Application Note

Energy and Chemicals

Analysis of Sulfides, Formaldehyde, and Organic Halides in High-Purity Hydrogen for Fuel Cell Vehicles

Using an Agilent 8890 GC/8355 SCD/ 5977 MSD System

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Abstract

This application note describes a robust analytical procedure for the detection of sulfides, formaldehyde, and organic halides in hydrogen for fuel cell vehicles. This analysis was executed using an Agilent 8890 gas chromatography (GC) system equipped with an Agilent 8355 sulfur chemiluminescence detector (SCD) and an Agilent 5977 mass spectrometer detector (MSD). Samples were preconcentrated using a thermal desorption system, followed by separation on an Agilent J&W DB-Sulfur SCD column. A purged two-way splitter was used to split the sample at a 3:1 ratio onto the SCD and MSD. This flexible configuration demonstrated excellent performance for these three categories of compounds. The correlation coefficients for all target compounds exceeded 0.9971, with reproducibility results varying between 0.3% and 7.9%. The detection limits for sulfides, formaldehyde, and organic halides were 0.01, 0.1, and 0.5 nmol/mol, respectively.

Introduction

Contrasted with traditional internal combustion engine vehicles, hydrogen fuel cell vehicles (FCVs) that use hydrogen as an energy source present many advantages. These advantages include superior conversion efficiency and zero emissions, thus being esteemed as another groundbreaking revolution in the automobile industry.[1] FCVs deploy proton exchange membrane fuel cells (PEMFCs), transforming chemical energy into electrical energy through the reaction between hydrogen and oxygen facilitated by a catalyst. The purity of hydrogen fundamentally determines the battery performance and lifespan. Hydrogen derived from fossil fuels, for example, referred to as grey hydrogen, is a substantial source. Grey hydrogen can include impurities, such as sulfides, carbon monoxide, carbon dioxide, ammonia, light hydrocarbons, formaldehyde, formic acid, and inert gases originating from the raw materials or the chemical reaction process.[2] Other colors of hydrogen from different sources may include various combinations of impurities as well. These impurities are crucial elements affecting the durability of the fuel cell. Sulfides are severe catalyst poisons, causing irreversible degradation of fuel cell performance even at part per trillion (ppt) levels. Both CO and CO_2 impurities in the hydrogen fuel can cause fuel cell performance degradation, with CO being more severe. Formaldehyde, an intermediate product in the process of hydrogen production from natural gas or methanol, has a poisoning mechanism like CO, but is more harmful. Trace amounts of ammonia can decrease the mass transfer ability of the electrolyte membrane, leading to irreversible degradation of the battery performance. Halides also irreversibly affect the performance of hydrogen fuel cells. Inert impurities in hydrogen (such as He, Ar, N_2) do not poison the fuel cell but dilute the hydrogen fuel, reducing the cell potential and leading to power loss.

To ensure the long-term stable operation of hydrogen fuel cells, various organizations have established quality standards for hydrogen used in FCVs. The International Organization for Standardization (ISO) and the Society of Automotive Engineers (SAE) in the United States have established specific standards for hydrogen used in PEMFCs, namely ISO 14687-2019[3] and SAE J2719-2015.[4] China has also established GB/T 37244-2018[5] to regulate the quality of hydrogen products. These standards consistently specify limits for certain impurities in hydrogen, such as sulfides not exceeding 0.004 µmol/mol, formaldehyde not exceeding 0.01 µmol/mol, and total halides not exceeding 0.05 µmol/mol. The GB/T 44243-2024[6] method details the determination of sulfide, formaldehyde, and organic halides in hydrogen for FCVs, gives reference instrument configurations, and also presents performance results.

In accordance with those standards, this study has established a comprehensive analytical method for multiple key trace impurities in hydrogen for FCVs. An analytical platform has been designed for seven sulfides, formaldehyde, and eight organic halides. Sulfides are detected using a GC/SCD, while formaldehyde and organic halides are detected using a GC/MSD. The detection limits of all compounds in this study fully met the requirements for hydrogen quality control described in ISO 14687-2019, SAE J2719-2015, and GB/T 37244-2018 methods.

Experimental

This work describes an 8890 GC configuration, complemented with both an SCD and an MSD, which facilitates the analysis of sulfides, formaldehyde, and organic halides in hydrogen using a single system. Samples from canisters were preconcentrated through a Markes Multi-Gas CIA Advantage-xr thermal desorption (TD) instrument and were subsequently transferred directly to an Agilent DB-Sulfur SCD column. A purged two-way splitter was used to split the column effluent at a 3:1 ratio to the SCD and MSD. Figure 1 shows the comprehensive flow path of the combined system. Tables 1 and 2 illustrate the instrument conditions and consumables used in the system.

