Designation: D7550 – 09

Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography [1]

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

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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.

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 loses of substances such as ammonium are insignificant.

7.2.1.2 *Calculations:*

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

Where:

MDCC = Minimum Detectable Cation Concentration
C1 = 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:*

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

Where:

PSV = planned sample volume, dscm

TMCC = analytical target minimum cation concentration, mg
STC = target contaminant concentration, mg/dscm
F = safety margin, $F \geq 1$

7.2.3 *Planned Sampling Time (PST)*—The planned sampling time is the time required to collect the minimum sample volume at the proposed volumetric sampling rate (VSR). The user should use an average volumetric sampling rate appropriate for the fuel source tested. If the VSR cannot be achieved in the field, the sampling time should be revised using the following equation to achieve the target PSV.

$$PST = PSV/VSR \tag{3}$$

PST = planned sampling time, unit time
PSV = planned sample volume, dscm
VSR = achievable volumetric sampling rate, dscm/unit time

7.3 *Sampling Operation*—Sample the required amount of gas as per the determination under 7.2. Upon completion of sampling, isolate the filter sampling module and remove it from the hydrogen sampling apparatus. Transfer filter sampling module to the sample recovery area. This area should be clean and rigorously free of cation contamination. Sample recovery should be performed in a laboratory.

8. Reagents and Materials

8.1 Ionic strength adjustor (ISA), pH adjusting solution.

8.2 Standard solutions - certified reference material quality. The following analytes as needed

8.2.1 *Ammonia* - 0.1M NH4Cl or 1400 ppm as N.

8.2.2 *Nitrate* - Stock 1000 mg/L as N Nitrate standard, which is equivalent to 4428.6 mg/L Nitrate as Nitrate. (Optional anion analysis)

8.2.3 *Sulfate* - 1000 mg/l sulfate standard. (Optional anion analysis)

8.2.4 *Sodium* - 100 mg/l sodium standard

8.2.5 *Potassium* - 100 mg/l potassium standard.

8.2.6 *Magnesium* - 100 mg/l magnesium standard.

8.2.7 *Calcium* -100 mg/l calcium standard.

8.3 *Calibration verification check standard*—As part of an overall QA/QC program calibration verification check standards should be analyzed with each set of samples in application of this standard test method. For example an ammonium calibration check standard at 28 mg NH3-N/L is prepared as follows.

8.3.1 Pipette 10 ml of 0.1M NH4Cl standard solution into a 500 ml volumetric flask and dilute to the mark with 0.04 N H2SO4. The Calibration verification check standard value is 0.002 M NH4Cl, or 28 mg NH3-N/L. Calibration Verification must be prepared prior to use.

8.4 *Methanesulfonic acid (MSA): 1.0 M*—Used in preparation of eluent for IC analysis

8.5 *Water*—Deionized or distilled to conform to Specifications D1193-99e1, Type 3. Water should be blank-checked for ammonium ion prior to use.

8.6 *Sulfuric Acid Solution*—0.1N 8.8

8.7 *IC Sparge gas (optional)*—Helium of high purity 99.995%, low nitrogen content.

9. Standards

9.1 Working standards are prepared each week and are stored in a refrigerator at 10 °C. Calibration is performed using the identical instrument parameters as are used in the analysis samples.

9.2 Prepare initial calibration standards using 1000 mg/l stock standards. Prepare at least four standards spanning the desired calibration range. For each calibration point, transfer the stock solution using a pipette directly into the appropriate sized volumetric flask, add 0.1 N H2SO4 and bring to volume using deionized water.

NOTE 1—Ammonium calibration standards will evolve ammonia over time at room temperature; therefore, they should be prepared as close as possible to use.

9.3 For analysis of cations present in the recovered sample solutions at 1 ppm or above a typical calibration curve can be prepared using the 1000 ppm stock standard by first preparing a 100 ppm standard. This standard is prepared by volumetrically adding 5 ml of stock standard to a 500 ml volumetric flask then adding deionized water to volume. Once the 10 ppm standard is prepared, a typical calibration set of points can be prepared as indicated in Table 1. Refrigerate the standards as necessary until ready to perform the analysis.

