

Gas Monitoring Systems in Support of Waste Tank 241-SY-101 Hydrogen Mitigation Task

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**GAS MONITORING SYSTEMS IN SUPPORT OF WASTE TANK 241-SY-101
HYDROGEN MITIGATION TASK**

**B. L. Philipp
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E. K. Straalsund**

INTRODUCTION

Twenty-four hazardous waste storage tanks at the Hanford Site in Richland Washington, are identified as having the potential to build up gases, including hydrogen, nitrous oxide and ammonia, to a flammable level. Because this behavior was not addressed adequately by the facility Safety Analyses, the U.S. Department of Energy (DOE) declared an Unreviewed Safety Question, placing the tanks on a Flammable Gas Watch List.

Westinghouse Hanford Company (WHC) identified Waste tank 241-SY-101 (SY-101) as presenting the most serious safety concern. Generated gases collect in the sludge layer near the bottom of the tank. The accumulation creates a buoyancy that eventually overcomes the density and bonding strength of the bottom layer. When this happens, the gases detach and travel upward through a liquid layer to the vapor space above the tank crust. This event typically occurs at 90-day intervals and is completed within a couple hours. This allows a rapid buildup of hydrogen to potentially flammable levels in the tank vapor space.

A mixer pump has been installed in tank SY-101. The goal is to control the buildup of flammable gases within the tank waste by generating a slow, continuous gas release. This requires monitoring of the tank vapor space for hydrogen to manage activities within and around the tanks. First, percent volume detection is needed to provide safety surveillance during any release of hydrogen to flammable levels. Secondly, accurate measurements in the 1 to 100 ppm range are required to detect small increases in tank background hydrogen level of 10 to 50 ppm. Increase in background hydrogen levels during the mixer pump operation indicate induced gas releases are mitigating tank hydrogen buildup.

The gas monitoring systems are located outdoors on a waste tank farm. To support system design transfer to other waste tanks, the gas sampling and monitoring equipment installation was designed to accommodate the following worst case environmental and sampling requirements:

- Waste tank external conditions
 - Air temperature variations from -29 to 49 °C
 - Relative humidity from 5 to 100%
 - Wind speeds up to 50 km per hour
 - Moisture in the form of rain, sleet, snow, and hail
 - Radiation levels exterior to the tank of 100 mrem per hour
 - Blowing dust and nearby lightning strikes.

- Gas sampling conditions
 - Vapor space pressure from -12 to 60 inches of water gauge
 - Vapor space temperature from 10 to 100 °C
 - Condensed vapor pH from 8 to 12
 - Tank vapor space and gas samples are assumed to be a Flammable Gas class 1, division 1, group B hazard at all times, defined by NFPA 497, (NFPA 1975) NEC article 504 (NFPA 1993), and ANSI/ISA RP 12.6 (ANSI/ISA 1987). (All components that come in contact with the sample gas were designed or qualified as Intrinsically Safe. The area outside the sample stream is unclassified because of two engineered barriers.)
 - The tank vapor space may contain, unknown concentrations of air, hydrogen, nitrous oxide, ammonia, water vapor, carbon dioxide, carbon monoxide, and other gases.

Gas sampling and monitoring systems have been developed and installed by WHC, in cooperation with Los Alamos National Laboratory, to support the SY-101 waste tank hydrogen mitigation task.

The gas monitoring systems provided the following range of measurements:

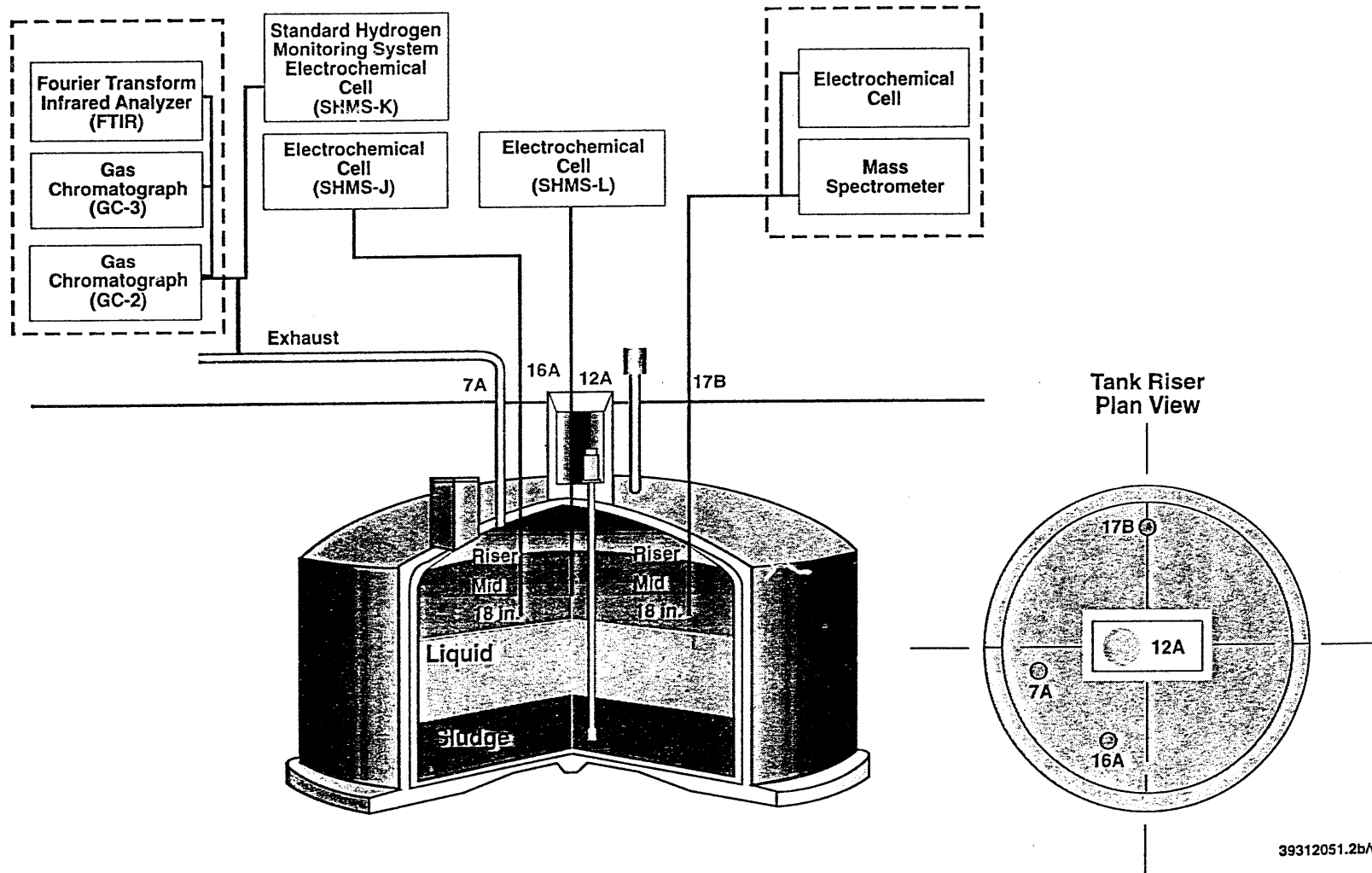
- Hydrogen detection accuracy $\pm 0.2\% \text{H}_2$ in the 0 to 10% H_2 range in a continuous real time mode
- Hydrogen detection accuracy $\pm 10.0\%$ of full scale in the 100 to 2,000 ppm H_2 range in a continuous real time mode
- Hydrogen analytical accuracy $\pm 2\text{ppm}$ in the 0 to 50 ppm range, $\pm 4\text{ppm}$ in the 50 to 100 ppm range, and $\pm 10\%$ of reading in the 100 ppm to 10% by volume range
- Nitrous oxide analytical accuracy of $\pm 10\%$ of reading from 3 ppm to 5% by volume range
- Ammonia analytical accuracy of $\pm 10\%$ of reading from 1 ppm to 5% by volume range

Figure 1 shows the waste tank configuration and the relative location of gas monitoring systems. Figure 2 graphically presents the instrumentation detection ranges.