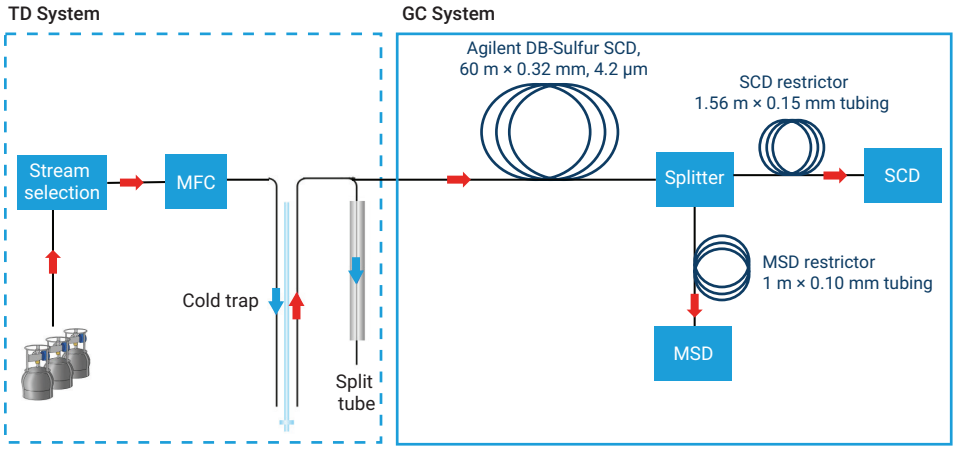

Figure 1. Schematic illustration of the flow path of the TD and Agilent 8890 GC/SCD/MSD system.

Table 1. TD parameters.

Instrument	Multi-Gas UNITY-xr, Multi-Gas CIA Advantage-xr
Cold Trap	MKI-U-T14H2S-2S
General	
Flow Path Temperature	120 °C
Sampling Line Temperature	120 °C
Presampling	
Sample Purge Time	2 min
Sample Purge Flow	50 mL/min
Sampling	
Sample Volume	8 to 800 mL
Sampling Flow	20, 50 mL/min
Post Sampling Purge	
Post-Sampling Purge Time	4 min
Post-Sampling Purge Flow	50 mL/min
Trap Setting	
Trap Purge Time	1 min
Trap Purge Flow	50 mL/min
Trap Low Temperature	–30 °C
Trap High Temperature	280 °C
Trap Desorption Time	3 min
Desorb Split Flow	3 mL/min

Table 2. GC conditions.

Parameter	Value
Agilent 8890 GC	
Column	Agilent J&W DB-Sulfur SCD, 60 m × 0.32 mm, 4.2 µm (p/n G3903-63001)
Carrier Gas	Helium, constant flow DB-Sulfur SCD column: 3 mL/min SCD restrictor: 3 mL/min MSD restrictor: 1 mL/min
Oven Program	35 °C (5 min), 20 °C/min to 220 °C (5 min)
CFT Device	Purged 2-way splitter (p/n G3180-60501)
SCD Restrictor	1.56 m × 0.15 mm id deactivated fused silica tubing (p/n 160-2625-10)
MSD Restrictor	1 m × 0.10 mm id deactivated fused silica tubing (p/n 160-2635-10)
Agilent 8355 SCD	
Burner Temperature	800 °C
Base Temperature	250 °C
Upper H_2 Flow	38 mL/min
Lower H_2 Flow	8 mL/min
Oxidizer Flow (Air)	50 mL/min
O_3 Generator Flow	42.14 mL/min
Burner Pressure	383 Torr
Reaction Cell Pressure	4.9 Torr
Data Rate	10 Hz
Agilent 5977 MSD	
Ion Source Temperature	230 °C
Quad Temperature	150 °C
Tune File	Etune.u
Acquisition Type	Scan/SIM (scan for organic halides; SIM for formaldehyde)

In this study, gas standards were purchased from Zhongce Standards Technology Co., Ltd. (Chengdu, China). Detailed work was performed on three classes of compounds that were preserved in two passivated cylinders. The first cylinder contained seven sulfides, while the second one contained formaldehyde and eight organic halides. The concentrations of all the substances under investigation were approximately 1 µmol/mol, as illustrated in Tables 3 and 4.

Prior to the establishment of the calibration curve, it was imperative to dilute the 1 µmol/mol gas standard to the anticipated concentration. In this study, a static dilution instrument was used to dilute the gas standard into canisters, using varying dilution factors for different compound types. Once the canisters were filled with the anticipated concentration of the gas standard, varied volumes were introduced by the Multi-Gas CIA Advantage-xr TD system to achieve different calibration levels. The details are displayed in Tables 5, 6, and 7. To minimize the adsorption of active compounds such as sulfides and formaldehyde, all parts of the sample flow path, including the tubing, regulator, and canister should be passivated.

Table 3. Standard mix gas for sulfides.