10. Analysis

10.1 As necessary, take the recovered samples out of the refrigerator and let them sit until they reach room temperature.

10.2 Prepare a matrix spike by transfering the sample to a clean beaker, and adding an appropriate amount of the 10 ppm cation standard prepared under section 10 to make a 1 ppm cation spiked sample.

10.3 Charge the IC eluent reservoir with freshly prepared eluent. Turn on all supply gases and pump the eluent through the system for at lease 30 min before starting calibration. Make sure baseline and background conductivity are low.

TABLE 1 Calibration Curve Data Points

Calibration Level	Target Concentration (ppm)	Amount of 10 ppm Standard (ml)	Final Volume
1	2.0	20	100
2	1.5	15	100
3	1.0	10	100
4	0.5	5	100
5	0.1	1	100

10.4 Fill autosampler vials with about 5ml of standard, control, or sample. Place the vials into the autosampler tray. A typical run list is shown below but these elements should be randomized in an effort to eliminate sampling errors:

Vial number	Sample I.D.
1	Deionized water
2 - 5	Standards five different levels from low to high
6	Control
7	Reagent Blank
8	Sample #1
9	Sample #1 Duplicate (as necessary)
10	Sample #1 Matrix Spike
11	Sample #1 Matrix Spike Duplicate (as necessary)
12	Control
13 - 17	Standards five different levels from low to high
18	Eluent Blank
19	Deionized water

11. Calculations

11.1 *Calibration Standards:*

11.1.1 *Response Factors (RF):*

$$RF = Analyte\ Response\ Curve\ Area/Analyte\ Concentration\ (ug/ml) \tag{4}$$

11.1.2 *Average Calibration Factor (RF_{ave}):*

$$RF_{ave} = (RF_1+RF_2+RF_3+RF_4+RF_5)/5 \tag{5}$$

Where:

RF_1 = Response factor for calibration level 1
RF_2 = Response factor for calibration level 2
RF_3 = Response factor for calibration level 3
RF_4 = Response factor for calibration level 4
RF_5 = Response factor for calibration level 5

11.2 *Cation measurement % RSD:*

$$\%RSD = Standard\ deviation/RF_{ave} \times 100 \tag{6}$$

11.3 *Control % RPD:*

$$\%RPD = |(xRF - RFdaily)|/|(xRF+RFdaily)/2| \times 100 \tag{7}$$

11.4 *Total Cation captured (TCC):*

$$TAC = ((A_{ave}/RF_{ave}) - B_x) \times V_R \tag{8}$$

A_{ave} = Average Area of analyte peak
RF_{ave} = Average Calibration Factor
B_x = Blank background concentration of blank
V_R = Total recovered volume, ml 12.5

11.5 *Corrected gas volume (V_{gas}):*

$$V_{gas} = [(Q\ x\ I/29.92) \times 520 \times E](460+D) \tag{9}$$

Q = Measured gas volume
I = Gas meter internal pressure
D = Gas meter temperature in °F
E = Gas meter correction factor

11.6 *Cation content in sample gas (ppmv) :*

$$Conc.\ (ppmv)NH3 = ((TAC+(ug/sample) \times W_a/W_i)/V_{gas})/(.0409*17) \tag{10}$$

W_a = formula weight of cation parent (for example, NH3, NaCl, etc.)
W_i = formula weight of cation
V_{gas} = Corrected volume of gas sample

11.7 *Quality Assurance:*

11.7.1 *Relative percent difference (RPD) between duplicate measurements:*

$$RPD = (C1 - C2)/Cave*100 \tag{11}$$

11.7.2 *Relative percent accuracy (RPA) of the calculated concentration for Calibration Verification:*

$$RPA = (Cave - 28)/28*100 \tag{12}$$

11.7.3 *Matrix spike percent recovery (%R) impinger train:*

$$\%R = (Cspike*0.102 - Csample*0.101)/0.2*100 \tag{13}$$

11.7.4 *Matrix spike recovery analysis:*

$$Spike\ Recovery\ (\%) = \frac{(MS - C_{sample})}{C_{spike}} \times 100 \tag{14}$$

MS = Matrix Spike concentration
C_{sample} = Concentration of sample
C_{spike} = Concentration of Spike

