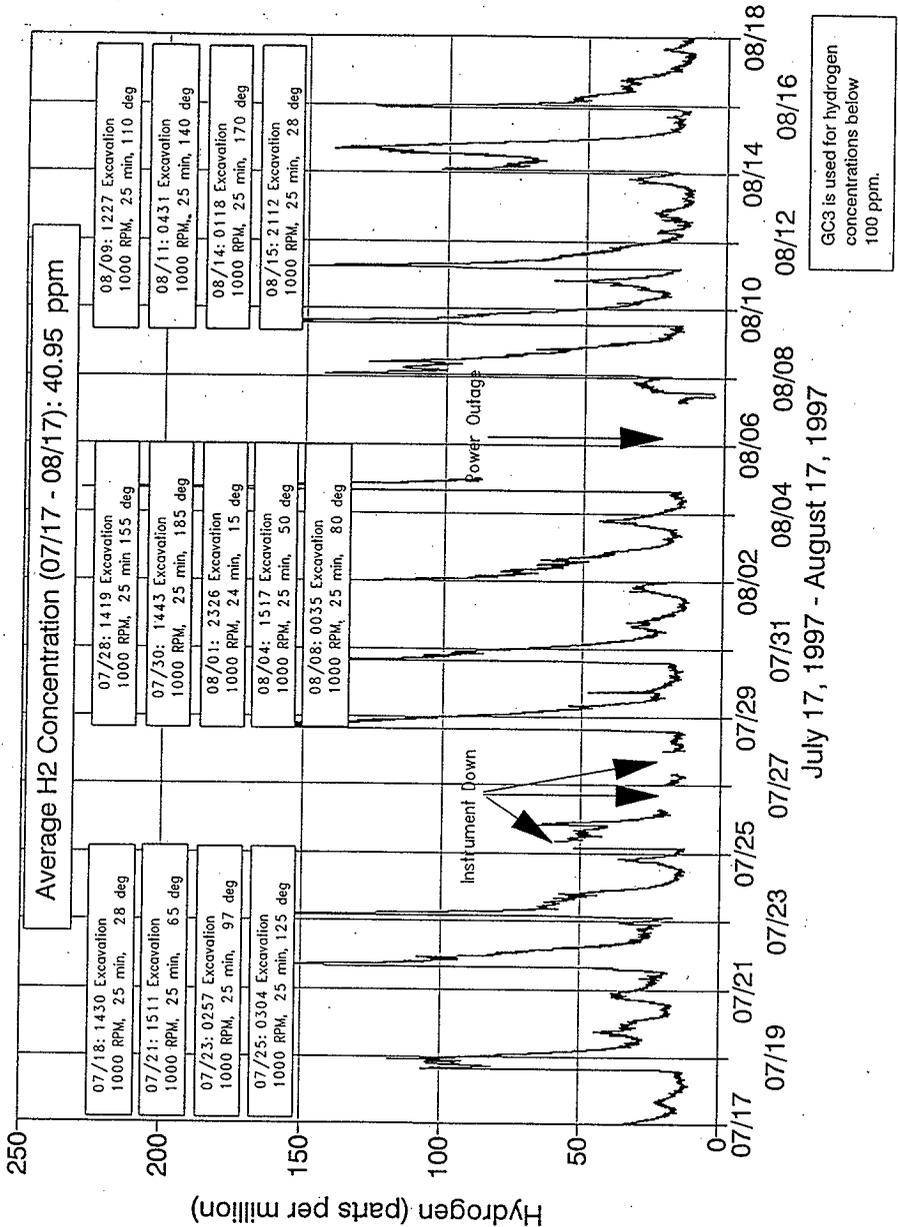
AW101 NH3, Low range FTIR



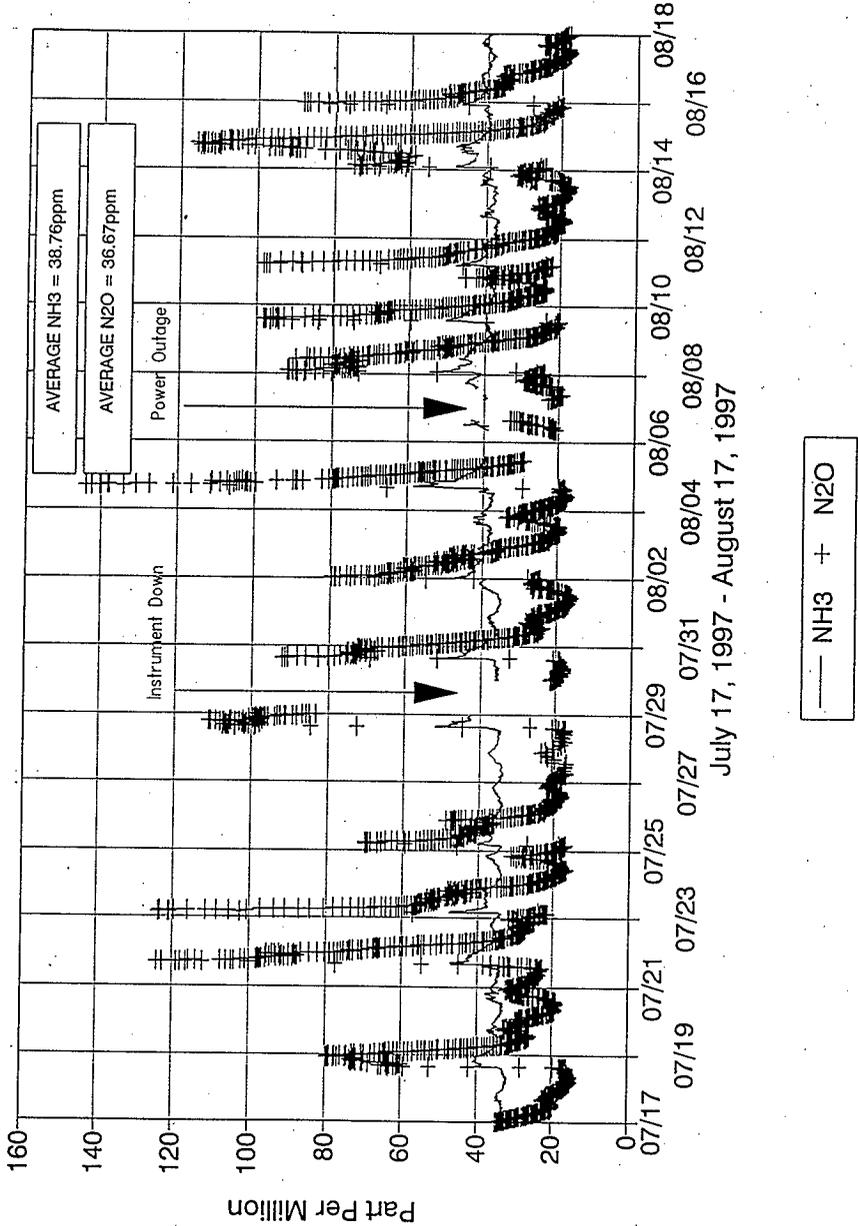
NH3 from AW Stack



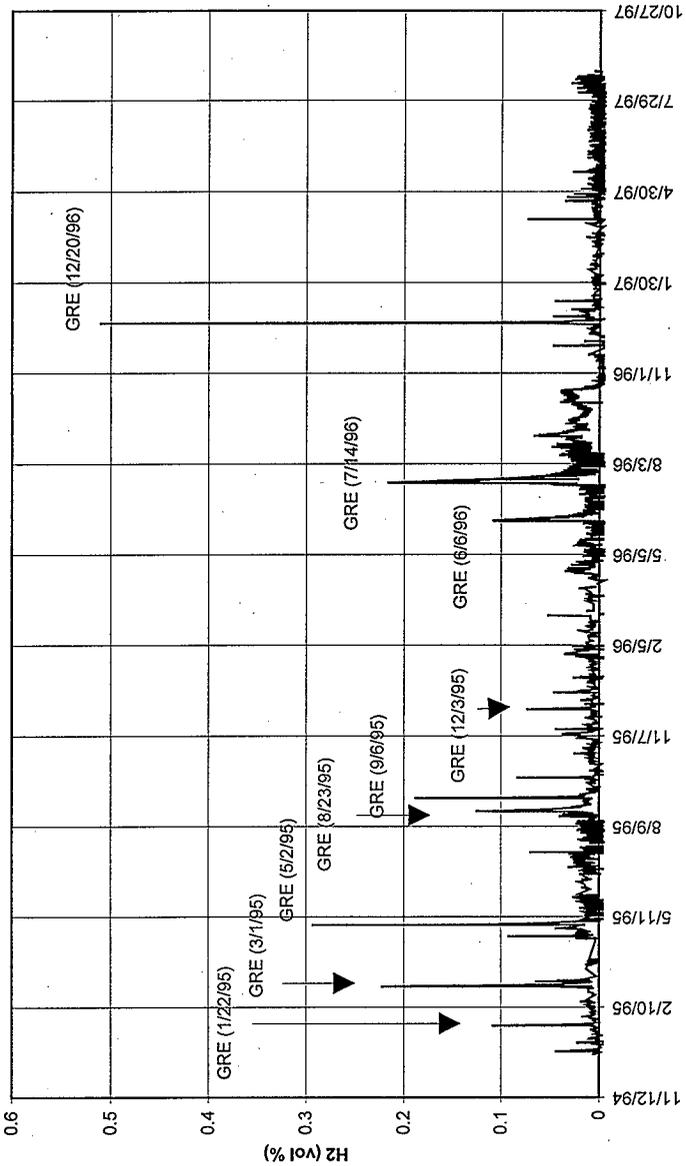
