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Application News

Ion Chromatograph, High Performance Liquid Chromatograph

Analysis of Inorganic Halogens, Formic Acid, Ammonia, and Formaldehyde as Impurities in Fuel Cell Grade Hydrogen Based on ISO14687 Grade D

Hiroyuki Aikawa, Jiang Yujing, Ayano Tanabe

User Benefits

- This analysis meets the standard values of ISO14687 Grade D.
- Simultaneous analysis of inorganic halogens and formic acid is possible.
- Since organic solvents are not used for extraction during pretreatment, environmental impact is reduced.

■ Introduction

Hydrogen is expected to be a new power and heat source to reduce greenhouse gases. Hydrogen is an easily available substance that can be produced from the electrolysis of water in our daily lives. However, when used in fuel cells, it is necessary to control impurities in hydrogen gas because certain impurities introduced during the manufacturing process deteriorate the electrode and electrolyte membrane, reducing the performance of the fuel cell or shortening its life. This section presents an example of analysis of inorganic halogens, formic acid, ammonia, and formaldehyde in hydrogen based on the standard values described in ISO 14687 Grade D [1)].

■ Hydrogen Impurity Specifications in ISO14687 Grade D

ISO14687 Grade D specifies impurities in hydrogen that affect the quality of fuel cell vehicles. Table 1 lists the applicable ingredients, standard values, concentrations (µg/L) converted by ion chromatograph (IC)/high-performance liquid chromatograph (HPLC), and equipment used.

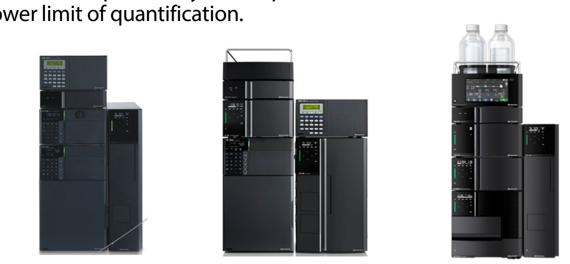
Table 1 Substances and specifications in ISO14687 Grade D

Ingredients of interest	Specified value (µmol/mol)	IC/HPLC Converted concentration (µg/L)	Equipment use d
Inorganic halogen (hydrogen chloride) *1	0.05	28	Suppressor IC
Formic acid *2	0.2	92	
Ammonia	0.1	26	Non-suppressor IC
Formaldehyde	0.2	141	HPLC

*1 The value of hydrogen chloride is shown as a representative value.
*2 Deleted in the 2025 edition

■ Analysis of Inorganic Halogens, Formic Acid, and Ammonia by IC

A suppressor IC (Fig.1, left) was used for inorganic halogen analysis. Since IC can selectively measure ions in a sample, it is less affected by contaminants than other methods, and inorganic halogens can be measured with high accuracy. Three components of inorganic halogens were simultaneously measured: chloride ion (Cl) as hydrochloric acid, bromide ion (Br) as hydrogen bromide, and formic acid (HCOOH). Table 2 shows the analytical conditions, Fig. 2 shows the chromatograms of each 50 µg/L standard sample, and Fig. 3 shows the calibration curves for the concentration range of 25 µg/L to 1000 µg/L. As shown in Fig. 3, the linearity was greater than 0.9999 in all cases. Table 3 shows the repeatability for 7 replicates at concentrations near the lower limit of quantification.



Suppressor IC (HIC-ESP) | Non-suppressor IC (HIC-NS) | HPLC(Nexera™ lite)

Fig.1 Equipment used

Table 2 Analysis conditions (inorganic halogens)

System	: HIC-ESP
Column	: Shim-pack™ IC-SA2 (250 mm × 4.0 mm I.D., 9 µm) *1
Guard Column	: Shim-pack IC-SA2(G) (10 mm × 4.6 mm I.D., 9 µm) *2
Mobile Phase	: 12 mM $NaHCO_3$ + 0.6 mM Na_2CO_3
Flow Rate	: 0.8 mL/min
Column Temp.	: 30 °C
Injection Vol.	: 100 µL
Vial	: 4 mL, Polypropylene *3
Detection	: Conductivity