11.7.5 *Matrix Spikes % RPD:*

$$\%RPD = \frac{|(SR\ (\%) - SD\ (\%))| \times 100}{|(SR(\%)+SD(\%))/2|} \tag{15}$$

SR = Spike Recovery
SD = Spike Duplicate Recovery

12. Quality Control

12.1 Standard Operating Procedures (SOPs) SOPs should be generated in each laboratory describing and documenting the activities such as: *(1)* assembly, calibration, leak check, and operation of specific sampling systems and equipment used, *(2)* preparation, storage, shipment, and handling of samples, *(3)* calibration, and operation of the analytical system, addressing the specific equipment used, *(4)* impinger train component storage and cleaning, and *(5)* all aspects of data recording and processing, including lists of computer hardware and software used.

12.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the laboratory personnel conducting the sample collection, transport and analyses.

12.3 *Spiked Samples*—A spiked sample is analyzed each day or every fifth sample as part of a QA/QC program. An acceptable recovery for cations present at the greater of 0.1 ppmv should fall within 10% of the theoretical amounts to verify nominal system performance.

12.4 *Controls*—A cation control sample should be analyzed after ever 5 samples to verify continued acceptable instrument performance. Typically, the determination should be within 10% of the actual value of each component in the control to verify acceptable system performance.

12.5 Post sample calibration curve verification – The calibration standards can be reanalyzed to confirm the calibration curve initially generated is valid for all samples analyzed. Analysis of the individual calibration standards should result in determinations within 10 percent of the actual values of each calibration level.

13. Laboratory Practices

13.1 *Sample Receipt:*

13.1.1 The overall condition of each sample is recorded in a dedicated logbook. Each filter must possess sample identification information or be imprinted with an alphanumeric identification. Include, the date sample was collected, the laboratory receipt date, and initials of recipient.

NOTE 2—A log containing the usage and history of each filter module should be kept. This historical record is valuable in tracking filter modules that have been contaminated or otherwise compromised.

14. Interferences and Limitations

14.1 *Interferences:*

14.1.1 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually high sample is encountered, it should be followed by an analysis of eluent blanks to check for cross-contamination.

14.1.2 Samples can be contaminated by leakage or diffusion of sample gas from the filter module during shipment and storage. A field sample blank taken through sampling and subsequent storage and handling can serve as a check for such contamination.

14.1.3 The purity of deionized water, absorbing solutions, and eluent are of important consideration in the determination of allowable blank concentrations.

14.1.4 Chromatographic conditions need to be selected such that cationic species do not co-elute with each other.

15. Filter Preparation and Sample Recovery

15.1 Nylon filters, used in speciation sampling, are washed with DI water rigorously free of cations and dried in a temperature and moisture controlled environment free of cation contamination prior to use.

NOTE 3—Un-washed nylon filters frequently contain significant background cation concentrations.

NOTE 4— While performing filter recovery and extraction operations, analysts must ensure that they are not the source of contamination by using dust free gloves and wearing breathing filters or masks.

15.2 After sampling, the filter sampling module is dissembled in an environment rigorously free of cation contamination. The filters are removed using tweezers or forceps. Filters are stored in a – 10 °C freezer.

15.3 Filter Extraction

15.3.1 Filters are removed from the – 10°C freezer and allow to equilibrate to room temperature. For each sample set, at least one blank filter is extracted according to the same procedure as used for bona fide samples.

15.3.2 Forceps are used to transfer the filters to a cation free 50 mL beaker.

15.3.3 Deionized water (25 ml) is added to each beaker. A Teflon coated stir bar is added, the beaker is covered with a watch glass, and the solution is heated to nearly boiling with stirring. After 1 hour, the solution is allowed to cool to room temperature. The solution is decanted into a 50 ml volumetric flask and water is added to make 50 ml.

16. Precision and Bias

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

16.1.1 *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. (Experimental results to be determined)

16.1.2 *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)

16.2 *Bias*—The procedure in Test Method D7550 Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography has no known bias.

17. Keywords

17.1 ammonia; calcium; cations; fuel cells; gaseous fuels; hydrogen; ion chromatography; magnesium; PEM; potassium; proton exchange membrane; sampling; sodium