Tank 241-SY-101 Gas Chromatograph 3 Hydrogen



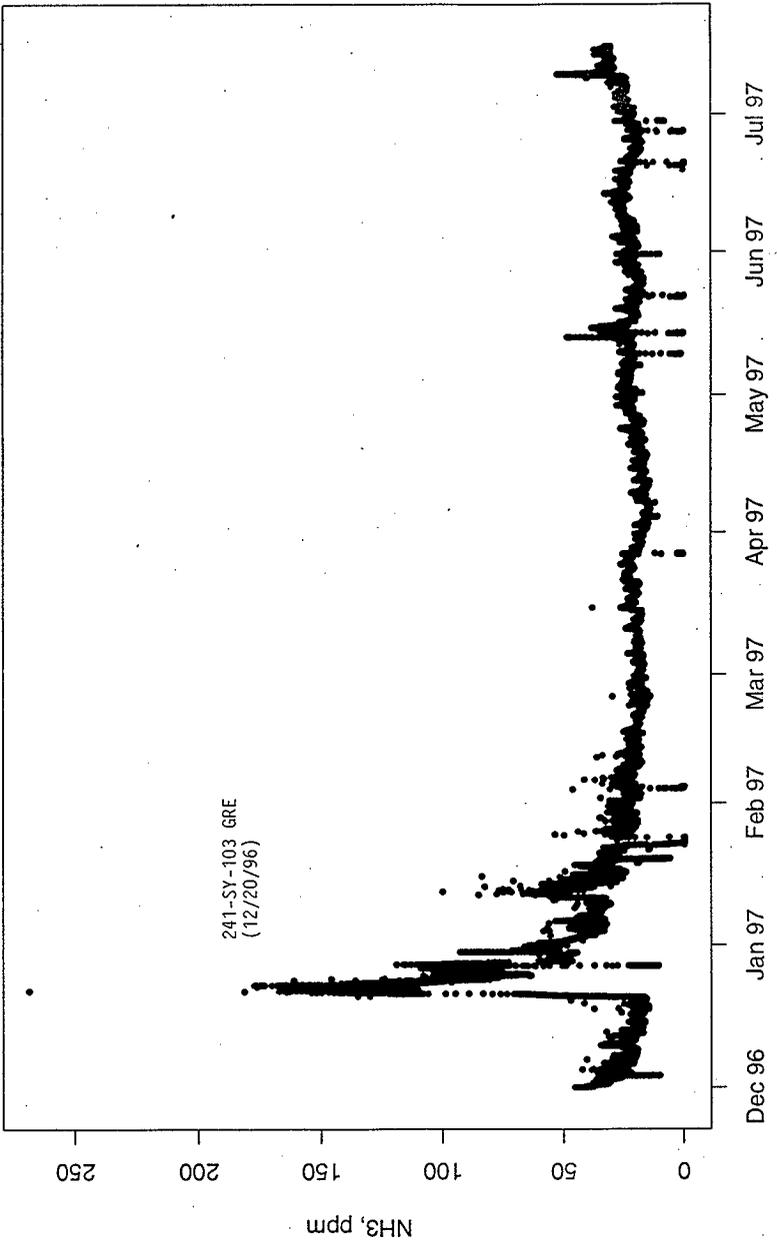
Tank 241-SY-101 FTIR Gas Compositions



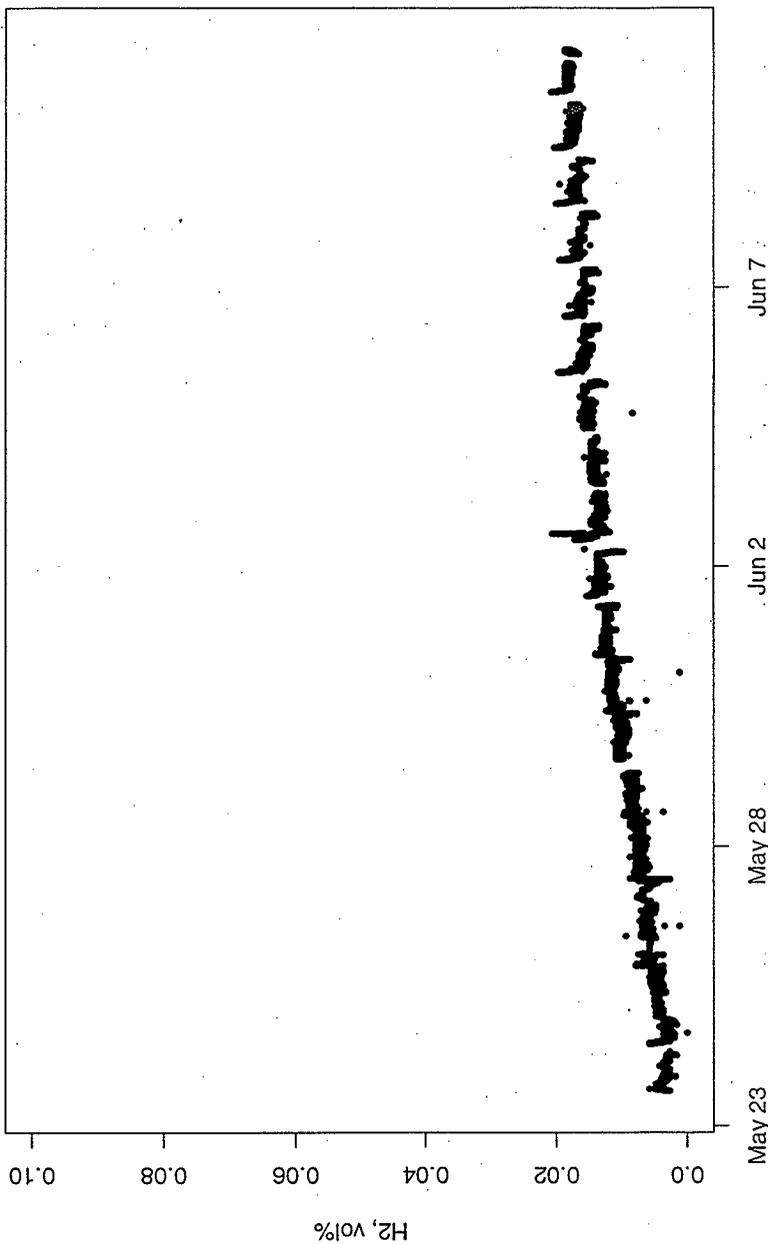
241-SY-103 SHMS HYDROGEN (narrow range)



