

Industrial

Determination of sulfur-containing compounds, formaldehyde, and organic halides in hydrogen for proton-exchange membrane fuel cell vehicles

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Keywords

Hydrogen, sulfur-containing compounds, formaldehyde, organic halides, gas chromatography-mass spectrometry, GC-MS, thermal desorption, Multi-Gas UNITY-CIA *Advantage-xr*

Goal

The goal of this application note is to demonstrate a suitable analytical method that can be applied for the determination of sulfur-containing compounds, formaldehyde, and organic halides in hydrogen used for proton-exchange membrane fuel cell vehicles in compliance with the Chinese regulation (GB/T 37244-2018) by using thermal desorption coupled to gas chromatography-mass spectrometry and sulfur chemiluminescence detection (SCD).

Introduction

The past energy crisis and global warming led researchers to find alternative cleaner and emission-free energy sources. Hydrogen has been identified as a very promising energy carrier or fuel due to its exceptional energy per mass content. The proton-exchange membrane fuel cell (PEMFC) has garnered considerable attention and represents a breakthrough technology for automotive applications due to its capability to convert hydrogen and oxygen into electricity with only water as a by-product. Studies have shown that impurities such as CO, CO₂, NH₃, formaldehyde, halogenated compounds, and sulfur-containing compounds in hydrogen can cause serious damage to the performance of PEMFC by reducing its service life. Therefore, an accurate assessment of hydrogen purity is extremely important. This application note is focused on the determination of sulfur-containing compounds, formaldehyde, and organic halide impurities in hydrogen gas.

Experimental

Instrumentation

In this study, a Thermo Scientific™ TRACE™ 1610 GC, configured with a sulfur chemiluminescence detector (PAC SeNSE™ SCD, PAC AC Analytical Controls) through a Thermo Scientific™ iConnect™ Generic Detector Interface module (GDI) and connected to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer, was combined with a Markes International™ Multi-Gas UNITY-CIA *Advantage-xr*™ for impurities concentration before GC-MS analysis.

The Markes UNITY-CIA *Advantage-xr* is an inert, multi-channel pre-concentrator that allows for the automated analysis of volatile compounds, down to C₂ hydrocarbons, without the inconvenience of using a cryogen fluid. It provides an ideal solution for laboratories who need a versatile thermal desorption (TD) system able to handle canisters and bags as well as on-line monitoring and single sorbent-tube desorption. The Multi-Gas Enabled UNITY-CIA *Advantage-xr* is certified for operation with a choice of three carrier gases: helium, nitrogen, and hydrogen, and it is required for analyzing hydrogen gas with on-line collection.

In this study, an aliquot of hydrogen was collected into an inert container, such as a canister. The hydrogen gas sample was drawn across the focusing trap where impurities were concentrated before being transferred to the GC for analysis. Grab sampling is predominantly used when there is a need to measure highly volatile compounds, such as formaldehyde and hydrogen sulfide, which cannot be sampled using sorbent tubes.

Chromatographic separation was achieved on a Restek™ Rtx™-1 column (60 m × 0.32 mm × 5 μm, P/N 10180), which provides long lifetime and very low bleed at high operating temperatures. The dual detector configuration MS-SCD was achieved by

splitting the eluent after the analytical column between the two detectors with a ratio of 3 (SCD):1 (MS), by means of the Thermo Scientific™ Dual-Detector Microfluidic Kit. The SCD detector was used for quantifying sulfur-containing compounds, while the single quadrupole MS was used to quantify formaldehyde and organic halides in SIM mode.

The Multi-Gas UNITY-CIA *Advantage-xr* and GC-MS experimental conditions optimized in this study are reported in Table 1. The list of selected ions for MS analysis is detailed in Table 2, while the full list of the target analytes is reported in Table 3.

Data acquisition, processing, and reporting

MS and SCD data were acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated control of the Multi-Gas UNITY-CIA *Advantage-xr* instrument ensures full automation of the analytical workflow, from sampling to data acquisition, combined with an intuitive user interface for data analysis, processing, customizable reporting, and storage in compliance with the Federal Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11). The SCD detector was controlled through the local user interface.

