TECHNICAL REPORT

ANSI/ISA–TR92.06.03–2008 (R2013)

A Technical Report prepared by ISA and registered with ANSI

Feasibility of Chlorine Detection Instrument Testing

Reaffirmed 10 March 2013

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)

ANSI/ISA–TR92.06.03–2008 (R2013)
Feasibility of Chlorine Detection Instrument Testing

ISBN: 978-1-937560-96-6

Copyright © 2013 by ISA. All rights reserved. Printed in the United States of America.
No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise), without the prior written permission of the Publisher.

ISA
67 Alexander Drive
P.O. Box 12277
Research Triangle Park, North Carolina 27709

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)

PREFACE

This preface, all footnotes, and annexes are included for informational purposes and are not a part of ISA-TR92.06.02-2008 (R2013).

This recommended practice has been prepared as a part of the service of ISA toward a goal of uniformity in the field of instrumentation. To be of real value, this document should not be static but should be subject to periodic review. Toward this end, the Society welcomes all comments and criticisms and asks that they be addressed to the Standards and Practices Board Secretary; ISA; 67 Alexander Drive; P. O. Box 12277; Research Triangle Park, NC 27709; Telephone (919) 549-8411; Fax (919) 549-8288; Internet: standards@isa.org.

The ISA Standards and Practices Department is aware of the growing need for attention to the metric system of units in general, and the International System of Units (SI) in particular, in the preparation of instrumentation standards. The Department is further aware of the benefits to USA users of ISA standards of incorporating suitable references to the SI (and the metric system) in their business and professional dealings with other countries. Toward this end, this Department will endeavour to introduce SI-acceptable metric units in all new and revised standards, recommended practices, and technical reports to the greatest extent possible. IEEE/ASTM SI 10, *American National Standard for Metric Practice*, and future revisions, will be the reference guide for definitions, symbols, abbreviations, and conversion factors.

It is the policy of ISA to encourage and welcome the participation of all concerned individuals and interests in the development of ISA standards, recommended practices, and technical reports.

Participation in the ISA standards-making process by an individual in no way constitutes endorsement by the employer of that individual, of ISA, or of any of the standards that ISA develops.

CAUTION — ISA DOES NOT TAKE ANY POSITION WITH RESPECT TO THE EXISTENCE OR VALIDITY OF ANY PATENT RIGHTS ASSERTED IN CONNECTION WITH THIS DOCUMENT, AND ISA DISCLAIMS LIABILITY FOR THE INFRINGEMENT OF ANY PATENT RESULTING FROM THE USE OF THIS DOCUMENT. USERS ARE ADVISED THAT DETERMINATION OF THE VALIDITY OF ANY PATENT RIGHTS, AND THE RISK OF INFRINGEMENT OF SUCH RIGHTS, IS ENTIRELY THEIR OWN RESPONSIBILITY.

PURSUANT TO ISA'S PATENT POLICY, ONE OR MORE PATENT HOLDERS OR PATENT APPLICANTS MAY HAVE DISCLOSED PATENTS THAT COULD BE INFRINGED BY USE OF THIS DOCUMENT AND EXECUTED A LETTER OF ASSURANCE COMMITTING TO THE GRANTING OF A LICENSE ON A WORLDWIDE, NON-DISCRIMINATORY BASIS, WITH A FAIR AND REASONABLE ROYALTY RATE AND FAIR AND REASONABLE TERMS AND CONDITIONS. FOR MORE INFORMATION ON SUCH DISCLOSURES AND LETTERS OF ASSURANCE, CONTACT ISA OR VISIT WWW.ISA.ORG/STANDARDSPATENTS.

OTHER PATENTS OR PATENT CLAIMS MAY EXIST FOR WHICH A DISCLOSURE OR LETTER OF ASSURANCE HAS NOT BEEN RECEIVED. ISA IS NOT RESPONSIBLE FOR IDENTIFYING PATENTS OR PATENT APPLICATIONS FOR WHICH A LICENSE MAY BE REQUIRED, FOR CONDUCTING INQUIRIES INTO THE LEGAL VALIDITY OR SCOPE OF PATENTS, OR DETERMINING WHETHER ANY LICENSING TERMS OR CONDITIONS PROVIDED IN CONNECTION WITH SUBMISSION OF A LETTER OF ASSURANCE, IF ANY, OR IN ANY LICENSING AGREEMENTS ARE REASONABLE OR NON-DISCRIMINATORY.

