Standard Test Method for Analysis of Oxygen in Gaseous Fuels (Electrochemical Sensor Method)[1]

ε^1 NOTE—This standard was revised editorially in October 2013 to reflect dual designation.

1. Scope

1.1 This test method is for the determination of oxygen (O_2) in gaseous fuels and fuel type gases. It is applicable to the measurement of oxygen in natural gas and other gaseous fuels. This method can be used to measure oxygen in helium, hydrogen, nitrogen, argon, carbon dioxide, mixed gases, process gases, and ambient air. The applicable range is 0.1 ppm(v) to 25% by volume.

1.2 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4150 Terminology Relating to Gaseous Fuels

D5503 Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation

3. Terminology

3.1 For general terminology see Terminology D4150.

3.2 *Definitions:*

3.2.1 *electrochemical sensor*—A chemical sensor that quantitatively measures an analyte by the electrical output produced by the sensor.

3.2.2 *span calibration*—The adjustment of the transmitter electronics to the sensor's signal output for a given oxygen standard.

3.2.3 *zero calibration*—The adjustment of the transmitter electronics to the sensor's signal output for a sample gas containing less than 0.1ppm(v) oxygen.

4. Summary of Test Method

4.1 Measurement of oxygen is accomplished by comparing the electrical signal produced by an unknown sample with that of a known standard using an oxygen specific electrochemical sensor. A gaseous sample at constant flow and temperature is passed over the electrochemical cell. Oxygen diffuses into the sensor and reacts chemically at the sensing electrode to produce an electrical current output proportional to the oxygen concentration in the gas phase. Experience has shown that the types of sensors supplied with equipment used in this standard typically have a linear response over the ranges of application which remains stable during the sensor's useful life. The analyzer consists of a sensor, a sample flow system, and the electronics to accurately determine the sensor signal.

5. Significance and Use

5.1 This test method is primarily used to monitor the concentration of oxygen in gases to verify gas quality for operational needs and contractual obligations. Oxygen content is a major factor influencing internal corrosion, fuel quality, gas quality, and user and operator safety.

6. Interferences

6.1 Interfering gases such as oxides of sulfur, oxides of nitrogen, and hydrogen sulfide can produce false readings and reduce the expected life of the sensor. Scrubbers are used to remove these compounds. Special sensors suitable for gas containing high fractions of carbon dioxide are available from manufacturers.

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[1] This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.12 on On-Line/At-Line Analysis of Gaseous Fuels.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

7. Apparatus

7.1 *Sensor*—The sealed sensor is contained in a housing constructed of stainless steel or other non-permeable material. The sensor contains a cathode and an anode in an electrolyte solution. A fluorocarbon membrane allows the oxygen from the sample to diffuse into the sensor. Oxygen in the sample is reduced at the cathode and is simultaneously oxidized at the anode. The electrons released at the surface of the anode flow to the cathode surface when an external electrical path is provided. The current is proportional to the amount of oxygen reaching the cathode and is used to measure the oxygen concentration in the gas phase. The electrochemical reactions for a lead anode cell are as follows:

$$O_2+2H_2O+4e^-\rightarrow 4OH \quad \text{(cathode half reaction)}$$

$$2Pb+4OH^-\rightarrow 2PbO+2H_2O+4e^- \quad \text{(anode half reaction)}$$

$$2Pb+O_2\rightarrow 2PbO \quad \text{(overall cell reaction)}$$

Any electrochemical cell with different materials can be employed if the cell can give the same performance for selective oxygen detection with similar sensitivity.

7.2 *Electronics*—Various electronic circuits are used to amplify and filter the sensor signal. The signal output may be corrected for the gas sample temperature.

7.3 *Output*—Automatic digital or range selectable analog display of parts per million or percent oxygen reading by volume.

7.4 *Sampling System*—Sample gas must be introduced to the sensor of the analyzer. A flow control metering valve is positioned upstream of the analyzer to provide a gas sample flow rate of 0.5 to 2 L/min [1 to 5 SCFM]. If necessary, a pressure regulator with a metallic diaphragm can be used upstream of the flow control valve to provide 35 to 200 kPa [5 to 30 psig] inlet pressure. A leak-free sample pump may be used for low pressure sampling. Stainless steel tubing and connections should be used to minimize any air intrusion into the sampling system. Gas scrubbers may be necessary to remove interfering gases such as oxides of sulfur, oxides of nitrogen, and hydrogen sulfide. A suitable coalescing or particulate filter can be used to remove condensation, moisture, and/or particulates to prevent erroneous analysis readings and damage to the sensor. A meter, such as a rotameter, is used to monitor the sample gas flow through the analyzer.

8. Hazards

8.1 Use safe and proper venting if using this method for the analysis of hazardous or flammable gases. Failure to follow manufacturer's instructions for the instrumentation used in this test method may result in a hazardous condition.

8.2 Do not open the sensor. The sensor contains a corrosive liquid electrolyte that could be harmful if touched or ingested. Refer to the Material Safety Data Sheet provided by the sensor manufacturer.