SY Farm Stack Ammonia

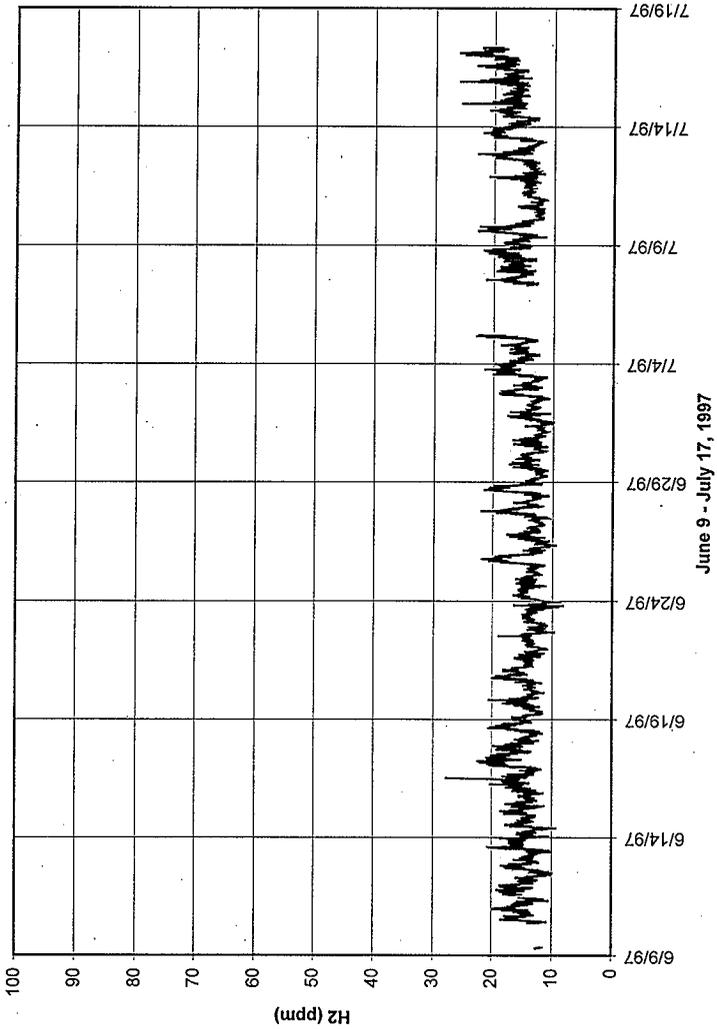


AY102 Hydrogen
(wide range Whittaker cell)