ISA REQUESTS THAT ANYONE REVIEWING THIS DOCUMENT WHO IS AWARE OF ANY PATENTS THAT MAY IMPACT IMPLEMENTATION OF THE DOCUMENT NOTIFY THE ISA STANDARDS AND PRACTICES DEPARTMENT OF THE PATENT AND ITS OWNER.

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)

ADDITIONALLY, THE USE OF THIS DOCUMENT MAY INVOLVE HAZARDOUS MATERIALS, OPERATIONS OR EQUIPMENT. THE DOCUMENT CANNOT ANTICIPATE ALL POSSIBLE APPLICATIONS OR ADDRESS ALL POSSIBLE SAFETY ISSUES ASSOCIATED WITH USE IN HAZARDOUS CONDITIONS. THE USER OF THIS DOCUMENT MUST EXERCISE SOUND PROFESSIONAL JUDGMENT CONCERNING ITS USE AND APPLICABILITY UNDER THE USER'S PARTICULAR CIRCUMSTANCES. THE USER MUST ALSO CONSIDER THE APPLICABILITY OF ANY GOVERNMENTAL REGULATORY LIMITATIONS AND ESTABLISHED SAFETY AND HEALTH PRACTICES BEFORE IMPLEMENTING THIS DOCUMENT.

THE USER OF THIS DOCUMENT SHOULD BE AWARE THAT THIS DOCUMENT MAY BE IMPACTED BY ELECTRONIC SECURITY ISSUES. THE COMMITTEE HAS NOT YET ADDRESSED THE POTENTIAL ISSUES IN THIS VERSION.

The following members of ISA Committee ISA92 approved ANSI/ISA-TR92.06.03-2008:

NAME	COMPANY
Jon Miller, Chair	Detector Electronics Corporation
Robert Seitz, Vice Chair	Artech Engineering
Mark Coppler, Managing Director	Ametek Inc.
Chris Brown	Enmet Corporation
Patrick Byrne	FM Approvals
Robert Masi	Detcon Inc.
David Mills	Underwriters Laboratories Inc.
Alex Spataru	The Adept Group Inc.
Jerry Thomason	Omni Industrial Systems Inc.

ANSI/ISA-TR.06.03-2008 was approved for publication by the ISA Standards and Practices Board on 15 November 2007.

NAME	COMPANY
T. McAvinew, Vice President	Jacobs Engineering Group
M. Coppler	Ametek Inc.
E. Cosman	The Dow Chemical Company
B. Dumortier	Schneider Electric
D. Dunn	Aramco Services Company
J. Gilsinn	NIST/MEL
E. Icayan	ACES Inc.
J. Jamison	Husky Energy Inc.
K. Lindner	Endress + Hauser Process Solutions AG
V. Maggioli	Feltronics Corporation
A. McCauley	Chagrin Valley Controls Inc.
G. McFarland	Emerson Process Mgmt. Pwr & Water Solutions
R. Reimer	Rockwell Automation
N. Sands	DuPont
H. Sasajima	Yamatake Corporation
T. Schnaare	Rosemount Inc.
J. Tatera	Tatera & Associates Inc.
I. Verhappen	MTL Instrument Group
R. Webb	ICS Secure LLC
W. Weidman	Worley Parsons
J. Weiss	Applied Control Solutions LLC
M. Widmeyer	Consultant
M. Zielinski	Emerson Process Management

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)

The following members of ISA92 reaffirmed this document.

NAME	COMPANY
J. Miller, Chairman	Detector Electronics Corporation
R. Seitz, Vice Chairman	Artech Engineering
M. Coppler, Managing Director	Det Norske Veritas Certification Inc.
S. Baliga	General Monitors
W. Bennett	Mine Safety Appliances Co.
T. Crawford	Intertek Testing Services
G. Garcha	GE Energy
R. Goins	Lyondell Basell
K. Hedrick	MSHA Approval & Certification Center
S. Henney	FM Approvals
C. Lucarino	Sensient
R. Masi	Detcon Inc.
D. Mills	Underwriters Laboratories Inc.
L. Owen	Dooley Tackaberry Inc.
A. Skinner	GMI Gas Measurement Instruments LLC
J. Stratman	Honeywell Analytics Inc.
J. Thomason	Omni Industrial Systems Inc.
A. Vial	Shell Exploration & Production Co.
D. Wechsler	American Chemistry Council

This technical report was approved by the Standards and Practices Board on 16 January 2013.