Standard and sample preparation

Standard preparation

A gaseous standard mixture of the compounds as listed in Table 3 was used to assess linearity, limits of detection (LODs), and peak area repeatability (%RSD). Calibration curves for the investigated analytes were prepared in canisters by diluting the gaseous mix with carrier-gas-grade nitrogen by using a gas diluter. The calibration curve for sulfur-containing compounds ranged from 0.1 to 10 nmol/mol; for formaldehyde, from 1 to 400 nmol/mol; and for organic halides, from 1 to 100 nmol/mol.

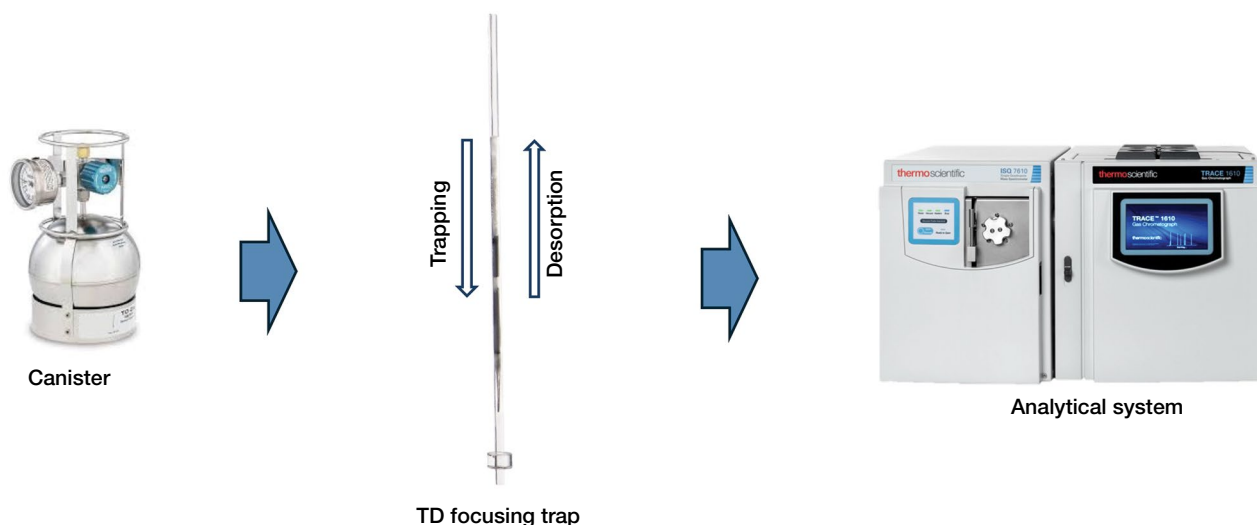


Figure 1. Workflow schematic for assessment of impurities in hydrogen

LODs were assessed using a calibration standard at 0.01 nmol/mol for sulfur-containing compounds, 0.1 nmol/mol for formaldehyde, and 0.5 nmol/mol for organic halides. Peak area repeatability was assessed by preparing n=7 sample replicates at 0.05 nmol/mol for sulfur-containing compounds and 1 nmol/mol for formaldehyde and organic halides.

Table 1. Experimental conditions for hydrogen impurity assessment

Parameter	Condition
Sample preconcentration	
Sampling instrument	Markes Multi Gas CIA <i>Advantage-xr</i>
Sampling volume	Up to 800 mL
Thermal desorption instrument	Markes Multi Gas UNITY-xr
Gas circuit temperature	120 °C
Sampling rate	50 mL/min
After sampling	
Gas circuit purging and cleaning	At 50 mL/min for 4 min
Cold trap purging and cleaning	At 50 mL/min for 1 min
Carrier gas	High-purity helium
Carrier flow rate	6 mL/min
GC oven temperature program	
Initial temperature	40 °C
Equilibrium time	1 min
Hold time 1	5 min
Heating rate 1	10 °C/min
Temperature 2	100 °C
Hold time 2	1 min
Heating rate 2	20 °C/min
Final temperature	220 °C
Final hold time	2 min
Sulfur chemiluminescence detector (SCD)	
Top heater	700 °C
Bottom heater	950 °C
Base	350 °C
Hydrogen flow	Base, 12 mL/min Top, 130 mL/min
Base PC (He)	25 kPa (\approx 40 mL/min)
Oxygen flow rate	30 mL/min
Furnace vacuum	<300 Torr
Cell vacuum	<50 Torr
Mass spectrometry (MS)	
Acquisition mode	SIM/ FULL SCAN
Scan range	29, 30, <i>m/z</i> 33–200
Ion source temperature	EI, 280 °C
Transfer line temperature	250 °C