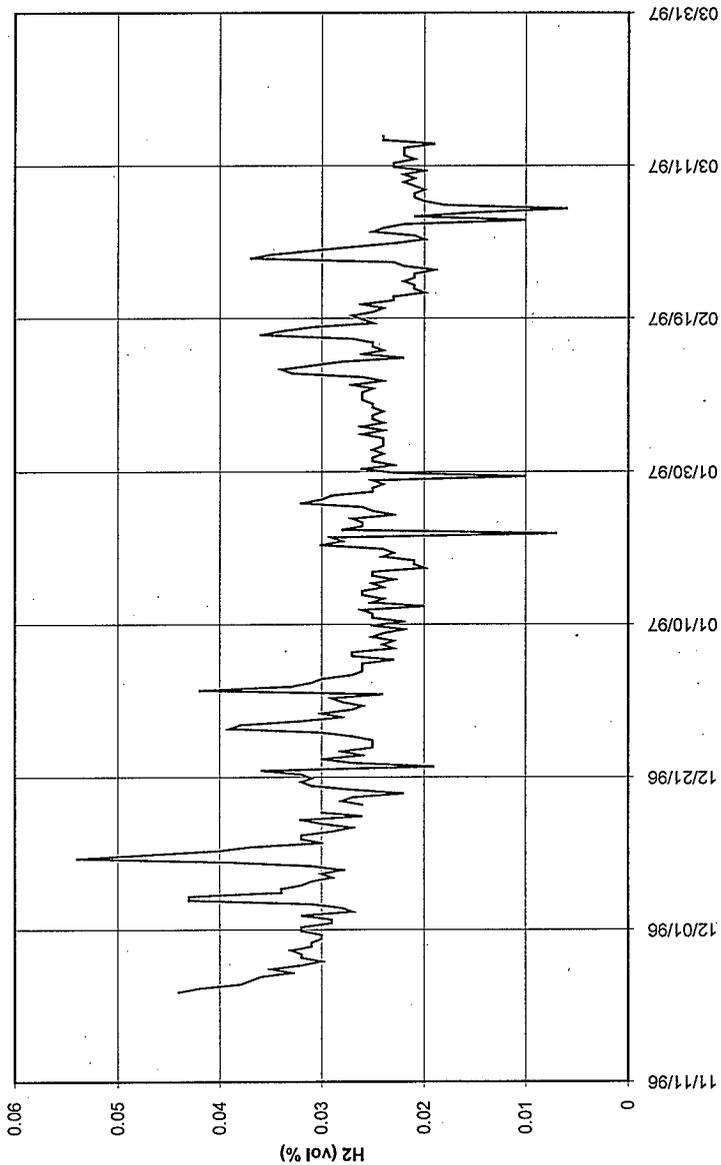


H₂, vol%

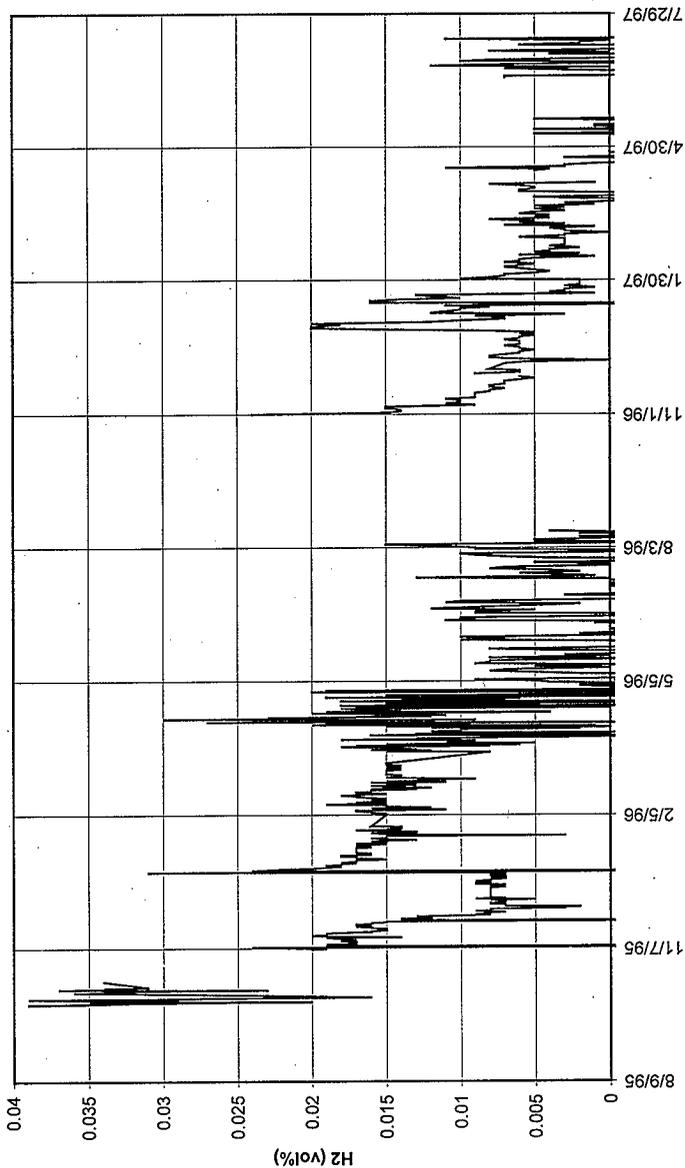
241-AY-102 GC Hydrogen



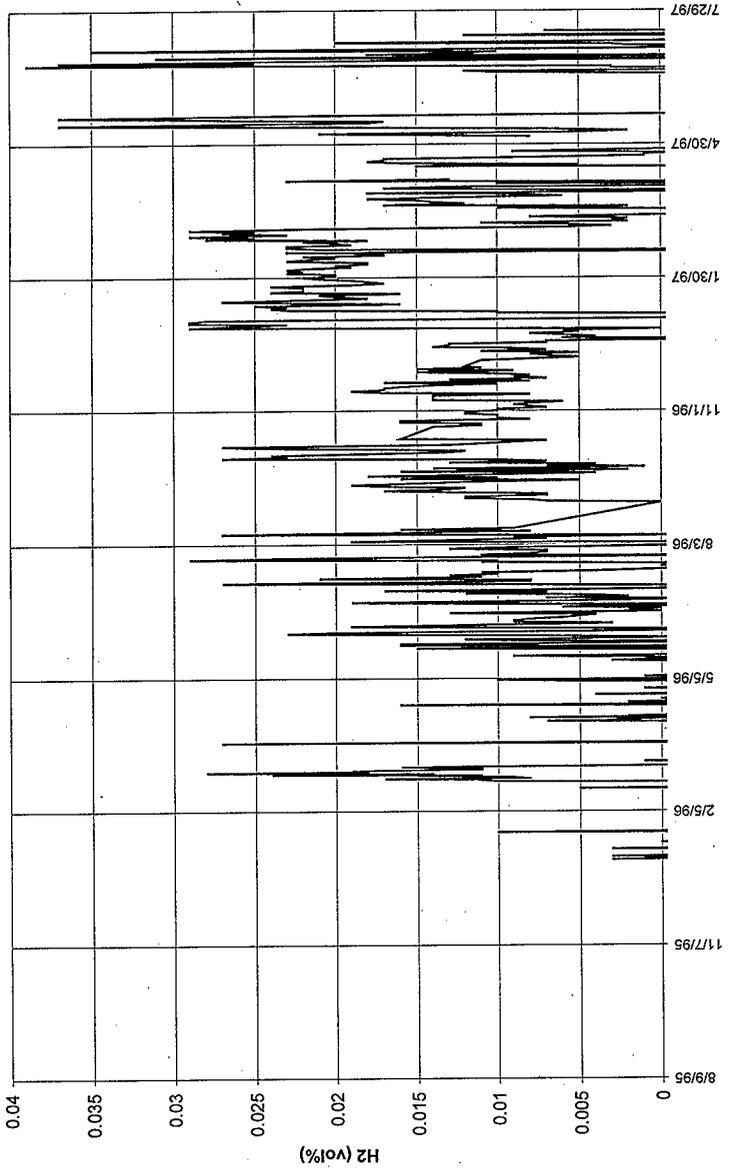
241-AX-101 SHMS HYDROGEN (narrow range)



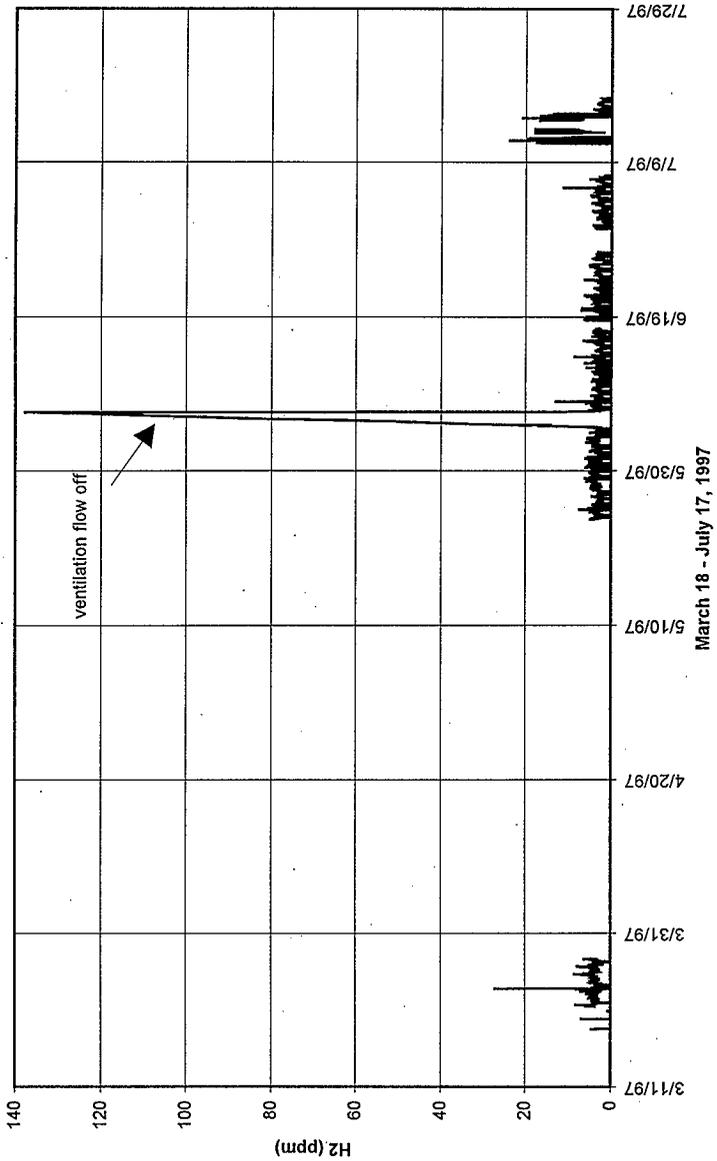
241-BY-103 SHMS HYDROGEN (narrow range)



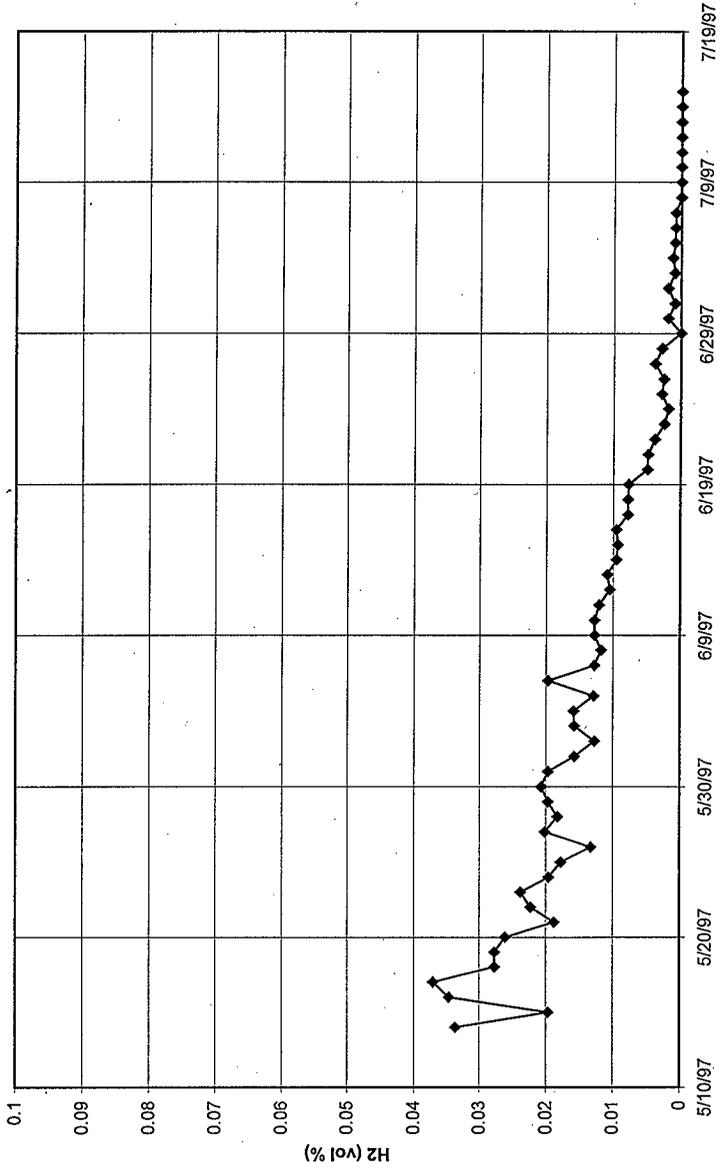
241-BY-109 SHMS HYDROGEN (narrow range)