Number	Compound Name	Formula	Concentration (µmol/mol)
1	Hydrogen sulfide	H_2S	1.01
2	Carbonyl sulfide	COS	1.01
3	Ethyl mercaptan	C_2H_6S	1.02
4	Dimethyl sulfide	C_2H_6S	1.05
5	Carbon disulfide	CS_2	0.993
6	Thiophene	C_4H_4S	1.03
7	Dimethyl disulfide	$C_2H_6S_2$	0.998
Balance Gas	N_2		

Table 4. Standard mix gas for formaldehyde and organic halides.

Number	Compound Name	Formula	Concentration (µmol/mol)
1	Chloromethane	CH_3Cl	0.978
2	Bromomethane	CH_3Br	1.00
3	Trichloromonofluoromethane	CCl_3F	0.999
4	Methylene chloride	CH_2Cl_2	0.983
5	*cis*-1,2-Dichloroethylene	$C_2H_2Cl_2$	1.01
6	Trichloromethane	$CHCl_3$	0.996
7	Tetrachloroethylene	C_2Cl_4	1.01
8	Chlorobenzene	C_6H_5Cl	1.01
9	Formaldehyde	CH_2O	1.01
Balance Gas	N_2		

Table 5. Preparation of calibration mixture for sulfides.

Parameter	Value						
Sample Concentration in Canister (nmol/mol)	10						
Sample Volume (mL)	8	16	40	80	160	320	800
Calibration Concentration (nmol/mol)	0.1	0.2	0.5	1	2	4	10

Table 6. Preparation of calibration mixture for formaldehyde.

Parameter	Value							
Sample Concentration in Canister (nmol/mol)	100						1,000	
Sample Volume (mL)	8	40	80	160	320	800	160	320
Calibration Concentration (nmol/mol)	1	5	10	20	40	100	200	400

Table 7. Preparation of calibration mixture for organic halides.

Parameter	Value						
Sample Concentration in Canister (nmol/mol)	100						
Sample Volume (mL)	8	40	64	80	160	400	800
Calibration Concentration (nmol/mol)	1	5	8	10	20	50	100

Results and discussion

Sulfides analysis on SCD

In the analysis of ultratrace sulfides, the passivation of the complete sample flow path was of utmost importance. This passivation included the inert gas cylinders, regulator, connecting tubing, the inert flow path of the static dilutor, canister, column, and detector. Prior to running samples, it was imperative to purge the system flow path with helium and to perform a blank test. This procedure ensured that the residual components remained beneath the method detection limit of the targeted compounds, thereby not influencing the sample measurement. To ascertain that the blank fulfilled the requisite criteria, the carrier gas purity needed to be equal to or exceed 99.999%. It was also advisable to install a sulfur filter (part number CP17989) within the flow path capable of eliminating sulfur-specific compounds such as H_2S, COS, and SO_2 from gas streams. It is important to note that this filter should be positioned as proximately as possible to the GC system.

The samples were initially concentrated using a TD system, followed by transfer to a GC/SCD for analysis after the blank validation. Figure 2A demonstrates that the J&W DB-Sulfur SCD column, specifically tailored for sulfides, delivered symmetrical peak shapes and superior separation. The seven sulfides exhibited equal molar responses on the SCD detector, around 1 nmol/mol.

However, Figure 2B indicates that with the reduction of sample concentration, the adsorption of hydrogen sulfide becomes prominent at a concentration of 0.05 nmol/mol. In contrast to carbonyl sulfide, the same concentration of hydrogen sulfide resulted in a slightly diminished response. This variation became more pronounced as the sample concentration was further reduced.