NAME	COMPANY
E. Cosman, Vice President	The Dow Chemical Company
D. Bartusiak	ExxonMobil Chemical Co.
P. Brett	Honeywell Inc.
J. Campbell	Consultant
M. Coppler	Det Norske Veritas Certification Inc
B. Dumortier	Schneider Electric
D. Dunn	Aramco Services Co.
J. Federlein	Federlein & Assoc. Inc.
J. Gilsinn	NIST/EL
E. Icayan	ACES Inc.
J. Jamison	EnCana Corporation Ltd.
K. P. Lindner	Endress + Hauser Process Solutions AG
V. Maggioli	Feltronics Corp.
V. Mezzano	Fluor Corporation
T. McAvinew	Instrumentation and Control Engineering, LLC
C. Monchinski	Automated Control Concepts Inc.,
R. Reimer	Rockwell Automation
S. Russell	Valero Energy Corp.
N. Sands	DuPont
H. Sasajima	Azbil Corp.
T. Schnaare	Rosemount Inc.
J. Tatera	Tatera & Associates Inc.
I. Verhappen	Yokogawa Canada Inc.
W. Weidman	WCW Consulting
J. Weiss	Applied Control Solutions LLC
M. Wilkins	Yokogawa IA Global Marketing (USMK)
D. Zetterberg	Chevron Energy Technology Co.

Documents
Document Sharing Hub
Copyright International Society of Automation
Full document details: ANSI ISA TR92.06.03-2008 (2013)

This page intentionally left blank.

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)

Foreword

Workplace safety

Elemental chlorine is a strong oxidizing agent[1], 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 0.5ppm[2]. 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 accuracy[3] 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 humidity[5]

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] $Cl_2(g) + 2e \Longleftrightarrow 2Cl$; $E^{\circ} = 1.358V$ 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.

Documents
Document Sharing Hub
Copyright International Society of Automation
Full document details: ANSI ISA TR92.06.03-2008 (2013)

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 (Cl_2) detectors and not active chlorine species detectors; the humidity test may not be a valid performance criterion since the true chlorine (Cl_2) 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.

Publication of this Technical Report that has been registered with ANSI has been approved by ISA, 67 Alexander Drive, Research Triangle Park, NC 27709. This document is registered as a Technical Report according to the Procedures for the Registration of Technical Reports with ANSI. This document is not an American National Standard and the material contained herein is not normative in nature. Comments on the content of this document should be sent to ISA, 67 Alexander Drive, Research Triangle Park, NC 27709, E-mail: standards@isa.org.

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, Cl_2, Gas, HCl, HOCl, Hypochlorous acid, Humidity, Hydrochloric acid, Instrument, Precision, Sensor, Standard

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)

CONTENTS

1 Introduction 11
2 Review of chlorine chemistry 11
2.1 Chlorine 11
2.2 Chlorine oxides 12
2.3 Oxy acids and anions 13
2.4 Water solubility 13
2.5 Vapor phase reactions 13
3 Sensor manufacturer's specifications 14
3.1 Draeger 14
3.2 City Technology 14
3.3 Transient humidity effects 14
4 Experimental results 14
4.1 Overall approach 14
4.2 Chlorine instrument tests: Bacharach 15
4.3 Chlorine instrument tests: Mine Safety Appliances 15
4.4 Chlorine instrument tests: NCASI 17
4.5 Chlorine instrument tests: National Draeger 18
4.6 Equilibrium calculations 19
4.7 Titration of humidified chlorine 21
5 Discussion of results 22
5.1 Summary results from instrument/sensor tests 23
5.2 Specification in Standard ISA-92.06.01-1998, Section 7.14.1 24
6 Sources of chlorine test gas 24
6.1 Gas tanks 24
6.2 Electrochemical generators 25
6.3 Permeation Tubes 25
7 Analysis of chlorine gas concentration 25
7.1 Literature methods for chlorine test gas analysis 25
8 Recommendations for testing with chlorine 25
8.1 Experimental considerations 25
8.2 Correction for water vapor 26
9 Other gas performance standards 27
10 Acknowledgments 27

Documents
Document Sharing Hub

Copyright International Society of Automation

Full document details: ANSI ISA TR92.06.03-2008 (2013)