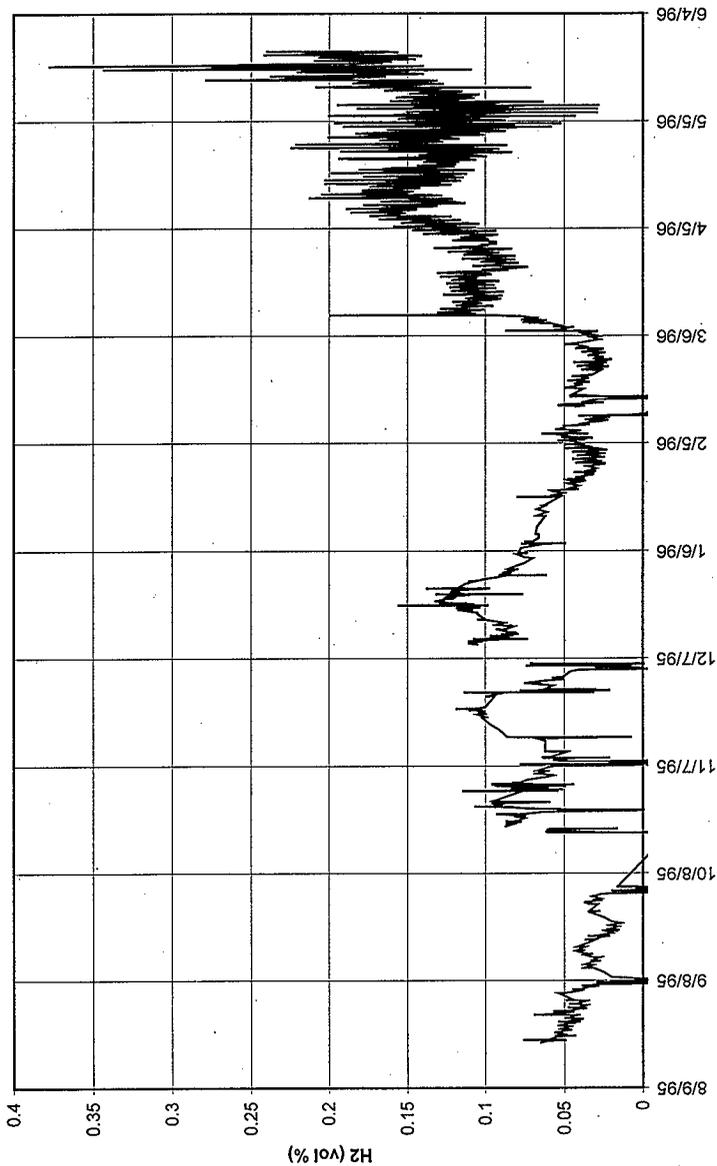
241-C-106 GC Hydrogen



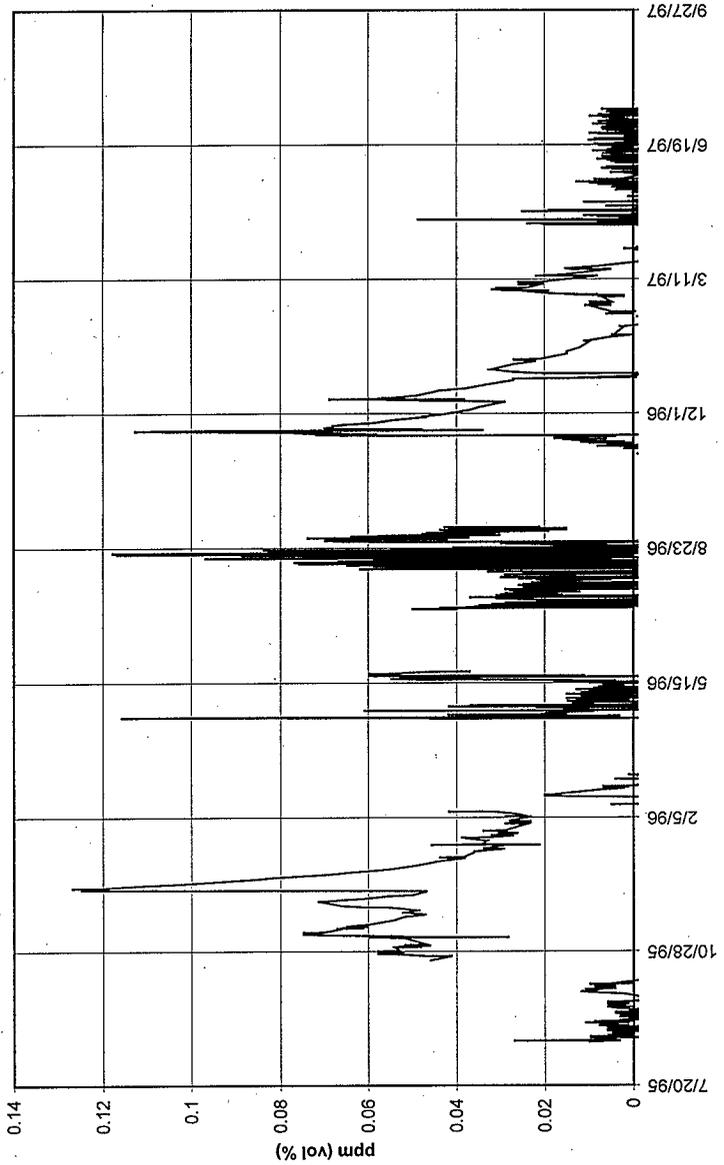
241-C-106 SHMS HYDROGEN (narrow range Whittaker cell)



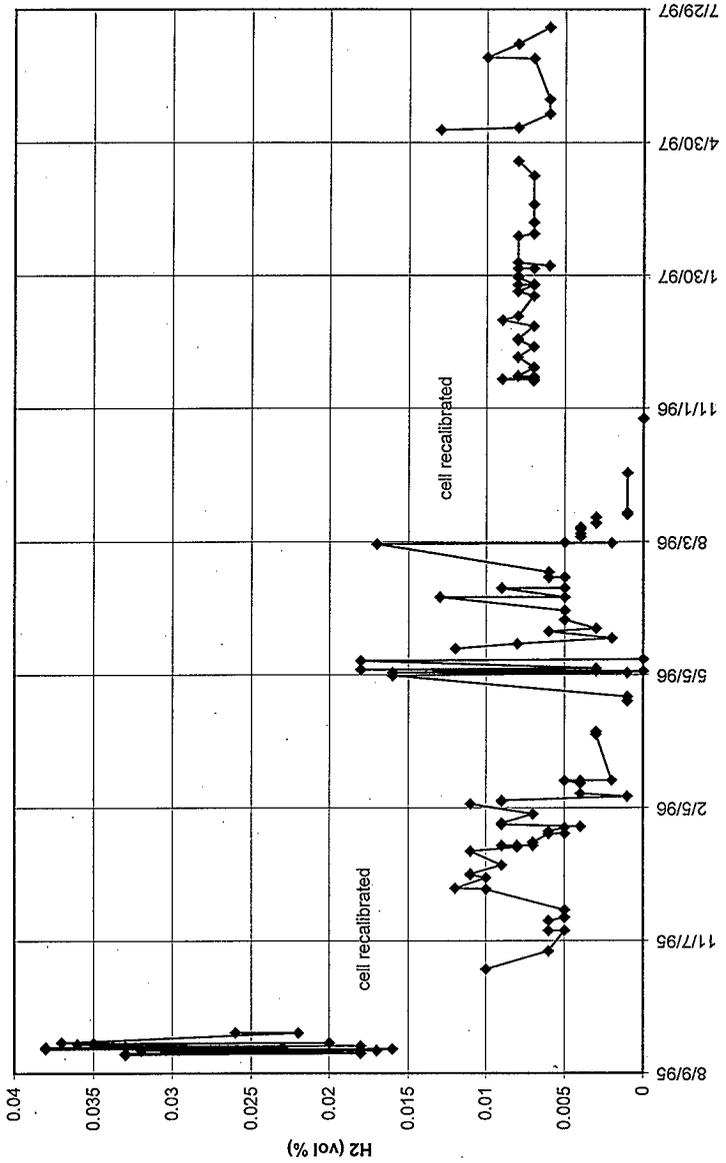
241-S-102 SHMS HYDROGEN (narrow range)