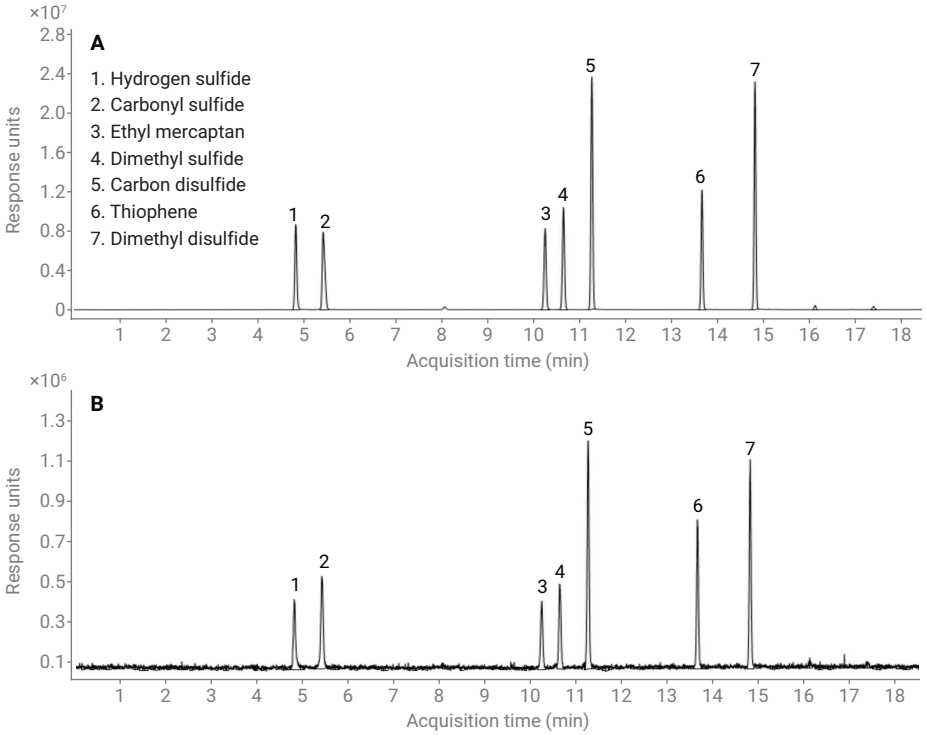

Figure 2. (A) SCD signal of sulfides at a concentration approximately 1 nmol/mol. (B) SCD signal of sulfides at a concentration approximately 0.05 nmol/mol.

A calibration procedure was carried out over multiple points with concentrations varying from 0.1 to 10 nmol/mol. For each component at every level of calibration, a response factor (RF) was determined. An average RF was then calculated, considering the mean RFs of the calibration curves for each component, along with its respective relative standard deviation (RSD). The RF %RSD was less than 18.2% for all substances analyzed. In relation to linear curve fitting that is enforced through the origin, the correlation coefficient (R^2) was found to be at least 0.998 for each component, as illustrated in Table 8.

Table 8. Linearity results for sulfides.

Compound	CF Formula (Origin: Force)	R^2	RF %RSD
Hydrogen Sulfide	y = 24,847,930.011358x	0.9994	18.17%
Carbonyl Sulfide	y = 28,166,440.860860x	0.9999	5.76%
Ethyl Mercaptan	y = 24,921,314.177000x	0.9986	10.84%
Dimethyl Sulfide	y = 28,160,991.568685x	0.9988	14.25%
Carbon Disulfide	y = 58,677,048.243978x	0.9993	5.41%
Thiophene	y = 28,359,517.901257x	0.9994	4.88%
Dimethyl Disulfide	y = 54,986,248.606198x	0.9994	7.83%

