



Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography¹

This standard is issued under the fixed designation D7550; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes a procedure for the determination of cations in hydrogen and other fuel cell feed gases. It has been successfully applied to other types of gaseous samples including air, engine exhaust, and landfill samples. An ion chromatograph/conductivity detector (IC/CD) system is used to determine cations. Sensitivity from low part per billion (ppb, µg/l, µg/kg) up to part per million (ppm, mg/l, mg/kg) concentration are achievable dependant on the amount of hydrogen or other fuel cell gas sampled. This test method can be applied to other gaseous samples requiring analysis of trace constituents provided an assessment of potential interferences has been accomplished.

1.2 The values stated in inch-pound units are to be regarded as standard. No other units of measurement are included in this 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

D1193 Specification for Reagent Water

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *density*—mass per unit of volume of the fuel gas or air being considered.

3.1.2 *gaseous fuel*—material to be tested, as sampled, without change of composition by drying or otherwise.

3.1.3 *relative humidity*—ratio of actual pressure of existing water vapor to maximum possible pressure of water vapor in the atmosphere at the same temperature, expressed as a percentage.

3.1.4 *relative density*—ratio of the density of the gaseous fuel, under the observed conditions of temperature and pressure, to the density of dried air, of normal carbon dioxide content (0.03%), at the same temperature and pressure.

3.1.5 *ion chromatography*—liquid chromatographic technique for the rapid separation of ionic species in solution using ion exchange columns and determined using a variety of flow-through detection system most commonly suppressed conductivity.

3.1.6 *ion chromatograph (IC)*—Instrument for performing ion chromatography.

3.1.7 *ion conductivity detector (ICD)*—instrument component that measures the total change in conductivity of the eluent and analytes flowing between two electrodes.

3.1.8 *chemical suppression*—technique using a chemical reaction to reduce the eluent conductivity and to enhance analyte response in ion chromatographic systems using a conductivity detector.

3.1.9 *electronic suppression*—technique using an electrochemical reaction to enhance analyte response in ion chromatographic systems using a conductivity detector.

3.1.10 *eluent*—solvent used to transport analytes through an ion chromatographic column, suppressor and detector.

3.1.11 *dscm*—dry standard cubic meter.

4. Summary of Test Method

4.1 Hydrogen or other fuel cell gas is passed through a hydrogen quality sampling apparatus containing a calibrated flow meter and a filter module loaded with a nylon filters (1.0 µm pore size). Alternative sampling apparatus can be used provided the fuel cell gas can be accurately measured and collected free of contamination. When necessary a pump is used to draw sample through the filter module. Filters are removed from the filter module weighed and extracted into volumetrically calibrated vessels. The recovered solutions are

¹ This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.14 on Hydrogen and Fuel Cells.

Current edition approved Sept. 1, 2009. Published October 2009. DOI: 10.1520/D7550-09.

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.

analyzed for cations using an ion chromatograph/conductivity detector (IC/CD) system. The cations present elute as peaks from the column. The area under the peaks is proportional to the amount in the sample. The sample amount is measured and compared to the amount found for standards used to generate a calibration curve. These functions/calculations are most commonly performed by chromatography software.

5. Significance and Use

5.1 Low operating temperature fuel cells such as proton exchange membrane (PEM) fuel cells require high purity hydrogen for maximum material performance and lifetime. Analysis to part-per-billion (ppb) concentration of individual cation contaminants such as potassium, sodium and ammonium in hydrogen and related fuel cell supply gases is necessary for assuring a feed gas of sufficient purity to satisfy fuel cell system needs. More specifically, cations such as ammonium causes irreversible performance degradation of proton exchange membranes used in low temperature fuel cells by reacting with protons in the membrane to form ammonium ions.

5.2 Although not intended for application to gases other than hydrogen and related fuel cell supply gases, techniques within this test method can be applied to other gaseous samples requiring cation analysis.