SYSTEM DESIGN DESCRIPTION

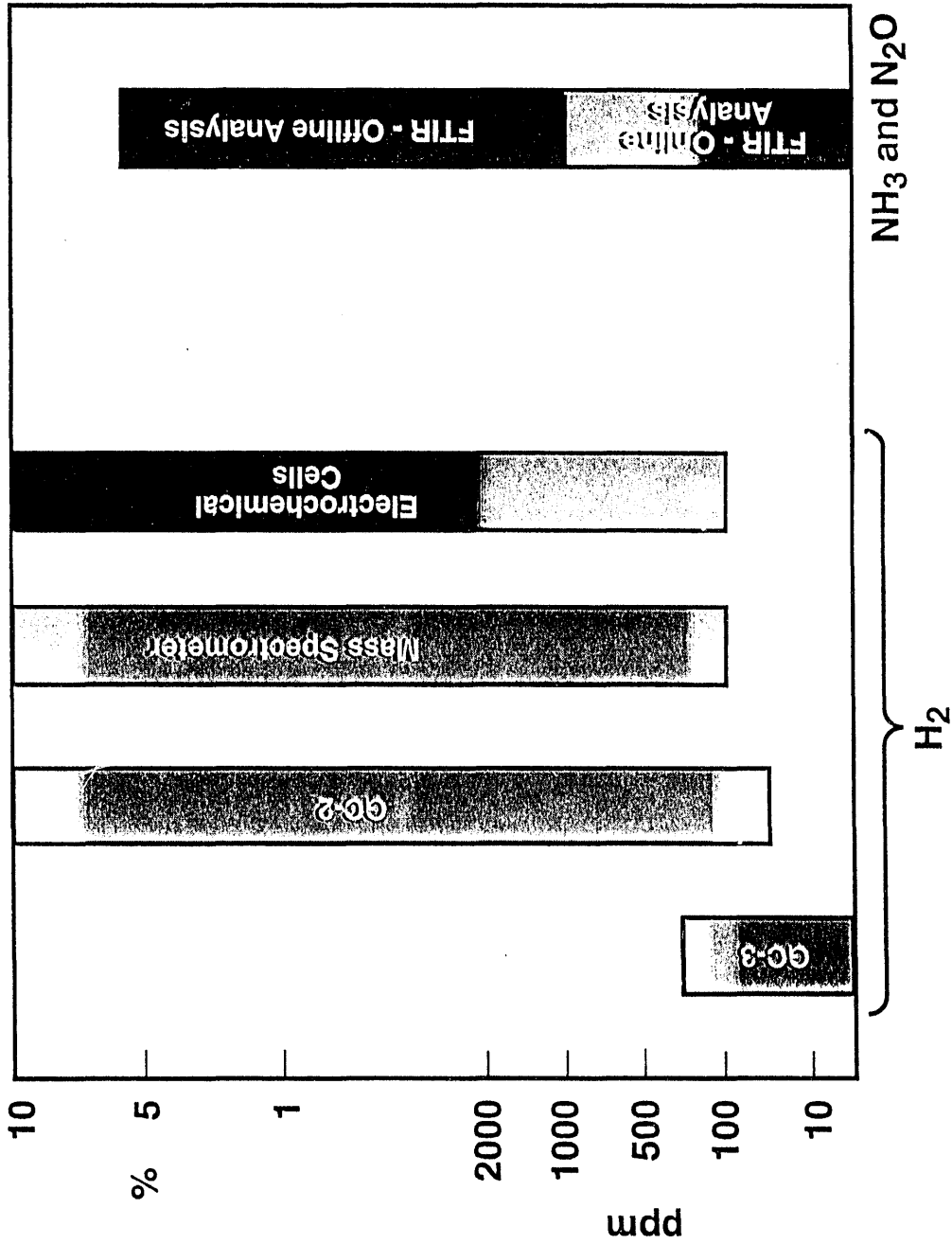
Three configurations of environmentally controlled enclosures support monitoring instrumentation and the gas sampling systems. Two 8-by-10-by-8-foot enclosures house the analytical instruments. Several

Figure 1. Gas Monitoring Instruments.