Table 2. Qualitative and quantitative ions for formaldehyde and organic halides

Component name	Qualitative ion (<i>m/z</i>)	Quantitative ion (<i>m/z</i>)
Methyl chloride	52	50
Methyl bromide	96	95
Trichlorofluoromethane	103	102
Dichloromethane	84	49
<i>Cis</i> -1,2-dichloroethylene	63	61
Trichloromethane	85	83
Tetrachlorethylene	129	166
Chlorobenzene	77	112
Formaldehyde	29	30

Table 3. Composition of the gaseous standard mix used for dilution and assessment of linearity and repeatability

	Sample no.	Component name	Mole fraction (μ mol/mol)
Sulfur-containing compound	S1	Hydrogen sulfide	0.9890
		Carbonyl sulfide	1.0000
		Ethyl mercaptan	0.9950
		Dimethyl sulfide	0.9930
		Carbon disulfide	0.9980
		Thiophene	0.9920
		Dimethyl disulfide	1.0000
Formaldehyde organic halides	S2	Nitrogen	Equilibrium
		Formaldehyde	0.960
		Methyl chloride	0.977
		Methyl bromide	1.000
		Trichlorofluoromethane	0.998
		Dichloromethane	0.983
		<i>Cis</i> -1,2-dichloroethylene	1.010
		Trichloromethane	0.996
		Tetrachlorethylene	1.010
		Chlorobenzene	1.010
Nitrogen	Equilibrium		

Results and discussion

Sulfur-containing compounds with SCD detector Chromatography

The use of a SCD detector provided a highly selective and sensitive detection of sulfur-containing compounds thanks to its capability of achieving high temperature combustion to generate sulfur monoxide (SO), which then reacts with ozone generating a chemiluminescent reaction. A typical chromatogram for sulfur-containing compounds obtained with a SCD detector is shown in Figure 2. The cross-bonded dimethyl polysiloxane stationary phase of the analytical column ensured Gaussian peak shapes and baseline separation with chromatographic peak resolution > 1 for all the target compounds.

Linearity

Linearity was assessed by analyzing a seven-point calibration curve in the range of 0.1 nmol/mol to 10 nmol/mol. Calibration curves were plotted by using a linear fit type forced to pass through the origin. All compounds showed a linear trend within the used calibration ranges with a coefficient of determination (R^2) ≥ 0.995 , relative response factor deviation compared to dimethyl sulfide $\leq 9\%$, and response factor RSD $\leq 10\%$, therefore

meeting the performance acceptance requirements stated in the Chinese regulation, as reported in Table 4. Some examples of calibration curves obtained for sulfur-containing compounds are reported in Figure 3.

Limits of detection (LODs)

As required by standard validation, the peak-to-peak signal-to-noise ratios (S/N) were assessed by analyzing a standard mix at a concentration level of 0.01 nmol/mol (Figure 4 and Table 5).

LODs were calculated at $3.143 \times$ standard deviation (S_0), using the standard at 0.05 nmol/mol over $n=7$ repetitions, with an injection volume in the pre-concentrator of 80 mL:

$$s_0 = \sqrt{\sum (x_i - \bar{x})^2 / (m - 1)}$$

$$x_{LOD} = 3.143 \times s_0$$

where:

x_i = concentration of each repetition

\bar{x} = mean of the x_i values

m = number of repetitions

For all analytes, the calculated LOD was close to 0.01 nmol/mol (Table 5).

