

TO:	All Marine Chemists and Marine Chemist Trainees
FROM:	Lawrence B. Russell, Principal Specialist
DATE:	07 APRIL 2023
SUBJECT:	Marine Field Service Safety Alert 01-23 – Check Sampling Hose Used with Portable Gas Detection Meter

Purpose

This Safety Alert highlights the risk of inaccurate gas detection readings that can occur when a defective sampling hose is used with a portable gas detection meter. Other factors that can affect the evaluation of the atmosphere of confined spaces and work areas are also presented. The incident that is the subject of this Safety Alert did not involve a Marine Chemist or shipyard employment. However, the lessons learned from this incident are important for Marine Chemists, Marine Chemist Trainees, and shipyard competent persons.

In this incident a portable gas detector failed to detect the presence of a flammable vapor. A repair involving hot work proceeded because the workers thought, based upon the atmosphere test results, no flammable vapor was present. The subsequent explosion resulted in a fatal injury. The accident investigation found that a significant contributor to the failure to detect the presence of a flammable vapor in the tank and work area was the flammable vapor being adsorbed on the inner surface of the sample tube. This meant that no flammable vapor reached the combustible gas indicator (CGI). The workers inaccurately concluded that the mixing vessel and work area were free of flammable vapor.

This incident highlights:

- The risk of adsorption if an unsuitable sample tube is used;
- The importance of verifying the effectiveness of gas detection equipment including the sampling hose;
- The importance of preparing tanks and pipelines for hot work; and
- The importance of properly conducting tests and a visual inspection.



Background

A fatal explosion at a chemical facility in July 2018 killed a welder who was carrying out maintenance work on a mixing vessel. Workers had checked the atmosphere with a combustible gas indicator before their work began. However, the gas monitor had failed to detect the presence of flammable vapor. Hot work proceeded because the workers believed that there was no flammable vapor in the mixing vessel.

Accident investigators discovered toluene residue inside the mixing vessel and some leaks were found in a supply pipeline outside of the mixing vessel. Investigators determined that toluene vapors had leaked into the vessel from faulty valves, producing a flammable atmosphere inside the mixing vessel.

Investigators found the gas test meter (specifically the CGI) had been incorrectly set up. The CGI took about 7 minutes to alarm on an exposure to toluene vapor. It should have taken less than 2 seconds. Further testing showed that a significant contributor to the failure of the CGI to detect the toluene vapor was the toluene vapor was adsorbed on the inner surface of the sample tube. This meant that when the portable gas detector was used during the incident, no flammable vapor had reached the CGI sensor before the gas-testing was completed.

Another factor identified by investigators was the CGI sensor had been calibrated for methane. Methane has a lower explosive limit (LEL) of 5% by volume which is greater than the LEL for toluene. According to the NIOSH Pocket Guide, toluene has an LEL of 1.1% by volume.

Pentane vs. Methane

When detecting a known combustible gas Industrial Scientific recommends that for best accuracy the portable gas meter should be calibrated to the gas which you are detecting whenever possible. For example, if you are testing the fuel system on and LNG-fueled vessel or a sewage tank, then the CGI sensor should be calibrated to methane. However, if the flammable or combustible gas that was last in the tank or space is a hydrocarbon or is unknown, then Industrial Scientific recommends that the CGI sensor is calibrated with a known concentration of pentane.

Combustible gases produce signals from the standard LEL type sensor at levels inversely proportional to the molecular weight of the gas. Light gases produce a higher signal than heavier gases. Methane being very light yields a very high signal on the typical sensor. Heavier hydrocarbons such as pentane and hexane produce a significantly lower signal than a gas such as methane. For this reason, it is advantageous to calibrate the CGI to pentane, because as lighter gases such as methane, hydrogen, propane, and ethane are detected, the response will be higher than normal, and all reading and alarm errors will side in the direction of safety. When calibrating with a lighter gas (methane), the instrument's ability to accurately detect the heavier compounds is somewhat diminished.

Example 1: The CGI that was calibrated to 50% LEL methane encounters a concentration of 15% LEL toluene. This concentration of toluene exceeds the NFPA 306 limits for confined space entry and hot work¹. However, in this example because the CGI is calibrated to methane, the display reading when detecting the concentration of 15% LEL toluene gas would only be 7% LEL. The portable gas detector is erroneously indicating that the conditions are safe for entry [NFPA 306-2019, 7.1.1(2)] and safe for hot work [NFPA 306-2019, 7.1.4(2)].

Example 2: The CGI was calibrated to 50% LEL pentane and is then exposed to the same concentration of toluene (15% LEL). Now, because the CGI is calibrated to the lighter gas (pentane), the CGI will read 14% LEL and produce and LEL alarm. Although the gas detector reading is not accurate, the instrument error is on the side of caution.

It can be easily deduced from these examples that the more appropriate calibration gas for use in general hydrocarbon combustible gas detection is pentane.

Instrument Response Time

In gas detector specifications the response time is usually defined as the time it takes the output of the sensor to reach 90% of its final value when subject to a step change in gas concentration at its sample point. The overall response time of a gas detector is governed by three factors:

- 1. The time taken to transport the sample to the sensor. For pumped (aspirated) systems the transport time is determined by the sample tube length, tube diameter, aspiration rate and diffusion rate from the flow system to the sensor.
- 2. The diffusion rate or the intrinsic time it takes for the gas-sensing mechanism to respond. This is dependent on the type of sensor that is installed in the gas meter (e.g., catalytic (pellistor), infrared, thermal conductivity, flame ionization, flame temperature, semiconductor, ultrasonic, photoionization).
- 3. The response time of the signal processing electronics.