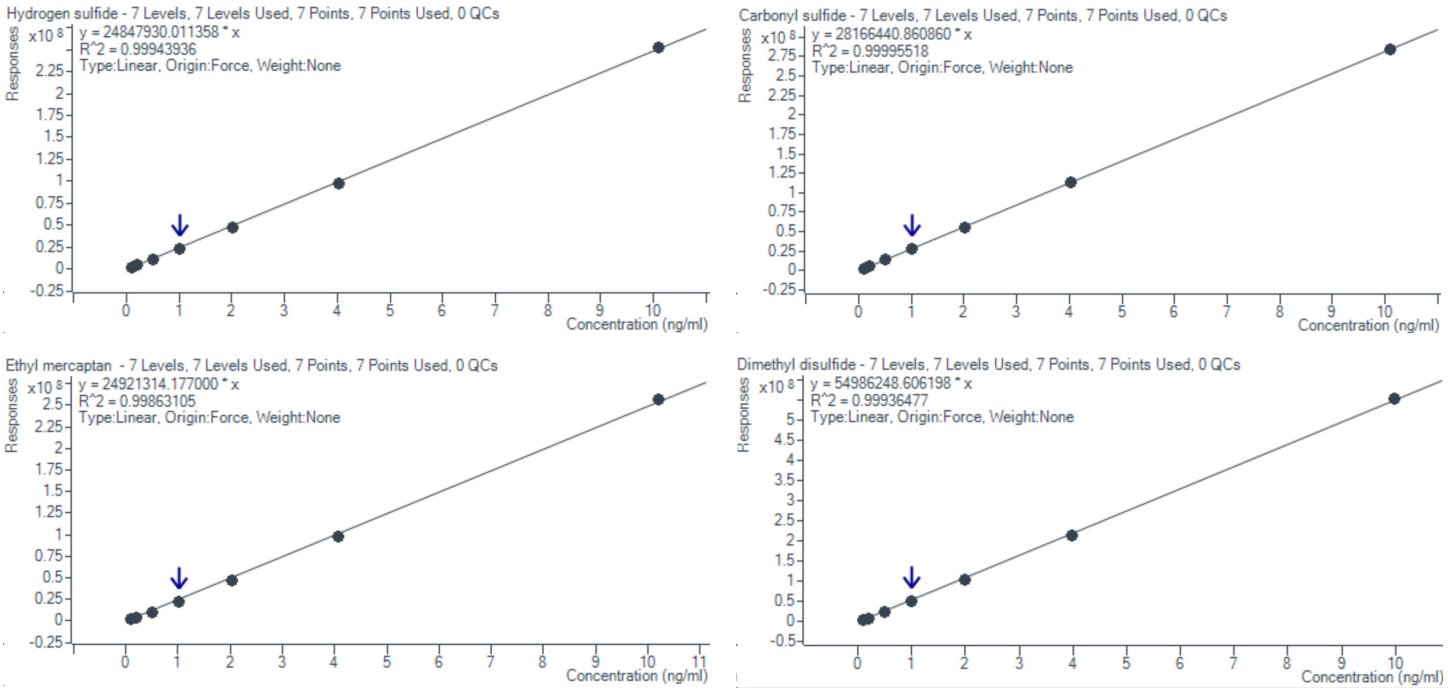

Figure 3. Calibration curves of some representative sulfides.

Repeatability was assessed by calculating the %RSD of the area from six replicate injections. This process was repeated for each analyte at both low and high concentrations (0.1 nmol/mol and 10 nmol/mol). As shown in Figure 4, the mean area %RSD for all analytes was 2.1%, with a maximum reaching 3.4%.

The evaluation of accuracy was also conducted in this study. For each concentration level of the sample, two consecutive injections were performed, followed by the calculation and averaging of the measured concentrations. The difference between this average value and the anticipated concentration value was computed, then divided by the anticipated concentration value, and ultimately multiplied by 100% to ascertain the definitive accuracy. The precise formula is presented in Equation 1.

$$\text{Accuracy} = (\overline{X} - X)/X \times 100\%$$

$\overline{X}$ = Average of measured concentration

X = Anticipated concentration

Equation 1. Accuracy calculation formula.

The determination of the measured concentration was facilitated by two distinct methods: the linear equation and the average response factor. The comprehensive results are shown in Table 9.

The SCD demonstrated exceptional selectivity and sensitivity towards sulfides. In this study, we established the method detection limit (MDL) by conducting seven replicated tests using a 0.05 nmol/mol gas standard. The concentration of each compound was calculated using a linear equation, followed by the calculation of the standard deviation and multiplication by 3.14 to determine the MDL. The study showed that the calculated detection limits for the seven sulfides were all under 0.01 nmol/mol, as illustrated in Table 10.

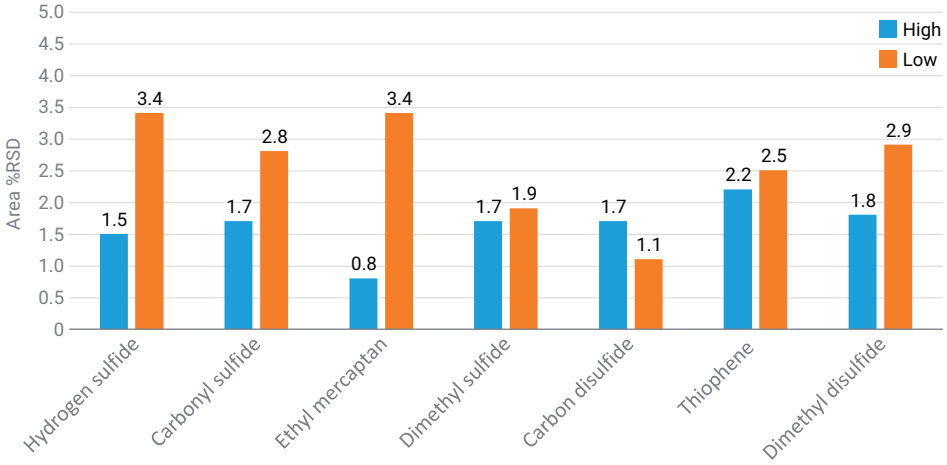

Figure 4. Repeatability results for sulfides at both low and high calibration levels.

Table 9. Accuracy results for sulfides across the calibration range.

Accuracy	Hydrogen Sulfide	Carbonyl Sulfide	Ethyl Mercaptan	Dimethyl Sulfide	Carbon Disulfide	Thiophene	Dimethyl disulfide
CF Formula	−30.37% ~ 2.78%	−8.77% ~ 2.27%	−24.59% ~ 1.98%	−29.36% ~ 2.99%	−11.04% ~ 11.44%	−9.06% ~ 13.49%	−18.80% ~ 2.86%
Average RF	−21.4% ~ 16.56%	−4.57% ~ 6.98%	−13.67% ~ 16.75%	−17.61% ~ 20.12%	−7.25% ~ 16.18%	−6.1% ~ 17.18%	−10.87% ~ 12.9%

Table 10. MDL results for sulfides.