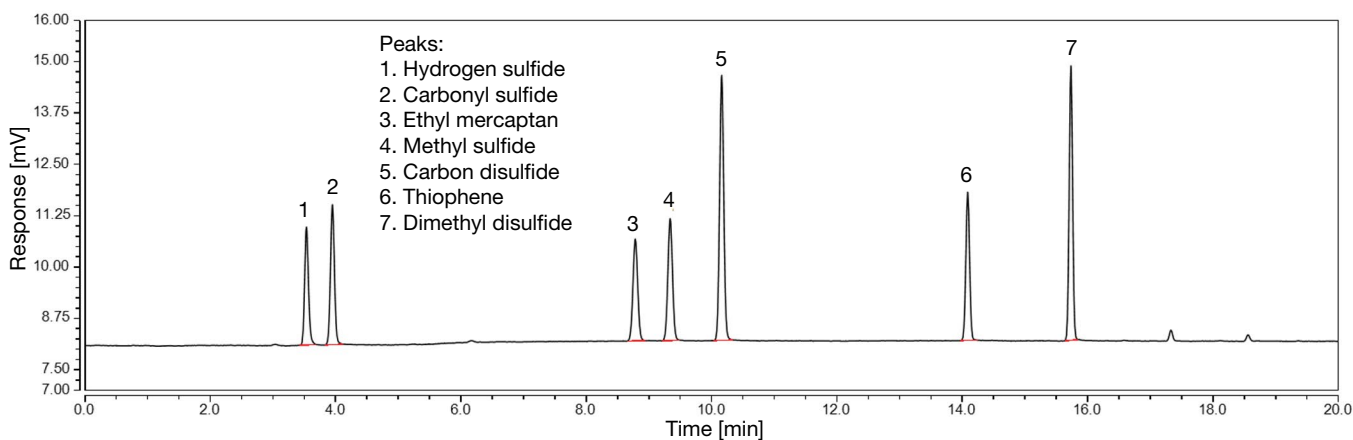


Figure 2. Typical chromatogram obtained for analysis of sulfur-containing compounds with the SCD detector

Table 4. Coefficient of determination (R^2), relative response factor deviation compared to dimethyl sulfide, average response factor and RF %RSD obtained for sulfur-containing compounds

Component	Slope (Forced through the origin)	Coefficient of determination R^2 ($R^2 > 0.995$)	RRF % (Relative response factor deviation vs dimethyl sulfide)	RF (Average response factor)	RF RSD % (Requirement RSD < 30%)
Hydrogen sulfide	0.2388	0.9997	8.46	0.2209	9.56
Carbonyl sulfide	0.2645	0.9988	6.77	0.2565	6.99
Ethyl mercaptan	0.2516	0.9997	3.52	0.2352	7.29
Dimethyl sulfide	0.2847	0.9996	0.00	0.2774	5.81
Carbon disulfide	0.5489	0.9995	8.72	0.5643	10.00
Thiophene	0.2811	0.9998	5.63	0.2752	5.12
Dimethyl disulfide	0.4711	0.9993	6.40	0.4703	6.59