Sample hoses should be as short as possible. The increase in response time should not exceed the response time of the gas detector without a sample hose plus the delay time specified in the gas detector manual or, where no time is specified in the manual, 1 second per foot (3 seconds per meter). The

¹ The concentration of flammable materials is below 10% of the lower explosive limit (LEL).

combination of gas detector and sample hose should be considered unsuitable where this time is exceeded.

Instrument Inspection, Maintenance & Calibration

According to the Health & Safety Executive (HSE-UK) the response time should also be considered in conjunction with the alarm level. The gas detector should be set to alarm at a level low enough to ensure the health and safety of people but high enough to prevent false alarms. False alarms are most likely to be caused by fluctuations in sensor output due to environmental changes (e.g., ambient temperature, pressure, or humidity), sensitivity to other gases or vapors, or sensor drift. If false alarms are a problem, then one option is to use two detectors - the alarm level must be registered by both detectors before the alarm activates.

Portable gas detection instruments should only be used if they are in good condition and functioning correctly. Every time you use your gas detection meter, inspect it for any damage prior to use; and periodically if the meter is being used for a prolonged period. Kinks, bends, blockages, and holes in the sample hose may affect the sample and give a false reading. A damaged battery or cracks in the instrument casing could make the gas meter unsafe or unreliable or both. Contamination, by water or dust, could give false readings and may damage the instrument. A damaged display can make the instrument difficult or impossible to read and a broken alarm may not register a hazardous situation. Any air inlet filters should be clean in order to allow an unrestricted airflow into the instrument. It is also important to check the integrity of other parts such as the carrying handle or case and shoulder strap.

NFPA 306, *Standard for the Control of Gas Hazards on Vessels*, Section 6.1 requires the accuracy and sampling integrity of instruments used by the Marine Chemist to be verified before each day's use. The calibration of the sensors shall be verified using a known concentration of test gas. The frequency of bump checks or function checks of the portable gas detector will depend on the manufacturer's recommendations and should include checking:

- That a zero reading is obtained in a clean atmosphere away from known sources of detectable gas or vapor.
- For a response to a known concentration of oxygen, flammable vapor and toxic gas with the sample hose attached.
- The battery charge level is adequate for the job.
- The logging period (if datalogging is required) to ensure all datapoints over the required duration of measurement can be stored in memory.

Cleaning and Testing Tanks and Pipelines

Investigators found toluene residue inside the mixing vessel and supply pipelines. There is no information available about this incident that details the extent of the tests and inspection that was performed prior to the commencement of the work. The importance of the preparation of the mixing vessel and the associated pipeline prior to hot work needs to be mentioned. If this work was done in a shipyard, marine terminal, or waterfront facility, then a Marine Chemist's Certificate would need to be posted before the work was started.

Prior to the issuance of the Marine Chemist's Certificate the mixing vessel would need to be cleaned so that the atmosphere met the conditions for the designation *Safe for Hot Work* or *Safe for Limited Hot Work* [NFPA 306-2019, 5.1.2]. In addition, all associated pipelines involved in the scope of work would have been flushed with water or blown with steam or air [NFPA 306-2019, 5.1.1].

As per NFPA 306, Section 6.2, a Marine Chemist would have to personally determine conditions and physically enter the mixing vessel (or look inside it) to conduct a visual inspection to the extent necessary to determine the atmospheric or fire hazards that may have existed. The Marine Chemist would have to:

- Conduct tests of the mixing vessel to ensure compliance with the minimum applicable requirements prior to issuing a Certificate [NFPA 306-2019, 6.2. and 6.2.1].
- Perform tests of the pipelines associated with the mixing vessel [NFPA 306-2019, 6.2.1(4)]
- Verify that the pipelines associated with the mixing vessel are either disconnected, blanked off, or otherwise blocked by a positive method, with the valves are positioned and tagged in such a manner to prevent or by written notice restrict operation [NFPA 306-2019, 6.2.1(5)].

Effective tank and pipeline preparation, accurate testing with a properly calibrated test meter, and a thorough visual inspection could have prevented this incident.

Conclusion

It is important that the gas detection equipment used to determine that a space or area is safe for entry or work is suitable for the intended purpose. Portable gas detection equipment needs to provide a sufficiently accurate and reliable indication of any hazardous material that may be present. In the incident presented in this Safety Alert, the CGI failed to detect a flammable atmosphere. Hot work proceeded based on the faulty test result. The hot work caused the ignition of a flammable atmosphere and a fatal injury. While there were errors in the selection and set-up of the gas detector, the most significant contributor to the failure of the gas detector was the adsorption of the flammable vapor on the surface of the sample hose before it could reach the CGI sensor. This Safety Alert is to remind Marine Chemists and Marine Chemist Trainees of the importance and need to ensure the suitability and function of the gas detection equipment you are using to assess workplace hazards. This assessment needs to include the sample hoses that you are using.

Questions or comments about this Safety Alert can be directed to the NFPA Marine Field Service.

References

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