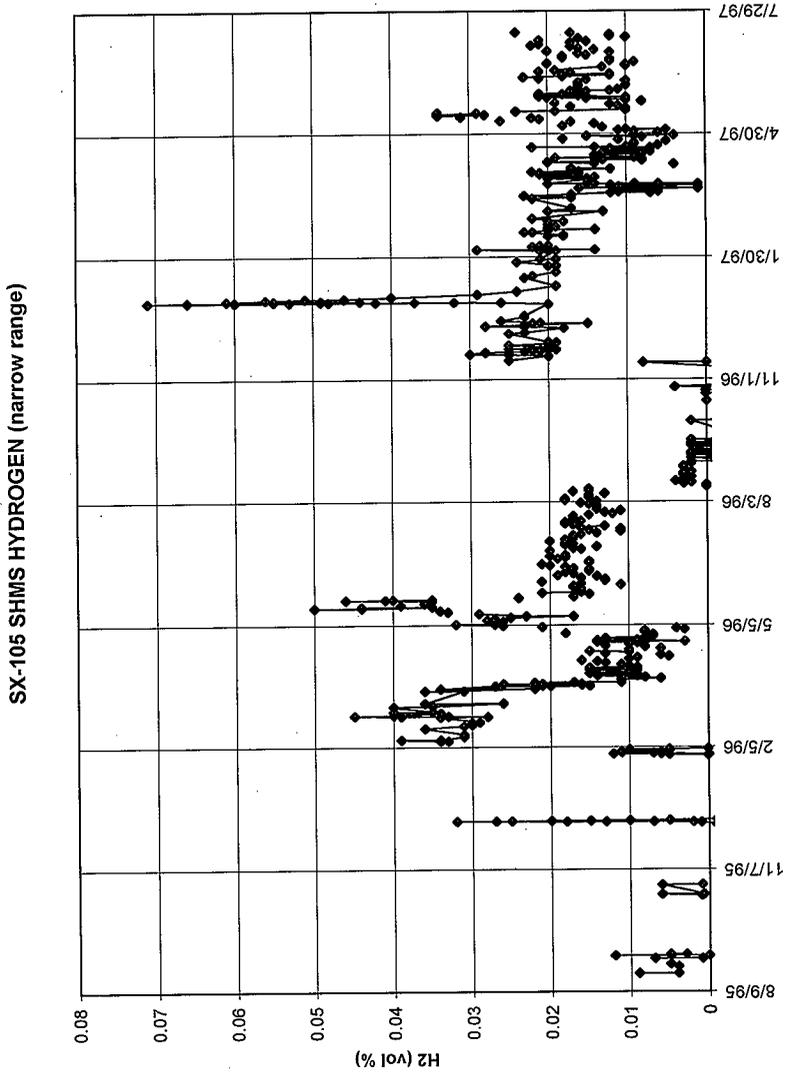


241-S-111 SHMS HYDROGEN (narrow range)

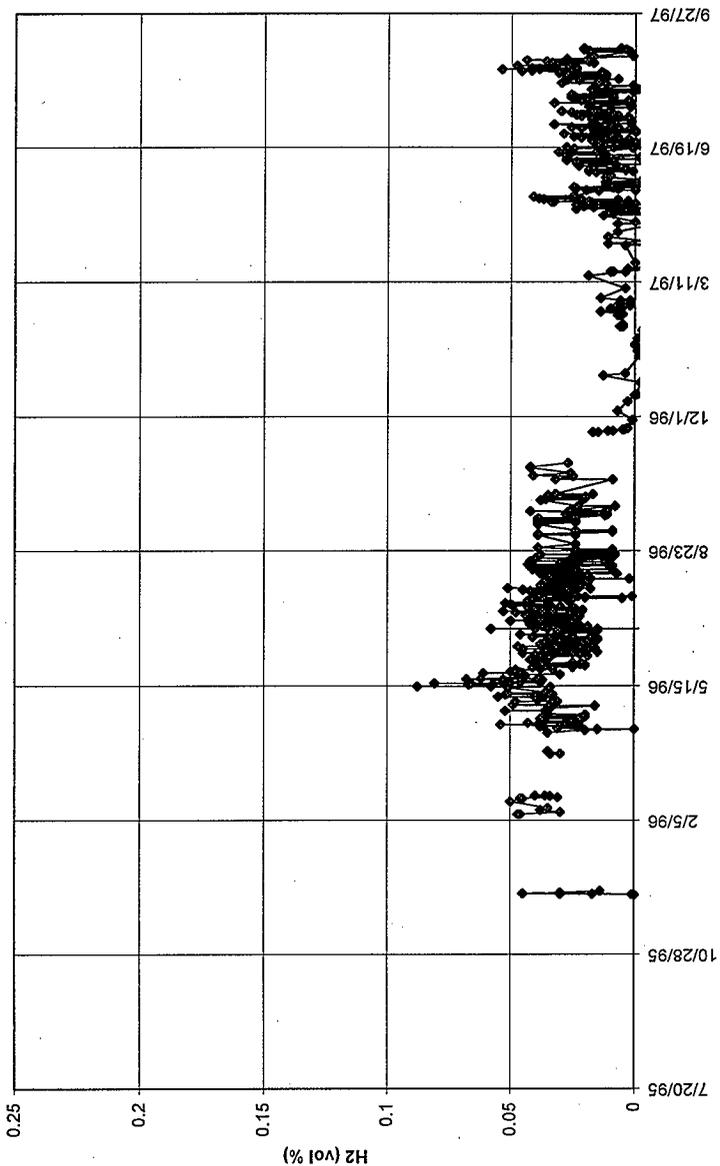


241-SX-101 SHMS HYDROGEN (wide range)