*1 P/N : 228-38983-91, *2 P/N : 228-38983-92, *3 P/N : 228-31537-91

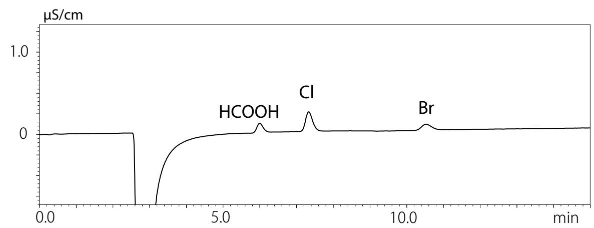


Fig.2 Chromatogram of inorganic halogens (50 µg/L each)

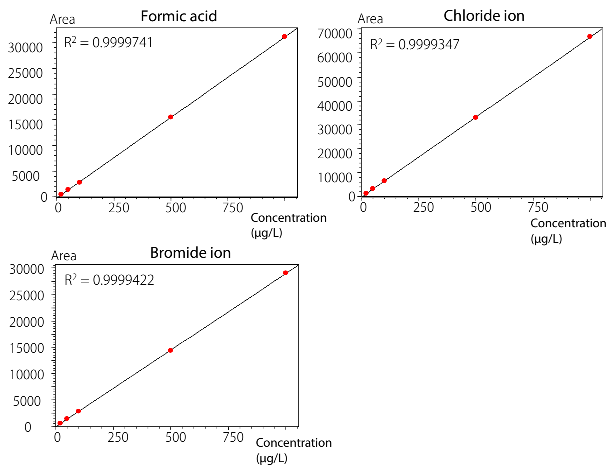


Fig.3 Calibration curves for inorganic halogens

Table 3 Repeatability of Inorganic Halogens (10 µg/L, n=7)

	Formic acid Concentration (µg/L)	Chloride ion Concentration (µg/L)	Bromide ion Concentration (µg/L)
1	10.1	9.48	9.12
2	10.4	9.66	9.33
3	10.6	9.56	8.47
4	10.6	9.48	9.11
5	10.7	9.89	9.90
6	10.8	9.74	8.77
7	11.1	9.68	9.84
Average	10.6	9.60	9.20
%RSD	2.91	1.55	5.68

Ammonia was determined as ammonium ion (NH4) using a non-suppressor IC (Fig.1, center). Table 4 shows the analytical conditions, Fig. 4 shows the chromatogram of a standard sample at a concentration near the specified value (25 µg/L), Fig. 5 shows the calibration curve prepared in the concentration range of 2.5 µg/L to 200 µg/L, and Table 5 shows the reproducibility at a concentration near the detection limit (10 µg/L). Both inorganic halogens and ammonia can be analyzed in the same apparatus by switching the mobile phase and column.

Table 4 Analysis Conditions (Ammonium ion)

System	: HIC-NS
Column	: Shim-pack IC-C4 (150 mm × 4.6 mm I.D., 7 µm) *1
Guard Column	: Shim-pack IC-GC4 (10 mm × 4.6 mm I.D., 7 µm) *2
Mobile Phase	: 2.5 mM Methane sulfonic acid
Flow Rate	: 1.0 mL/min
Column Temp.	: 40 ˚C
Injection Vol.	: 100 µL
Vial	: 4 mL, Polypropylene *3
Detection	Conductivity

*1 P/N : 228-41616-91, *2 P/N : 228-59900-91, *3 P/N : 228-31537-91

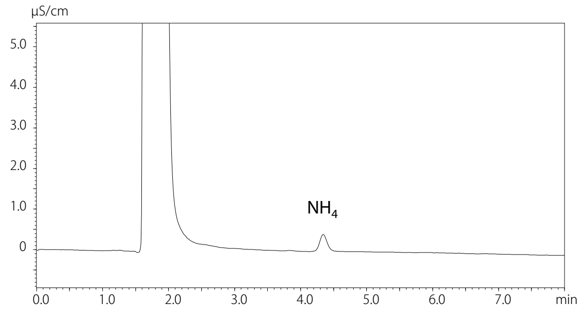


Fig.4 Chromatogram of ammonium ion (25 µg/L)

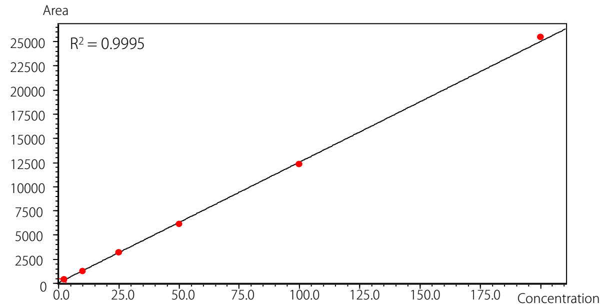


Fig.5 Calibration curve for ammonium ion

Table 5 Repeatability of ammonium ion (10 µg/L, n=7)