6. Equipment and Instrumentation

6.1 *Sampling Apparatus*—Development of a suitable hydrogen and other fuel cell feed gas sampling apparatus and appropriate sampling practices is on-going. Any appropriate apparatus can be used provided it can safely provide a contamination free filtered sample of a volumetrically measured fuel cell feed gas.

6.2 *Nylon filters* - 1.0 µm pore size.

6.3 *Metering System*—Typically, the metering system includes a thermometer(s) capable of measuring temperature to within 3 °C (5.4 °F), a dry gas meter capable of measuring volume to within 2 percent, and related equipment. An alternative to the thermometers and dry gas meters is an equivalent temperature compensated dry gas meter. When needed, a leak-free pump is interfaced between the filter module and the dry gas meter.

6.4 *Sampling Line*—The sampling line and any other sampling apparatus shall be made of material which is inert to the gas sampled and cations including ammonia.

6.5 IC Analysis:

6.5.1 Ion chromatograph (IC) standard manufacture fitted with a conductivity detector, autosampler, and interfaced to a computer or other data storage/collection device. The following conditions have been successfully used:

6.5.1.1 *Cation Exchange Separator Column*: IonPac CS12A (4×250mm).

6.5.1.2 *Cation Exchange Guard Column*: IonPac CG12A (4×50mm).

6.5.1.3 *Eluent*: 20mM MSA, Flow rate: 1.0 ml/min.

6.5.1.4 *Detection*: Suppressed conductivity, recycle mode

6.5.1.5 *Suppressor*: CSRS 300 (4mm).

6.5.2 *Type 1 Water* (Specification **D1193-06**).

6.5.3 *Graduated Cylinder*, various sizes as needed.

6.5.4 *Beakers*, 150 ml.

6.5.5 *Volumetric Pipettes*, Class A borosilicate glass, various sizes as needed.

6.5.6 *Volumetric Flasks*, Class A, various sizes as needed.

6.5.7 *Balance*, analytical, accurate to 0.1 g.

6.5.8 *Magnetic stirrer*, thermally insulated, and Teflon coated stirring bar.

6.5.9 *Micropipette*, 0.1 ml to 1 ml.

7. Apparatus

7.1 Sampling is accomplished using a hydrogen quality sampling adaptor (HQSA) or other appropriate sampling apparatus fitted with a filter module containing a nylon filter (1.0 µm pore size). The HQSA is appropriate for sampling of high pressure gas lines and is defined as apparatus used to interface with a hydrogen delivery receptacle such as a vehicle fueling nozzle and deliver sample to a collection vessel. Free flow of sample gas through the filter can be made by using a low pressure sample line or by drawing sample through the sample train using a pump. **Warning**—Caution, hydrogen and related flammable gas sampling should be accomplished in a well ventilated locale where hydrogen gas will not build up to explosive levels. **Warning**—Caution, hydrogen at high pressures is an explosion hazard and may spontaneously ignite creating an invisible flame when leaked through a seam or pinhole.

7.2 *Determining the Target Minimum Cation Concentration (TMCC)*—The user should identify the target minimum cation concentration needed for the application. When the determination of multiple cations is desired, the cation chosen should be the one likely to be present in the lowest concentration.

7.2.1 Determining the TMCC:

7.2.1.1 Assumptions: :

(1) All the cations in the sample are recovered from the filter

(2) Evaporative losses of substances such as ammonium are insignificant.

7.2.1.2 Calculations:

$$MDCC = C_1/V_R \quad (1)$$

Where:

MDCC = Minimum Detectable Cation Concentration

CI = lowest concentration on a calibration curve.

VR = assumed liquid volume for the recovery solution, ml

7.2.2 *Planned Sampling Volume (PSV)*— The planned sample volume is the volume of gas that must be sampled to collect for analysis a quantifiable mass of a particular cation. The PSV is based on the TMCC and the target contaminant concentration, and is further adjusted by a safety margin to assure quantification.

7.2.2.1 Calculations:

$$PSV = TMCC/STC \times F \quad (2)$$

Where:

PSV = planned sample volume, dm³