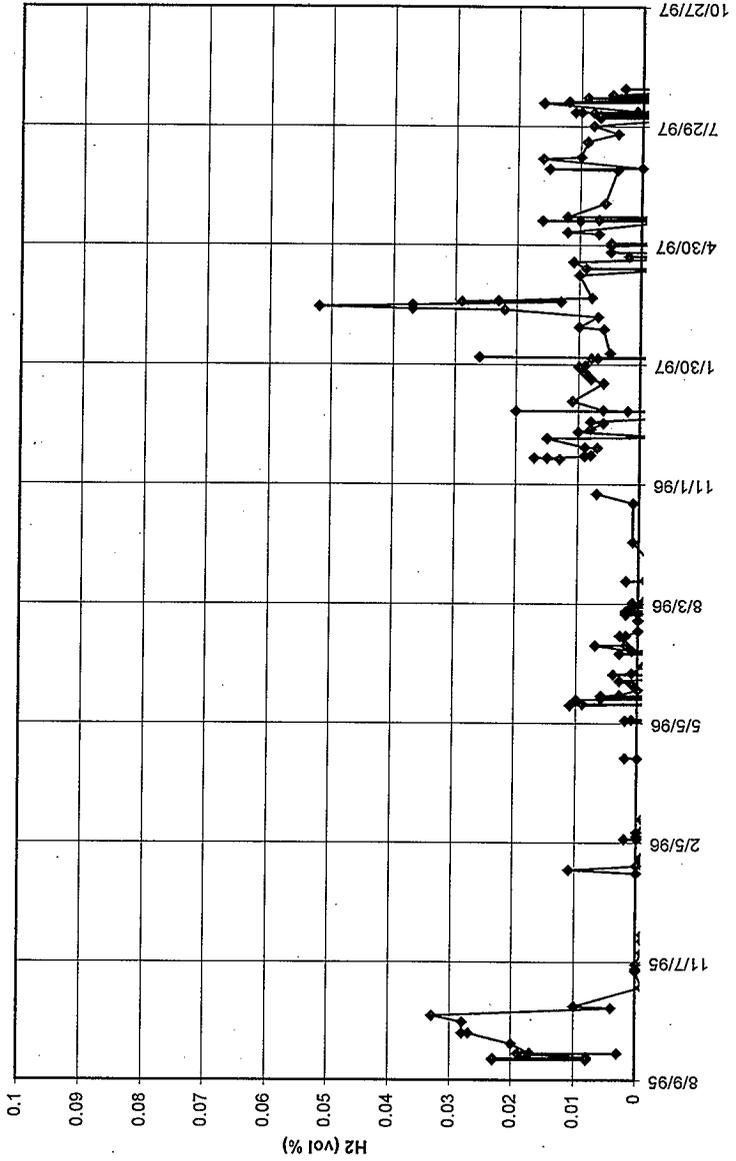




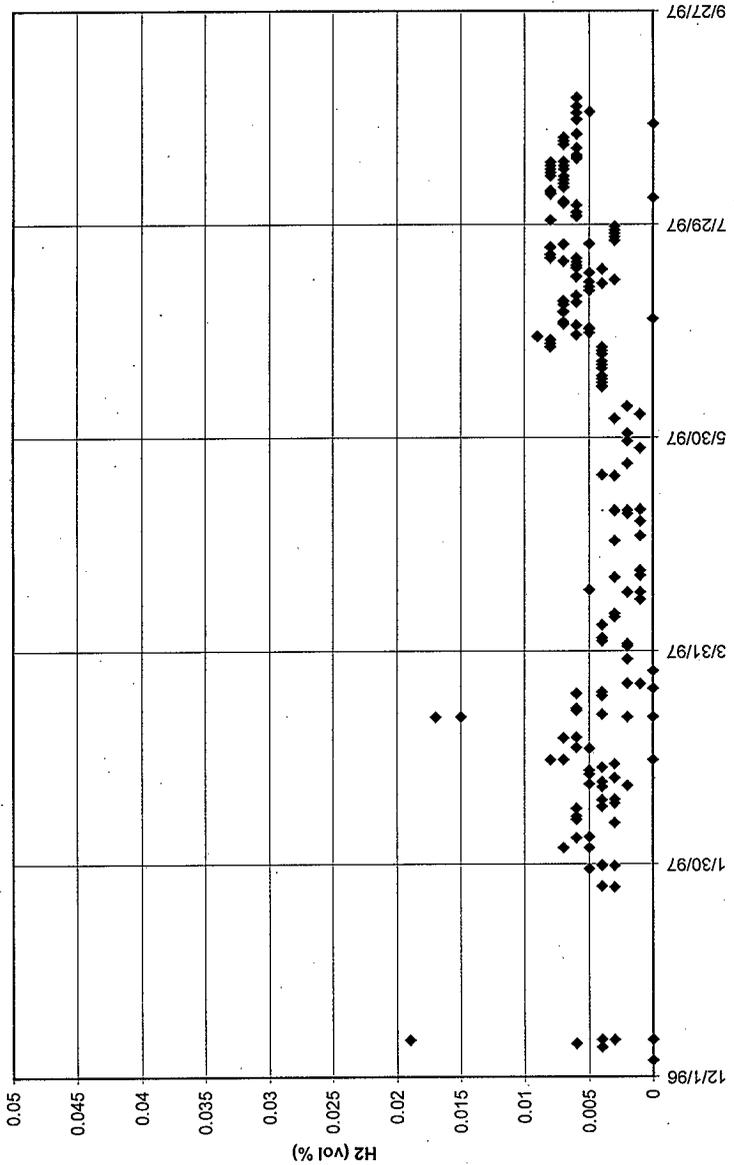
241-SX-106 SHIMS HYDROGEN (wide range)



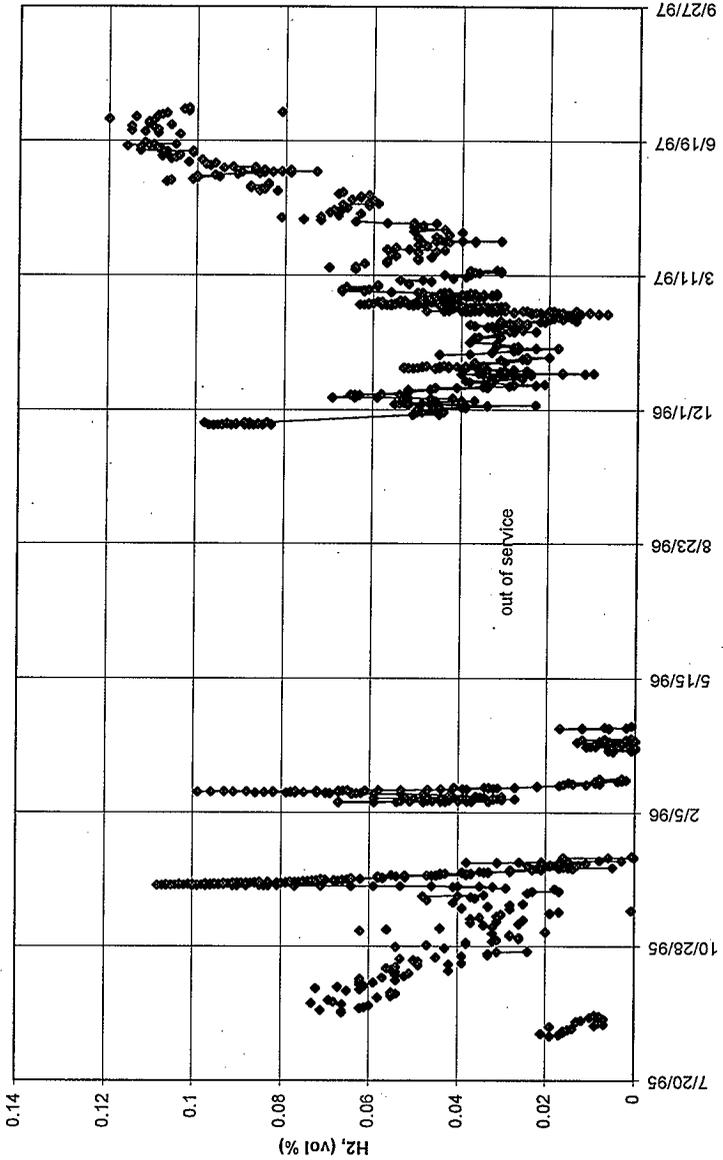
241-SX-109 SHMS HYDROGEN (wide range)



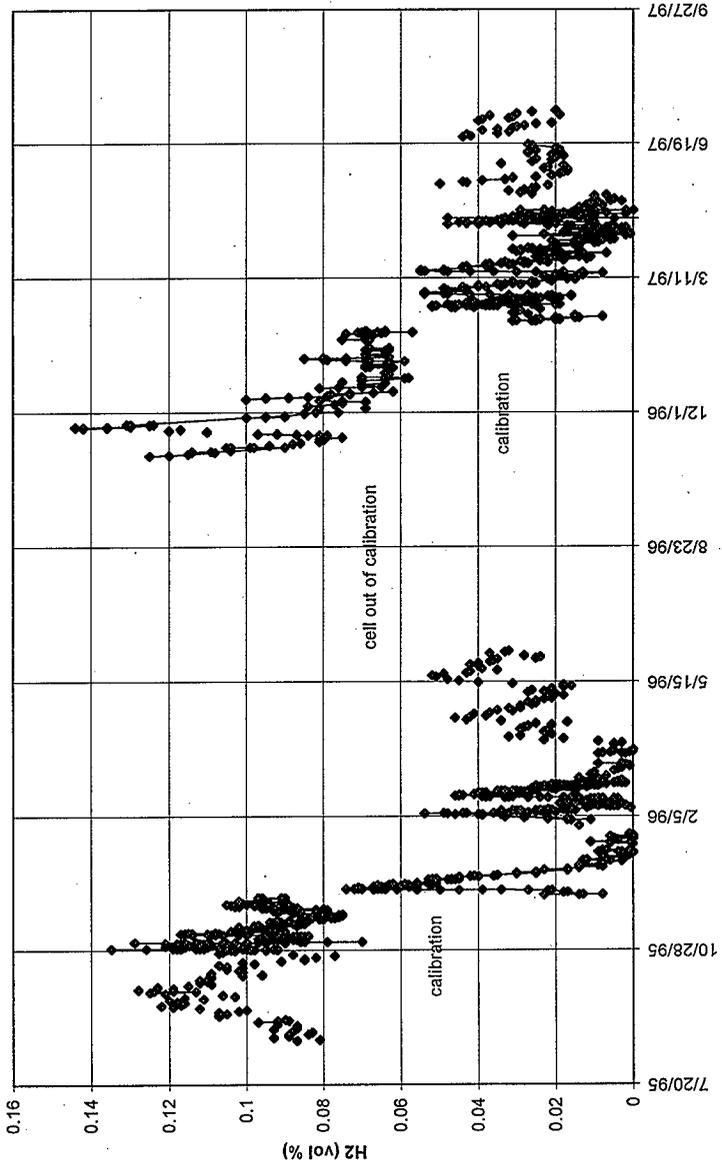
241-T-110 SHMS HYDROGEN (wide range)