	Retention time (min)	Peak area	Concentration (µg/L)
1	4.36	1315	9.99
2	4.36	1355	10.3
3	4.37	1380	10.5
4	4.37	1284	9.74
5	4.37	1292	9.80
6	4.37	1246	9.43
7	4.36	1318	10.0
Average	4.36	1313	9.97
%RSD	0.04	3.41	3.61

■ Analysis of Formaldehyde by HPLC

Formaldehyde (HCHO) may adsorb on the catalyst of a fuel cell and interfere with hydrogen generation. We used HPLC (right side of Figure 1) to measure formaldehyde. DNPH derivatization was performed according to the pretreatment protocol shown in Figure 6 and measured by HPLC. Table 6 shows the analytical conditions, Fig.7 shows the chromatogram of a standard sample at a concentration near the specified value (100 µg/L), Figure 8 shows the calibration curve prepared at a concentration range of 10 µg/L to 200 µg/L, and Table 6 shows the repeatability at a concentration near the lower limit of quantification (10 µg/L).

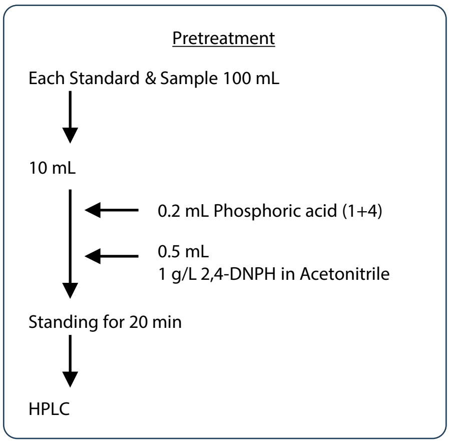


Fig.6 Pretreatment protocol for DNPH derivatization

Table 6 Analytical conditions (formaldehyde)

System	: Nexera™ lite
Column	: Shim-pack GIST-HP-C18-HP (150 mm × 3.0mm I.D., 3 µm) *1
Mobile Phase	: Water/Acetonitrile = 1 : 1
Flow Rate	: 1.0 mL/min
Column Temp.	: 40 ˚C
Injection Vol.	: 10 µL
Vial	: 1.5 mL, Glass *2
Detector	: UV 360 nm

*1 P/N : 227-30040-05, *2 P/N : 227-34500-02

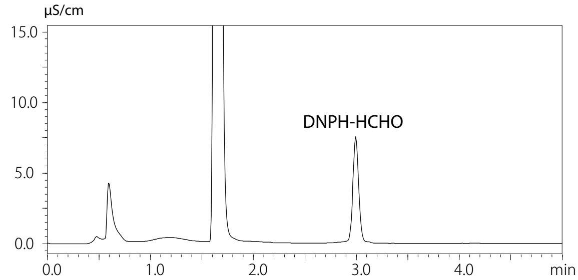


Fig.7 Chromatogram of formaldehyde (100 µg/L)

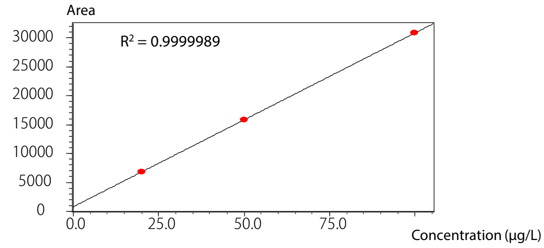


Fig.8 Calibration curve for formaldehyde

Table 7 Repeatability of formaldehyde (10 µg/L, n=7)

	Retention time (min)	Peak area	Concentration (µg/L)
1	3.23	2792	8.53
2	3.23	2865	8.98
3	3.23	2888	9.12
4	3.23	2877	9.05
5	3.23	2810	8.64
6	3.23	2894	9.15
7	3.23	2901	9.20
Average	3.23	2861	8.95
%RSD	0.00	1.50	2.92

■ Measurement of Hydrogen Gas

As shown in Fig.9, hydrogen from a G2 grade hydrogen cylinder was bubbled with ultrapure water in an impinger to absorb impurities. Two impingers were installed in the order of 1st impinger and 2nd impinger, and dissolved inorganic halogen, formic acid, ammonia, and formaldehyde were analyzed by analyzing water from each impinger. Table 8 shows the collection conditions. Fig.10 shows the chromatogram of anions (Formic acid, chloride, and bromide), Fig.11 shows the chromatogram of cations (ammonia), and Fig.12 shows the chromatogram of formaldehyde. No impurities were detected from either 1st impinger or 2nd impinger.

