1 Introduction

This report has been written to provide support to the work of the ISA92.06 Subcommittee responsible for drafting a performance standard for chlorine detection instruments. The scope of the standard is limited to those instruments intended for the determination of chlorine gas in air to enhance workplace safety. In Committee discussions two technical questions were raised; the first was the feasibility of generating chlorine gas concentrations with sufficient accuracy and precision necessary for the performance tests. The second question was whether there was a significant reaction between chlorine and water in the vapor phase since the extent of this reaction would impact the validity of the proposed humidity performance test.

The first part of the report discusses issues related to the question of the possible interaction of chlorine with water vapor in the gas phase. The latter part of the report discusses the generation of chlorine gas.

This report is divided into several sections. The first section provides a brief overview of the chemistry of chlorine and related compounds. This section is intended to provide an outline of the chemical basis for later discussions and to summarize the results obtained from literature searches. Since a standard is by necessity based on the current technology, the available information from sensor manufacturers is summarized so that a comparison between the proposed specifications and manufacturers' specifications can be made. Several instrument tests have been performed by both the NCASI and several manufacturers using both Draeger and City Technology chlorine sensors. These tests were aimed at finding the effect that humidity has on the response of the instrument to a nominal chlorine concentration. Lastly, a theoretical approach using free energy calculations was used to estimate the thermodynamic feasibility of the proposed vapor-phase reactions between chlorine and water.

The second part of the report addresses sources of chlorine test gas and the feasibility of generating chlorine test gas mixtures with sufficient accuracy and precision necessary to do the performance testing called for by the standard (ISA-92.06.01-1998). This section also provides information about the analysis of chlorine test gas mixtures and a short section with some practical experimental recommendations for working with chlorine.

2 Review of chlorine chemistry [6,7,8,9]

The chemistry of chlorine is briefly reviewed as relevant to this report. Particular emphasis is placed on the reactions of chlorine with water and the products and equilibrium formed. Further information may be found in the references cited.

2.1 Chlorine

Elemental chlorine is a greenish yellow diatomic gas, Cl_2, with a molecular weight of 70.9 g/mol; atomic number 17; mp -101.0°C, bp -34.05°C; and its density is approximately two and a half times that of air. Chlorine occurs most commonly in nature as the chloride ion in sea water and in salt deposits. It was first isolated in 1774 by Karl Scheele, who did not recognize it as an element; the elemental nature of chlorine

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6 Merck Index, 11th Edition, Publ. Merck & Co. Inc.,1989.

7 Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 1, John Wiley, New York, (1978).

8 F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Fourth Ed., Publ. John Wiley, New York, 1980.

9 G. C. White, The Handbook of Chlorination and Alternate Disinfectants, Third Ed., Publ. Van Nostrand Reinhold, New York (1992).