		Hydrogen Sulfide	Carbonyl Sulfide	Ethyl Mercaptan	Dimethyl Sulfide	Carbon Disulfide	Thiophene	Dimethyl Disulfide
Calculated Concentration (nmol/mol)	1	0.0505	0.0505	0.0510	0.0525	0.0497	0.0515	0.0499
	2	0.0510	0.0491	0.0505	0.0500	0.0490	0.0498	0.0501
	3	0.0498	0.0516	0.0520	0.0494	0.0488	0.0496	0.0518
	4	0.0505	0.0533	0.0523	0.0537	0.0518	0.0554	0.0529
	5	0.0544	0.0504	0.0526	0.0559	0.0514	0.0522	0.0528
	6	0.0528	0.0510	0.0533	0.0554	0.0499	0.0524	0.0526
	7	0.0501	0.0496	0.0513	0.0525	0.0491	0.0529	0.0523
	Mean	0.0513	0.0508	0.0518	0.0528	0.0499	0.0520	0.0518
	SD	0.0017	0.0014	0.0010	0.0025	0.0012	0.0020	0.0013
MDL (3.14 × SD) (nmol/mol)		0.0052	0.0044	0.0031	0.0078	0.0038	0.0062	0.0040

Formaldehyde and organic halides analysis on MSD

The MSD was used for the analysis of formaldehyde and organic halides, with the formaldehyde acquired in selected ion monitoring (SIM) mode and organic halides in full scan mode. Each compound quantification was accomplished by integrating the peak areas of their individual characteristic ions.

As shown in Figure 5, the DB-Sulfur column exhibited a superior symmetrical peak shape for formaldehyde, without the interference of any coeluting peaks. The area %RSD for formaldehyde was confirmed to be equal to or less than 1.9 at both 1 and 100 nmol/mol concentrations, as presented in Figure 8. Moreover, the calibration coefficient was established at 0.9971 (linear equation enforced through the origin), and the %RSD of the RF was 8.8% covering the concentration range from 1 to 400 nmol/mol, as shown in Table 11. The accuracy assessment was also conducted for formaldehyde, using the identical calculation formula used for sulfides (Equation 1). The detailed results of this evaluation can be seen in Table 12. The MDL was determined based on seven replicate analyses of a 1 nmol/mol gas standard, resulting in a calculated MDL value of 0.0832 nmol/mol for formaldehyde.

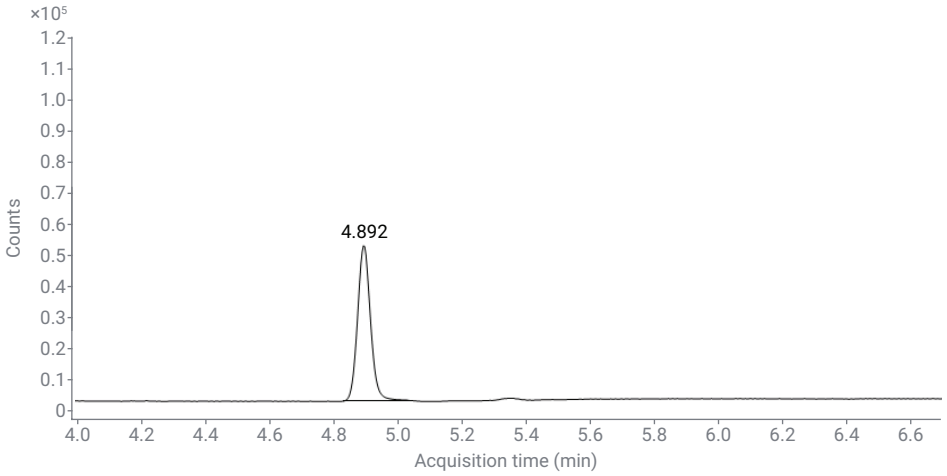

Figure 5. Total ion chromatogram of formaldehyde at the concentration of 10 nmol/mol in SIM mode.

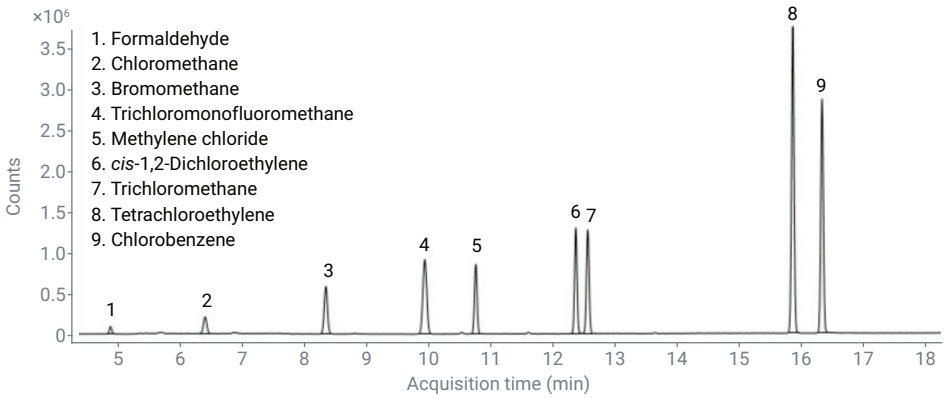

Figure 6. Total ion chromatogram of the target compounds at the concentration of 20 nmol/mol in scan mode.