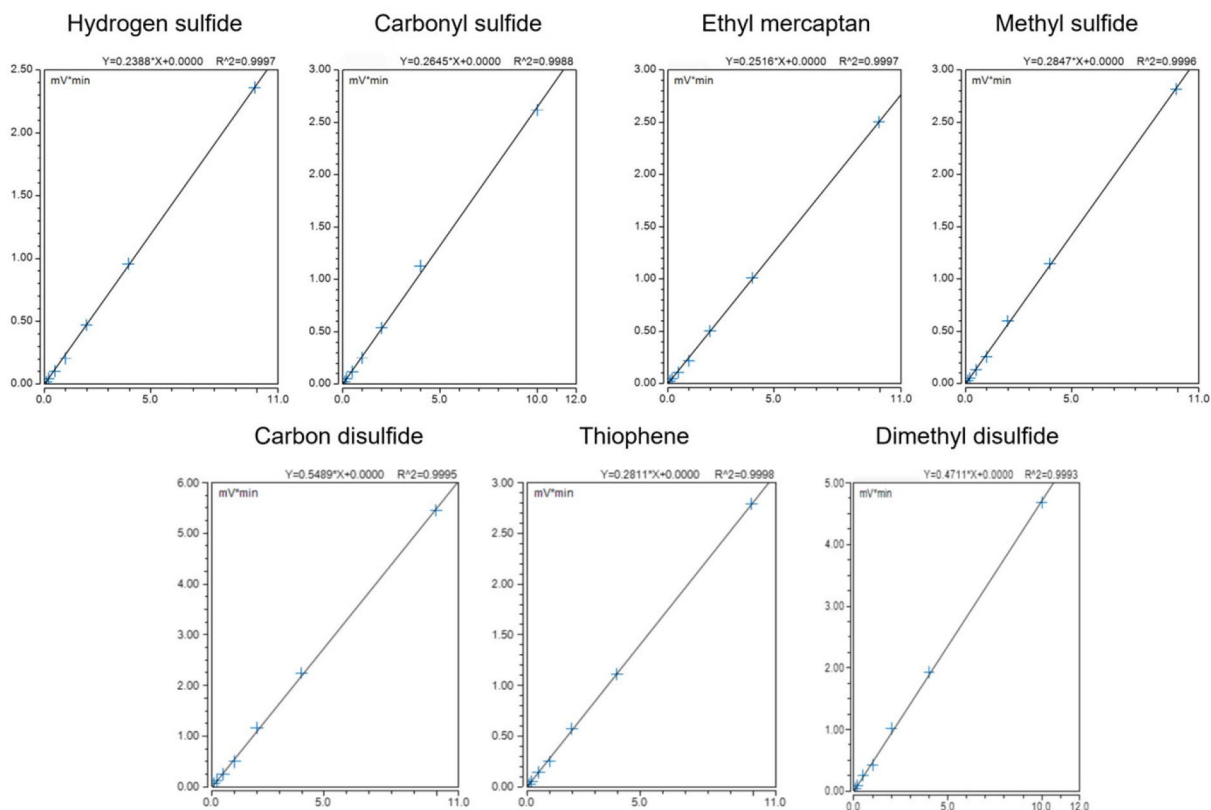


Figure 3. Calibration curves ranging from 0.1 to 10 nmol/mol obtained for sulfur-containing compounds

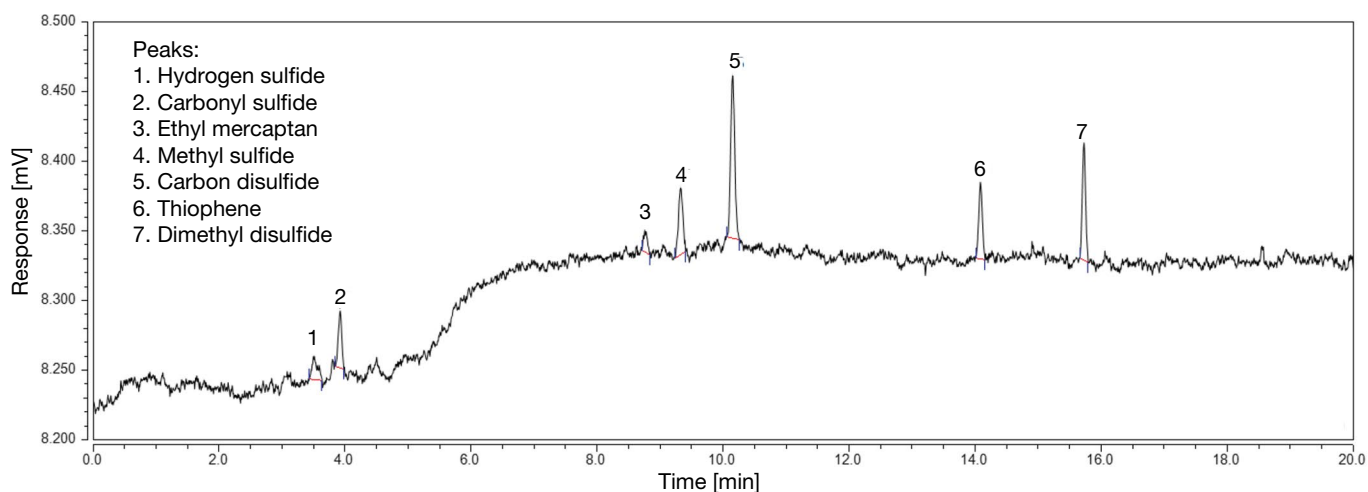


Figure 4. Example of SCD chromatogram for sulfur-containing compounds at a concentration level of 0.01 nmol/mol