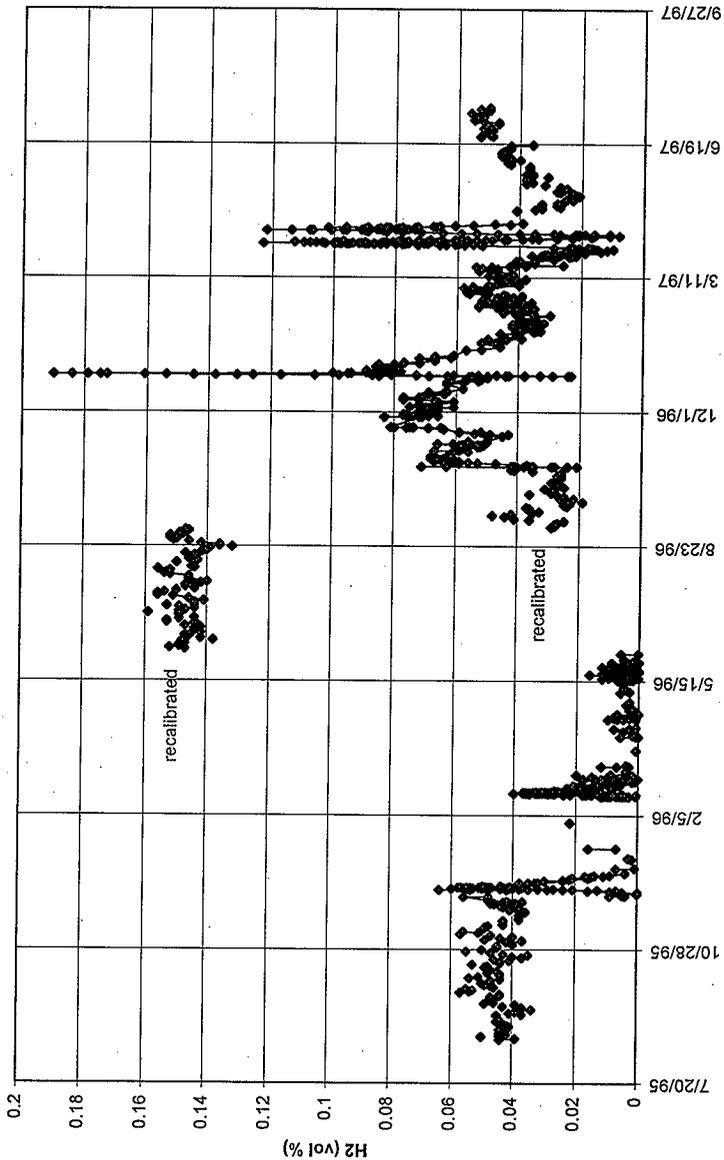
241-U-103 SHMS HYDROGEN (narrow range)



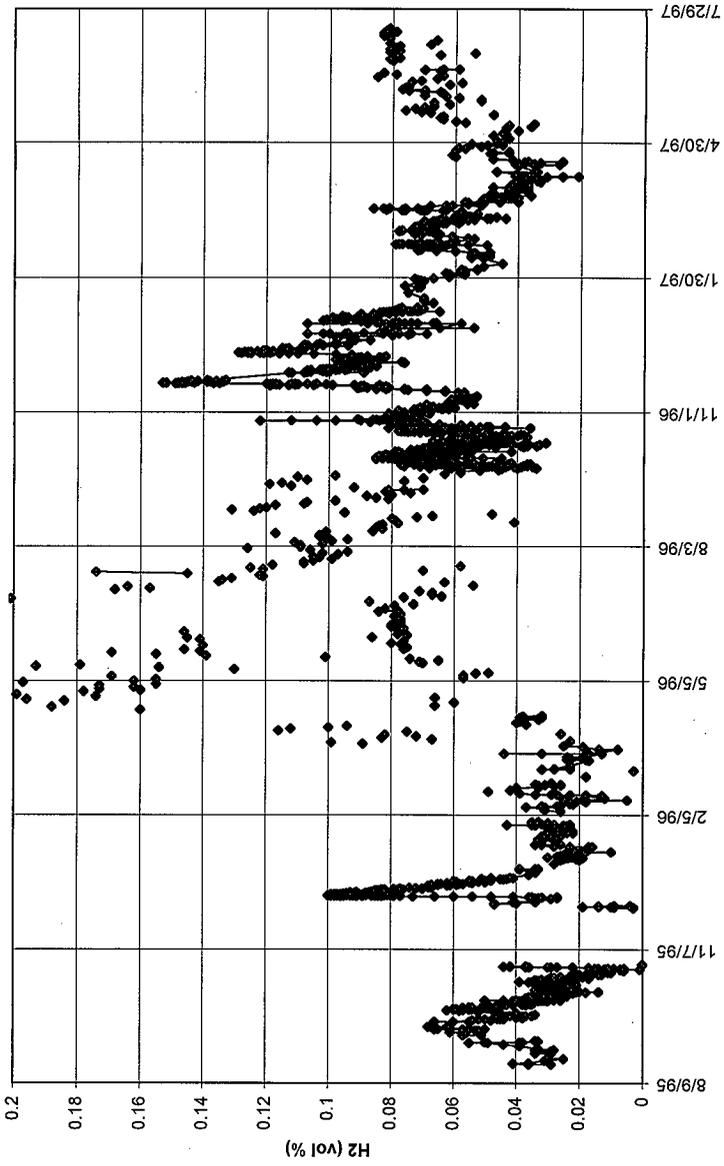
241-U-105 SHMS HYDROGEN (narrow range)



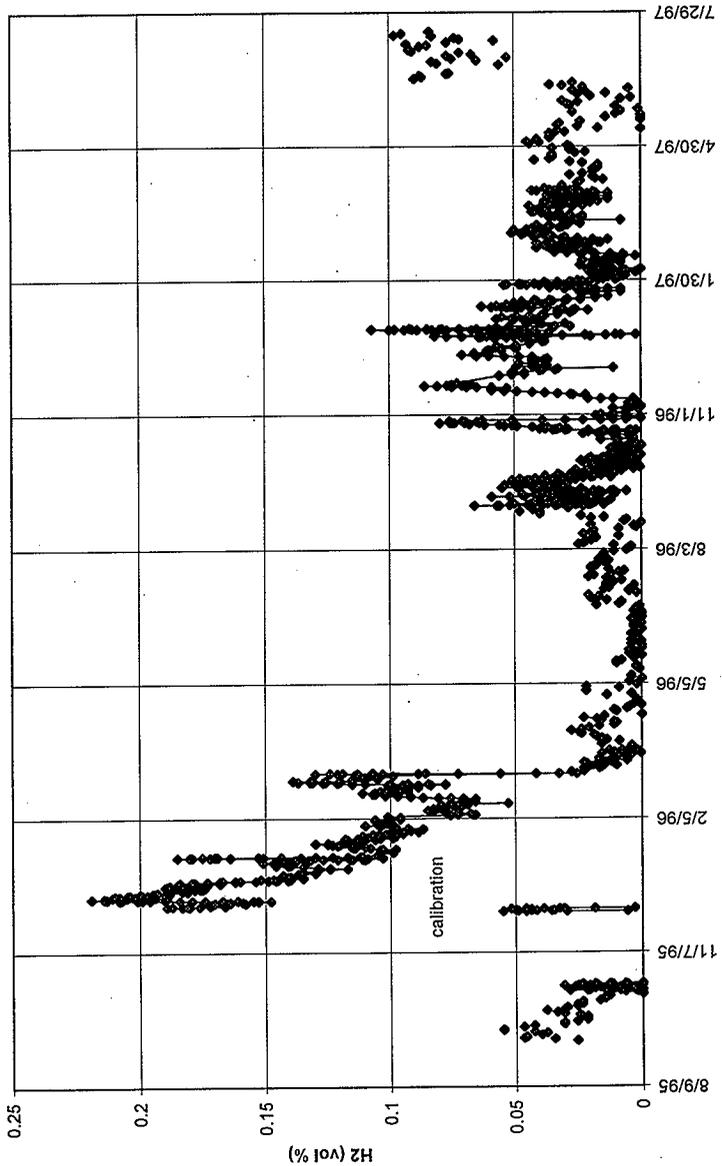
241-U-107 SHMS HYDROGEN (narrow range)



241-U-108 SHMS HYDROGEN (narrow range)



241-U-109 SHIMS HYDROGEN (narrow range)



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