

TECHNICAL REPORT

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Feasibility of Chlorine Detection Instrument Testing

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Feasibility of Chlorine Detection Instrument Testing

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Foreword

Workplace safety

Elemental chlorine is a strong oxidizing agent¹, and in water it disproportionates to form hypochlorous and hydrochloric acids. This high chemical reactivity is reflected in the toxicity of chlorine. The workplace exposure limit, TLV-TWA, is only 0.5ppm². Consequently safety requirements of chlorine are a high priority, and there is a considerable need for chlorine gas detection instruments for workplace safety. These instruments may be either fixed or portable; and there are many companies that manufacture instruments for chlorine gas detection in the workplace. In order to promote a safe work environment, the ISA92 Committee is developing performance standards for gas detection instruments for workplace safety. One of the subcommittees, ISA92.06, has the responsibility of developing a standard for chlorine gas detection.

Chlorine detection instrument performance tests

Several questions have been posed by the Committee about testing chlorine gas detection instruments. Since the TWA-TLV is low (0.5ppm), it is desirable for the tests to be performed near this chlorine concentration level. For the test to be valid, the concentration of the gas applied to the instrument under test has to be known to a significantly higher precision and accuracy³ than the allowed tolerance of the instrument response. As currently written, many of the instrument performance tests require the instrument to give a reading or activate an alarm based on a difference in gas concentration of 0.1ppm.⁴

Effect of humidity⁵

The standard for chlorine gas detection instruments (ISA-92.06.01-1998) includes a performance requirement that the instrument detect a chlorine gas test mixture of known concentration within set tolerances over a non-condensing humidity range between around 15 and 90+ percent. There has been a lot of debate within the Committee about whether this test is valid. There are two principal arguments in this discussion.

The first argument is that humidity is a very important parameter that should be tested since many of the locations where chlorine detection instruments are used are very humid. Many paper mills, for example, operate with the atmosphere almost constantly saturated with water vapor. Therefore, a performance standard for chlorine detection instruments should include a test of the effects of humidity on the chlorine sensor response.

¹ $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$; $E^\circ = 1.358\text{V}$ vs. SHE; CRC Handbook of Chemistry & Physics, 70th Edition, 1989-1990, R.C. Weast et al. (Eds.), Publ. CRC Press, Boca Raton, FL.

² 1994-1995 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, ACGIH.

³ For this discussion, accuracy is a measure of how close the nominal chlorine concentration is to the actual chlorine concentration. The precision is a measure of the variance of the chlorine concentration from the mean concentration upon repeating the same measurement many times.

⁴ This report assumes that the atmosphere and gas pressure is one standard atmosphere (1.01325 Bars). At constant pressure, and assuming ideal gas behavior, gas concentrations can be expressed as volume ratios, i.e. the volume of component divided by the total gas volume, written as, for example, percent (%) or parts per million (ppm).

⁵ Relative Humidity - The ratio of the quantity of water vapor present in the atmosphere to the quantity that would saturate at the existing temperature.

The second argument is that the test is not reasonable since chlorine may react with water in the vapor phase, forming other reactive species. If species such as hypochlorous acid (HOCl) are being formed, they may not diffuse into the detector in the same way as chlorine gas. The most common technology for detecting chlorine in the workplace uses electrochemical sensors. Typically these sensors contain a diffusion barrier consisting of a porous Teflon membrane, which the gas has to diffuse across to reach the electrode/electrolyte where the detection reaction occurs. If hypochlorous acid is formed in the gas phase, it is likely that it will absorb onto the first surface it meets, such as the porous membrane. The instrument would therefore read low under high humidity conditions because the real chlorine concentration had been decreased by the high humidity. Since this standard is for chlorine (Cl₂) detectors and not active chlorine species detectors; the humidity test may not be a valid performance criterion since the true chlorine (Cl₂) concentration would not be known at high humidities if these vapor-phase reactions occurred to a significant extent.

The Committee agreed to try to find out as much as possible about the reactions of chlorine with water vapor and combine these with experimental results to produce recommendations for ISA-92.06.01-1998.

This report is a summary of the results of this investigation.

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Abstract

This report has been written to answer questions about the feasibility of performing the tests described in the ISA standard for chlorine gas detection instruments (ISA-92.06.01-1998). The report discusses two questions; the first is the availability of a chlorine gas supply of sufficient accuracy and precision for performing the tests, and the second is the viability of testing a gas detection instrument with chlorine under a variety of humidity conditions. The report surveys the available chemical literature, presents experimental and calculated results of humidity testing, and summarizes information on test gas generation and analysis.

Key Words

Accuracy, Chlorine, Cl₂, Gas, HCl, HOCl, Hypochlorous acid, Humidity, Hydrochloric acid, Instrument, Precision, Sensor, Standard

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