Table 11. Linearity results for formaldehyde and organic halides

Compound	CF Formula (Origin: Force)	R^2	RF RSD%
Formaldehyde (1 to 400 nmol/mol)	y = 4,635.949359x	0.9971	8.80%
Chloromethane	y = 24,160.722741x	0.9999	3.17%
Bromomethane	y = 5,809.133480x	0.9994	5.23%
Trichloromonofluoromethane	y = 1,062.950309x	0.9999	7.09%
Methylene Chloride	y = 29,606.437470x	0.9989	10.04%
cis-1,2-Dichloroethylene	y = 44,517.394611x	0.9990	5.82%
Trichloromethane	y = 79,354.677026x	0.9995	5.30%
Tetrachloroethylene	y = 115,877.834523x	0.9987	15.39%
Chlorobenzene	y = 159,946.196181x	0.9996	3.72%

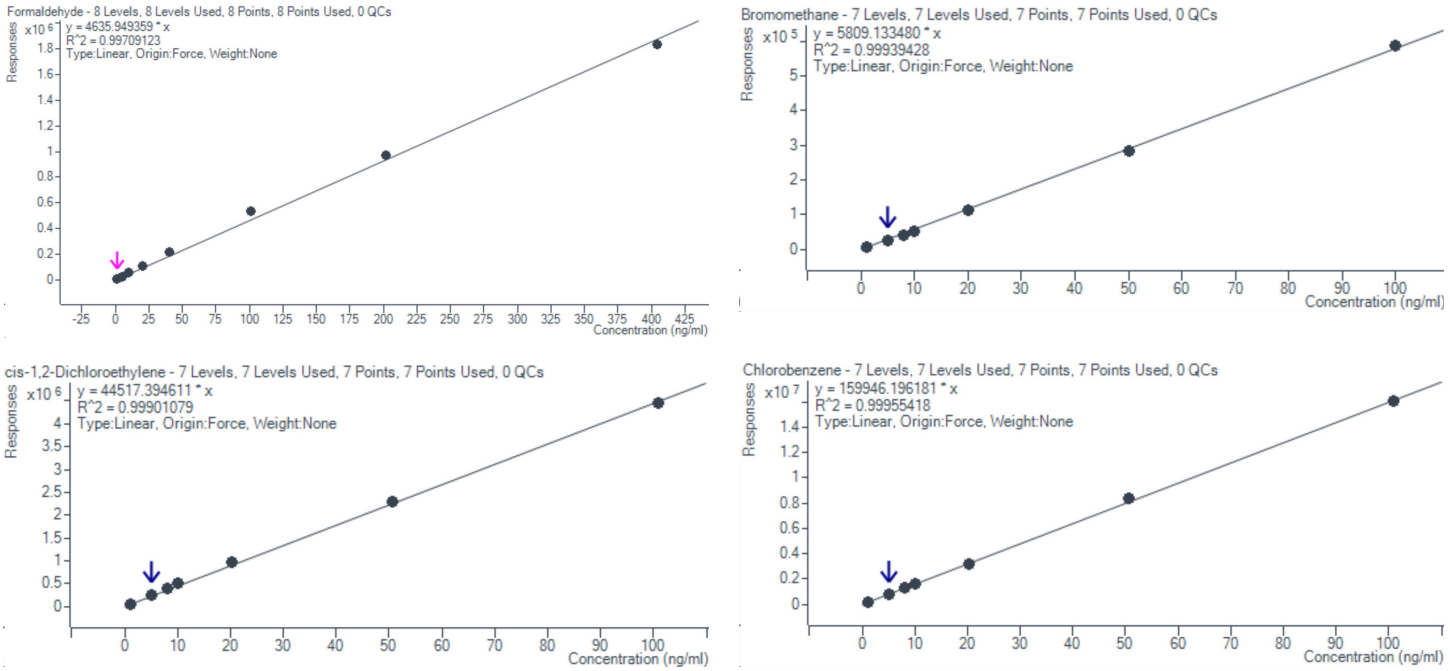

Figure 7. Calibration curves of formaldehyde and some representative organic halides.