Table 5. Calculated S/N for sulfur compounds at a concentration level of 0.01 nmol/mol and LOD calculated at $3.143 \times S_0$ using the standard at 0.05 nmol/mol (n=7)

Component	Calculated concentration (nmol/mol)	S/N (0.01 nmol/mol)	Calculated LOD (nmol/mol)
Hydrogen sulfide	0.0099	2.1	0.0137
Carbonyl sulfide	0.0100	4.2	0.0180
Ethyl mercaptan	0.0100	2.9	0.0086
Methyl sulfide	0.0099	8.3	0.0173
Carbon disulfide	0.0100	18.5	0.0186
Thiophene	0.0099	6.6	0.0156
Dimethyl disulfide	0.0100	10.5	0.0138

Repeatability

Peak area repeatability (%RSD) was evaluated on n=7 repetitions of a standard at 0.05 nmol/mol. The injection volume of the pre-concentrator was 80 mL. The calculated peak area RSDs were below 5% for all the investigated analytes as demonstrated in Figure 5 and Table 6.

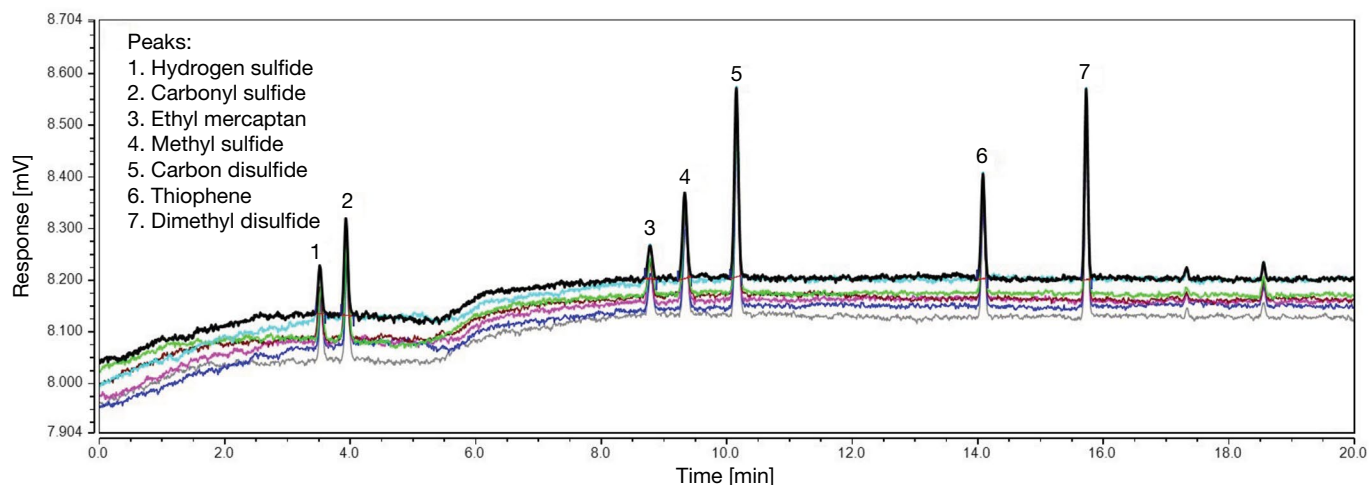


Figure 5. Overlaid chromatograms showing the peak area repeatability for sulfur-containing compounds obtained by analyzing n=7 standards at 0.05 nmol/mol

Table 6. Peak area (mV*min) as well as calculated %RSD for sulfur-containing compounds at 0.05 nmol/mol