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Figure 2. Applicable Detection Range by Instrument.



39312051.1b/w

Figure 2

modified 24-by-30-by-72-inch, National Electrical Manufacturer's Association (NEMA) Type 4-rated (NEMA 1991) enclosures house the hydrogen detection instrumentation.

The gas sampling and delivery systems use a common design. The sample is drawn from the vapor space and returned to the tank exhaust system. The stainless steel tubing is trace-heated to minimize condensate buildup during sample transport and to maintain the gas sample at a constant temperature. A positive-displacement, sealed-bellows vacuum pump conducts a particulate-filtered sample to the analysis instruments. The pump is downstream of the instruments to provide a near-atmospheric sample and to provide containment for potential contamination. Additional support process instrumentation monitors sample temperature, pressure, and flow.

The gas monitoring instruments use certified standard gases for periodic calibration. Suitable gas concentrations are used to qualify proper instrument operation. Further, the calibration gas pressures and temperatures are monitored and controlled to match the sample conditions.

The first analytical instrument installed for real time analysis was a magnetic-sector mass spectrometer. The mass spectrometer is used to detect and quantify hydrogen and other gas species present in the tank vapor. This instrument, along with grab samples, obtained data for the initial release gas characterization in May 1991. Detection of the gas species takes place at high vacuum pressures and involves a very small portion of the sample gas.

A small amount of sample gas flows into the mass spectrometer tube where the molecular separation of the gas occurs. A magnetic field propels the positive ions generated by the ion source through a focusing slit into an electron multiplier detection tube. The degree of ion deflection within the magnetic field depends on the ion's velocity as well as its mass-to-charge ratio. Altering the ion source potential will change the given ion velocity and allow different masses to be focused and detected.

An electrochemical cell was used to detect hydrogen in the range of 0 to 10% by volume. The cell was designed specifically for detecting hydrogen. It generates a millivolt signal, of nominally 1 mV per 1% hydrogen, as a function of gas partial pressure. The signal conditioner provides a local digital display as well as a 4-to-20-mA output signal proportional to the selected full scale range.

The cell reduces oxygen or oxidizes the hydrogen on a catalytically active electrode in contact with a gas permeable membrane. It is the membrane that is in contact with the sample. It acts as a diffusion barrier and keeps the active sensor components from contact with the sample stream. Hydrogen partial pressure is indicated by the millivolt signal level developed across the external resistive-temperature compensation network. The voltage results from the electron exchange occurring between the two internal electrodes joined by a highly ionized electrolyte solution. The sensor exhibits a linear response over a wide range of hydrogen concentrations. Concentration variations from 100 ppmv to 5%v are detected easily.

Initially, molybdenum disulfide (MOS) solid state sensors were used to detect hydrogen in the ranges of 0 to 100 ppm and 100 to 2,000 ppm. During the first measured gas release, it was discovered that their response was unpredictably affected by the gas stream constituents.

Two gas chromatographs (GC) are used to analyze the presence of hydrogen. The low-range hydrogen GC is a reduction gas analyzer. The GC is used to quantify the sample stream hydrogen content in the range of 0 to 100 ppm. In reduction gas detection, the hydrogen is passed through a heated bed of mercuric oxide where the hydrogen reacts to create mercury vapor. The resultant mercury vapor is quantitatively determined by an ultraviolet photometer located immediately downstream of the reaction bed. Mercury vapor is easy to measure, allowing the detector to be relatively sensitive.

The wide-range GC uses a thermal conductivity detector. This GC is used to quantify the sample stream hydrogen content in the range of 0 to 10% by volume. The system can detect hydrogen peaks as low as 100 ppm. The thermal conductivity detector uses thermistors in a bridge circuit. The circuit detects changes in resistance as the eluted gas species in a carrier gas are passed over one thermistor while maintaining the other as a reference.