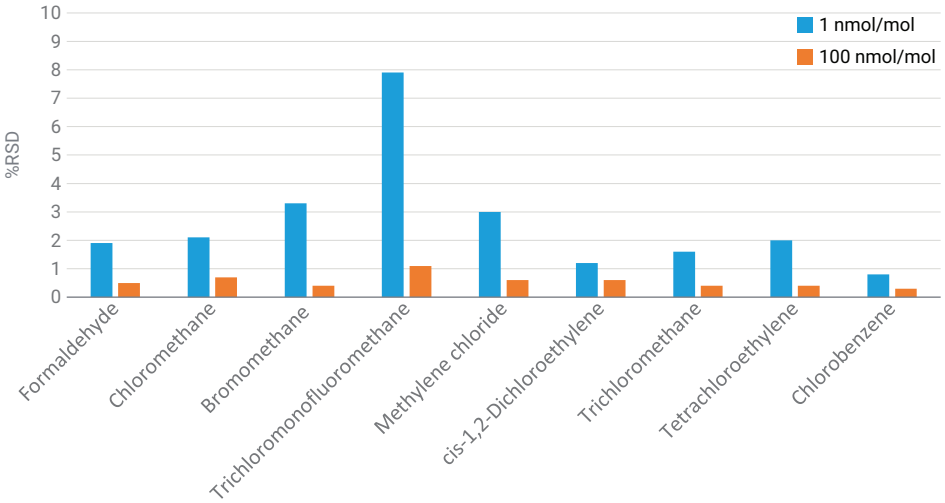

Figure 8. Repeatability results (n = 6) for formaldehyde and organic halides at concentrations of 1 nmol/mol and 100 nmol/mol.

The linearity of the eight organic halides was assessed across seven concentration levels, spanning from 1 to 100 nmol/mol. Correlation coefficients (R^2) for these components exhibited superior performance, exceeding 0.9987 (linear equation enforced through the origin), and the RSD of the RF was consistently less than 15.4%. Figure 7 provides illustrative calibration plots for selected typical compounds, while Table 11 presents comprehensive results for each individual compound. The repeatability results for the organic halides are shown in Figure 8, demonstrating area %RSDs ranging from 0.3 to 7.9%. Table 12 provides an overview of the accuracy results for the organic halides. The MDL was determined through seven replicate runs of a 1 nmol/mol gas standard. Table 13 shows these detailed results.

Table 12. Accuracy results of formaldehyde and organic halides.

Compound	Accuracy	
	CF Formula	Average RF
Formaldehyde	−10.55% ~ 5.1%	−7.70% ~ 8.45%
Chloromethane	−8.92% ~ 1.51%	−7.99% ~ 2.56%
Bromomethane	−11.09% ~ 0.81%	−5.01% ~ 7.71%
Trichloromonofluoromethane	−0.65% ~ 19.11%	−5.98% ~ 12.71%
Methylene Chloride	−1.1% ~ 28.04%	−12.03% ~ 13.90%
cis-1,2-Dichloroethylene	−1.23% ~ 18.2%	−9.11% ~ 8.77%
Trichloromethane	−1.08% ~ 17.44%	−6.63% ~ 10.85%
Tetrachloroethylene	−30.45% ~ 3.96%	−20.29% ~ 19.15%
Chlorobenzene	−8.00% ~ 3.84%	−6.31% ~ 5.75%

Table 13. MDLs for formaldehyde and organic halides.

		Formaldehyde	Chloromethane	Bromomethane	Trichloromono-fluoromethane	Methylene Chloride	*cis*-1,2-Dichloroethylene	Trichloromethane	Tetrachloro-ethylene	Chlorobenzene
Calculated Concentration (nmol/mol)	1	1.0783	0.9639	1.0059	0.9823	1.0039	1.0122	1.0005	1.0182	1.0124
	2	1.0418	0.9921	0.9941	1.0157	0.9621	1.0078	0.9915	1.0018	1.0076
	3	1.0056	0.9304	0.9696	0.9484	0.9439	0.9815	0.9685	0.9966	0.9897
	4	1.0370	0.9592	0.9780	0.9817	0.9435	1.0061	0.9868	1.0021	0.9926
	5	1.0115	0.9516	0.9945	1.0180	0.9461	0.9863	0.9678	0.9885	0.9906
	6	1.0069	0.9646	0.9580	0.9663	0.9206	0.9796	0.9744	0.9842	0.9688
	7	1.0131	0.9638	0.9933	0.9586	0.9241	1.0077	0.9778	0.9438	1.0090
	Mean	1.0277	0.9608	0.9848	0.9816	0.9492	0.9973	0.9810	0.9907	0.9958
	SD	0.0266	0.0184	0.0168	0.0270	0.0279	0.0142	0.0123	0.0234	0.0152
MDL (3.14 × SD) (nmol/mol)		0.0835	0.0577	0.0527	0.0846	0.0877	0.0445	0.0386	0.0735	0.0478

Conclusion

The Agilent 8890 Gas Chromatography system, equipped with a Multi-Gas CIA Advantage-xr TD and dual detection systems (SCD/MSD), is proficient in the analysis of ultratrace sulfides, trace formaldehyde, and organic halides in hydrogen for FCVs. Based on this system, exceptional analytical performance for these three distinct compound types has been achieved, fully satisfying the quality control criteria specified in ISO 14687-2019, SAE J2719-2015, and GB/T 37244-2018 methods.

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