Component name	Peak area response value (mV*min)							RSD %
	1	2	3	4	5	6	7	
Hydrogen sulfide	0.0072	0.0070	0.0071	0.0074	0.0077	0.0072	0.0066	4.74
Carbonyl sulfide	0.0141	0.0136	0.0137	0.0122	0.0140	0.0140	0.0138	4.81
Ethyl mercaptan	0.0070	0.0069	0.0066	0.0065	0.0065	0.0068	0.0061	4.59
Methyl sulfide	0.0140	0.0148	0.0150	0.0140	0.0142	0.0149	0.0143	2.98
Carbon disulfide	0.0289	0.0293	0.0295	0.0281	0.0273	0.0294	0.0280	2.96
Thiophene	0.0147	0.0143	0.0139	0.0144	0.0141	0.0146	0.0141	2.02
Dimethyl disulfide	0.0249	0.0242	0.0232	0.0239	0.0227	0.0234	0.0233	3.10

Formaldehyde and organic halides with a single quadrupole mass spectrometer

Chromatography

The dual detector configuration used in this study allowed for selective detection of sulfur-containing compounds through the SCD detector as well as formaldehyde and organic halides through the use of the MS detector. The single ion monitoring (SIM) acquisition mode allowed for targeted analysis of the compounds of interest by monitoring their characteristic ions, therefore improving confidence in analyte identification. A typical chromatogram for formaldehyde and organic halides is shown in Figure 6. Also in this case, the selected chromatographic column allowed for baseline resolution and Gaussian peak shapes.

Linearity

Linearity was assessed by diluting a concentrated gas standard mix to obtain an 8-point calibration curve with mole fractions ranging from 1 to 400 nmol/mol for formaldehyde, and a 7-point calibration curve ranging from 1 to 100 nmol/mol for organic halides.

Calibration curves were plotted by using a linear fit type forced to pass through the origin. All compounds showed a linear trend within the used calibration ranges with $R^2 \geq 0.995$ and relative standard deviation (%RSD) of response factors (RF) $\leq 11\%$, therefore meeting the acceptance requirements stated in the Chinese regulation of $R^2 \geq 0.995$ and RF RSD $< 30\%$, as reported in Table 7. Examples of calibration curves obtained for formaldehyde and organic halides are reported in Figure 7.

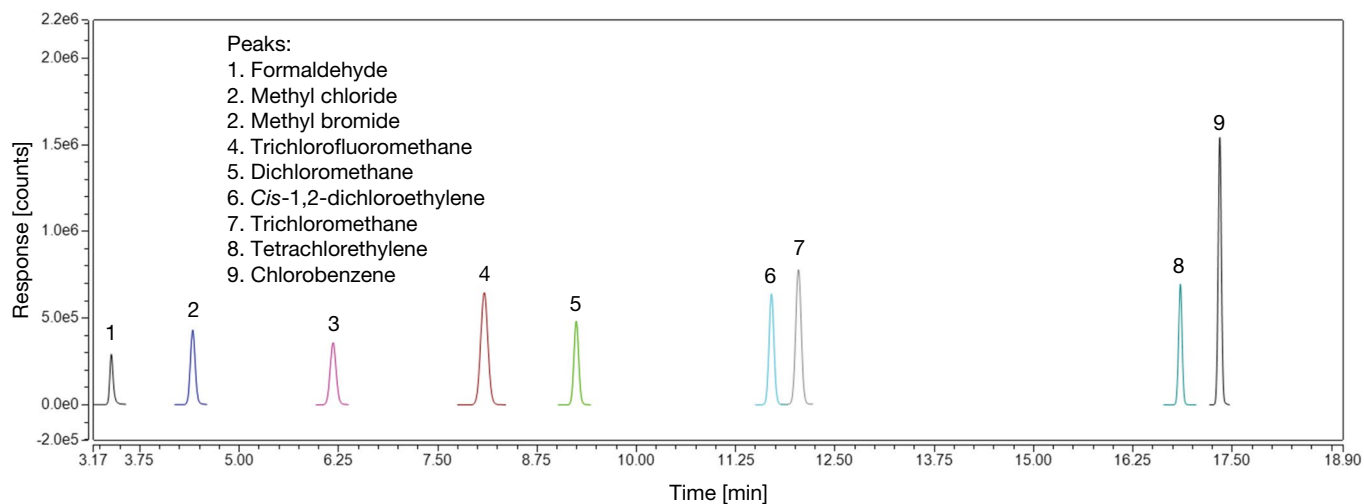


Figure 6. Example of SIM trace showing the chromatographic separation for formaldehyde and organic halides