A Fourier Transform Infrared (FTIR) spectrometer is used to measure gas species that absorb infrared (IR) energy such as ammonia, nitrous oxide, carbon dioxide, and other selected species. These gases may affect the tank vapor flammability. Because diatomic molecules are not affected significantly by IR, the FTIR cannot be used to analyze hydrogen concentrations. The FTIR analyzes the absorption spectra obtained from IR light transmitted through a sample gas chamber.

The monitoring instrumentation is locally and remotely displayed and controlled. A distributed data acquisition and control system interfaces process signals that are supervised from a control room located off the tank farm. Sample gas temperatures, pressures, and flows are controlled, monitored, and logged to ensure consistent analysis. The analytical instruments are controlled by local personal computers and are linked to the control room supervisory computer by modems or a local area network (LAN) using industry standard protocol. Nominally 1,000 analytical gas samples are taken, analyzed, transmitted, and stored daily. This large quantity of data is required to characterize adequately the tank vapor space during steady-state, pump-testing, and gas release events.

SUCCESSSES AND DISCOVERIES

As with any design, deployment, and testing activity, there are successes and failures associated with the project. Initial testing under laboratory conditions confirmed the MOS sensor's ability to detect ppm hydrogen in the presence of air. Initial input from the vendor discounted the need to test for interfering gases. Following initial deployment of the first sensor, the tank gas background signal showed close correlation to the mass spectrometer data. Not until deployment of the second sensor was a concern noted with sensor data correlation. The MOS sensors were shown to experience significant interferences to other gases during the February 2, 1993, SY-101 gas release.

The gas sampling pump motors initially experienced a short field life. The pump motor end bell bearing failed prematurely because of poor motor design. The motor manufacturer redesigned the end bell bearing configuration, and the pump manufacturer modified the counter balance and piston rod in the bellows pump to reduce vibration. These actions have increased the motor life significantly.

Initially, the mass spectrometer experienced frequent operational down time. The problems were attributed to the following:

- Rapidly developed hardware and software system to support a safety issue
- Difficulty of siting a laboratory instrument in a field environment
- Lack of care of support personnel working inside the instrumentation shelter during high work activity periods.

Additional work control and intense operational attention to the system performance significantly improved the system availability.

The GCs are robust instruments designed for field deployment. However, the computer interfaces and LAN software necessary to convey data outside the tank farm restriction barriers have caused significant downtime for these analytical instrument systems.

Several gas monitoring systems were situated in support of SY-101 vapor space gas characterization and monitoring. Both analytical and safety-related detection systems were deployed to meet project goals. The systems included a mass spectrometer, two GCs, an FTIR, and four electrochemical detection systems.

Site qualification testing of sampling and measurement systems proved the required performance. An initial site qualification test was performed on the low-range GC and the FTIR. Known certified gases and Hanford Site mixed gases were drawn into the gas sample tubing nominally 8 meters from the analytical instruments. The gases were accurately analyzed by the GC and FTIR. Tank background hydrogen concentrations have been measured with good correlation between the mass spectrometer, the low-range GC, and grab samples from several other riser locations. The high-range GC, mass spectrometer, and the electrochemical cells are able to accurately detect gas release concentrations of hydrogen. The February 2, 1993, and subsequent SY-101 tank hydrogen releases have been measured with good correlation between the electrochemical hydrogen monitors, the low- and high-range GCs, and the mass spectrometer. Other gases of interest measured by the FTIR and the mass spectrometer show good agreement with analyzed grab samples.

REFERENCES

ANSI/ISA, 1987, *Installation of Intrinsically Safe Systems for Hazardous (Classified Locations)*, ANSI/ISA RP 12.6, American National Standard Institute/Instrument Society of America, Research Triangle Park, North Carolina.

NFPA, 1993, *National Electrical Code*, NFPA 70, Code 504, "Intrinsically Safe Systems," National Fire Protection Association, Quincy, Massachusetts.

NEMA, 1991, *Enclosures for Electrical Equipment (1000 Volts Maximum)*, NEMA 250, National Electrical Manufacturer's Association, Washington, D.C.

NFPA 1975, *Hazardous Chemical Data*, NFPA 49, National Fire Protection Association, Quincy, Massachusetts.

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