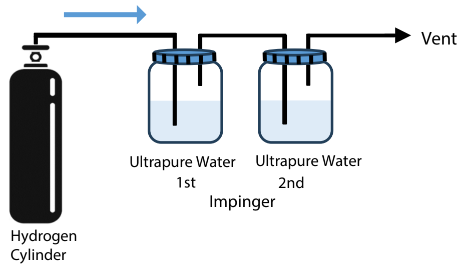


Fig.9 Collection of hydrogen gas impurities

Table 8 Conditions for collecting hydrogen gas impurities

Flow Rate	:	500 mL/min
Sampling Time	:	30 min
Water Amount in Impinger	:	40 mL for each
Material of Impinger	:	Perfluoroalkoxy alkanes 100mL volume

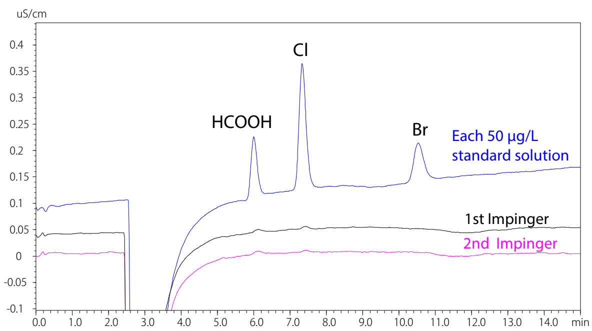


Fig.10 Chromatograms of hydrogen gas sample (inorganic halogen)

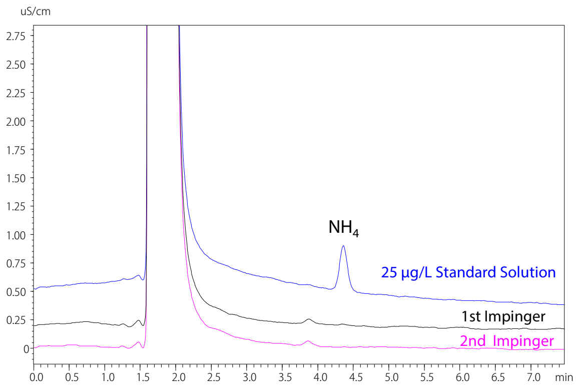


Fig.11 Chromatograms of hydrogen gas sample (ammonium ion)

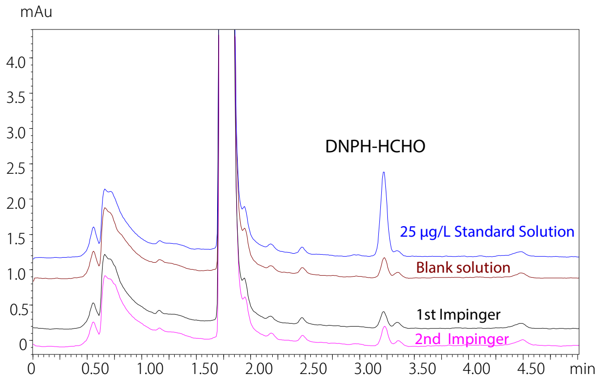


Fig.12 Chromatograms of hydrogen gas sample (formaldehyde)

■ Conclusion

Using an ion chromatograph and HPLC, we analyzed inorganic halogens, formic acid, ammonia, and formaldehyde, which are impurities in hydrogen, and confirmed that the results meet ISO 14687 Grade D standards. Inorganic halogens, formic acid, and ammonia can be analyzed using the same equipment by switching the analysis conditions. Simple pretreatment and a unified analysis procedure allow measurement without hesitation.

<References>

1) ISO 14687 Hydrogen fuel quality-product specification (2025)

<Related Applications>

1. Analysis of Ammonia as An Impurity in Fuel Cell Grade Hydrogen According to ISO 14687 Grade D Using A Gas Generator, Application News No. 01-01070

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