9. Preparation of Apparatus and Calibration

9.1 *Zero alibration*—In theory the oxygen sensor produces no signal when exposed to oxygen free sample gas. In reality, expect the sensor to generate an oxygen reading when sampling oxygen-free sample gas due to minor leakage in the sample line connections, residual oxygen in the sensor's electrolyte, and tolerances of the electronic components of the analyzer. Zero calibration is required after a new sensor is installed.

9.1.1 The sensor is exposed to the sample gas with less than 0.1 ppm oxygen. Follow the instrument manufacturer's recommended inlet sample flow rate and pressure, usually a flow rate of 1 liter per min or 2 SCFH is recommended for optimum performance.

9.1.2 Allow the analyzer output to stabilize. This may take up several hours if a new sensor has been installed.

9.1.3 Follow the instrument manufacturer's instructions for zero calibration of the instrument.

9.2 *Span Calibration of Instrument*—Certified gas standards can be obtained from a gas standard vendor. Span calibration is required after a new sensor is installed.

9.2.1 Flow the gas standard through the analyzer. The standard should approximate the sample gas to be tested and contain oxygen levels in the range of interest of the user.

9.2.2 Allow the analyzer output to stabilize. This may take several min.

9.2.3 Follow the instrument manufacturer's instructions for span calibration of the instrument.

10. Conditioning

10.1 Purge oxygen free or low ppm oxygen gas through the apparatus if it is not to be used immediately after calibration. Allow the display reading to stabilize before disconnecting. This is to minimize the oxygen exposure (reaction) to the sensor during storage or stand-by.

11. Procedure

11.1 *Sampling*—Due to the large volume of sample that may be required for this analysis it is advisable to analyze for oxygen at the sample source such as directly from a gas pipeline or storage vessel.

11.2 *Blank Analysis*—Sensor performance and sample system integrity may be verified by passing low oxygen content gas across the sensor. Higher than expected readings may be indicative of sensor failure or sample system leaks.

11.3 *Sample Analysis*—Prior to flowing sample gas to the sensor, establish the flow rate in the sample line, allow sample to vent to atmosphere long enough to purge the line free of air, then connect the sample gas to the sensor. Avoid any leaks in the tubing that transports the sample to the analyzer and make sure there are no restrictions in the analyzer outlet vent. Permanent sensor damage can occur from backpressure on the sensor. The sample conditions should closely approximate the calibration conditions for maximum accuracy.

11.4 The analyzer displays a direct readout of oxygen in the sample. Do not attempt to take a reading until the readout stabilizes. Standard connections are available for the signal output to a data logger or computer data system. Measurements below 10 ppm usually require 20 min if the sensor has been in service at ppm levels for at least two weeks, and 60 min if the sensor is new assuming the zero/purge/sample gas has an oxygen concentration below 1 ppm. Measurements above 100 ppm require less than 10 min.

11.5 *Quality Assurance*—The following quality assurance procedures are suggested.

11.5.1 *Calibration Check*—the primary calibration standard is reanalyzed daily. Results that vary by more than 5% of the accepted value indicate an analyzer or sampling problem and may warrant investigation.

11.5.2 *Secondary Calibration Check*—secondary standards may be analyzed as a crosscheck to assure primary standard validity. Results that vary by more than 10% of the accepted value may indicate a problem with the standard in use.

11.5.3 *Linearity Checks*—Known concentrations of oxygen at differing levels may be introduced to the sensor for analysis. Deviation from linearity may indicate sampling system leaks or sensor problems and should be investigated. Acceptable linearity limits are determined by the user's application.

12. Calculation or Interpretation of Results

12.1 If a sample scrubber is used for sensor protection from interfering gases the oxygen concentration should be corrected as follows:

$$X = A/(1 - B) \tag{1}$$

Where:

X = corrected oxygen in sample
A = oxygen reading
B = Mol Fraction of interfering gases removed by scrubber

12.2 Conversion from volume to mass concentration (W) of oxygen in milligrams per cubic meter at 25 degrees C and 760 mm Hg [101.3 kPa] is obtained by multiplying ppm by molecular weight and dividing by 24.45 (Molar Volume):

$$W = X(32/24.45) \tag{2}$$

Where:

W = mass concentration, mg/m^3, and
X = Oxygen concentration in sample, ppmv

13. Precision and Bias

13.1 *Precision*—The precision of this test method as determined by the statistical examination of the inter-laboratory test results is as follows.

13.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values by only one case in twenty. See Table 1.

TABLE 1 Repeatability of Oxygen Measurement at Various Levels

Concentration	Standard Deviation	Repeatability
1.34 ppm	0.02 ppm	0.05 ppm
10.24 ppm	0.05 ppm	0.15 ppm
103.3 ppm	0.11 ppm	0.31 ppm
0.20 %	0.01 %	0.02 %
20.0 %	0.04%	0.11 %

13.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only one case in twenty. (Experimental results to be determined.)

13.2 *Bias*—Since there is no accepted reference material for determining the bias, no statement on bias can be made.

14. Keywords

14.1 oxygen; natural gas