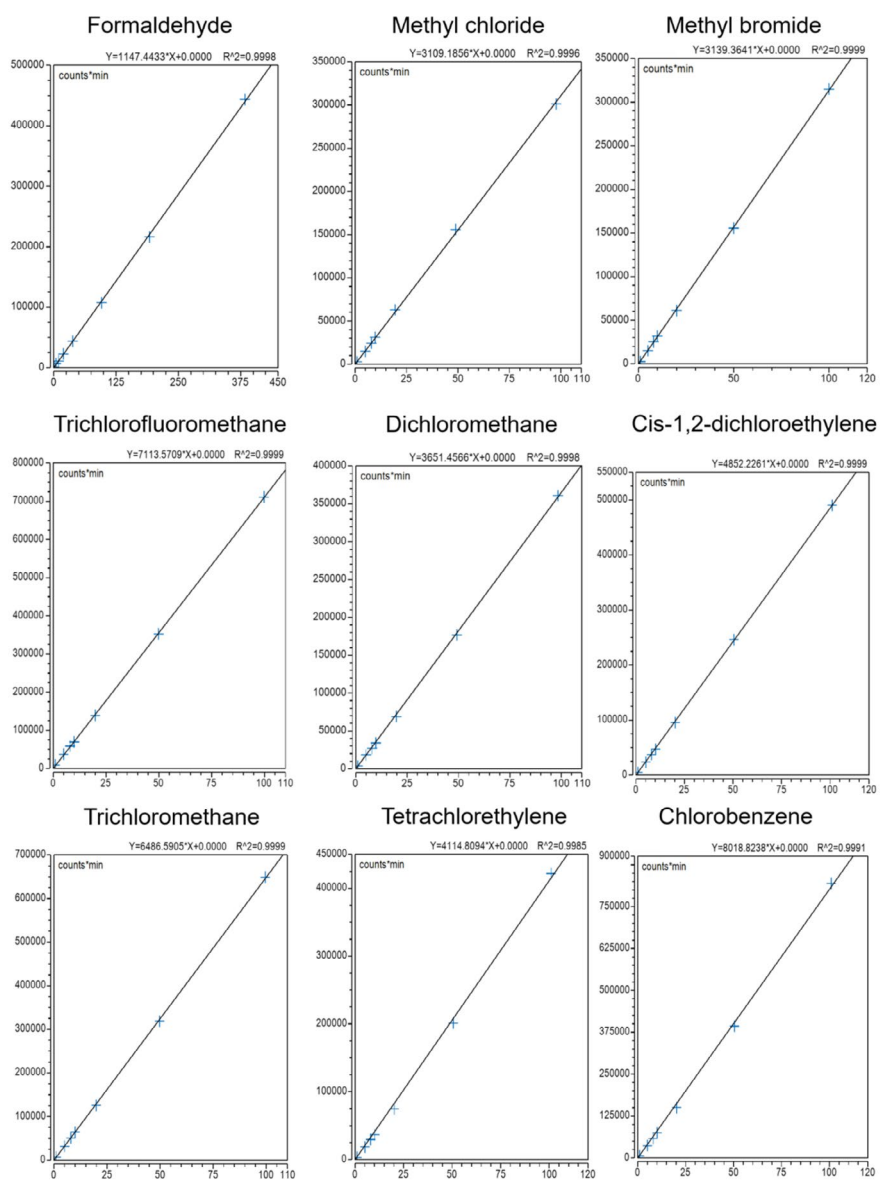


Figure 7. Calibration curves obtained for formaldehyde (calibration range: 1 to 400 nmol/mol) and organic halides (calibration range: 1 to 100 nmol/mol)

Table 7. R² and calculated RF %RSD obtained for formaldehyde and organic halides

Component	Slope (Forced through the origin)	Coefficient of determination (Requirement > 0.995)	RSD % of each component RF (Requirement < 30%)
Formaldehyde	1151.8661	0.9998	8.05
Methyl chloride	3109.1856	0.9996	7.18
Methyl bromide	3139.3642	0.9999	8.27
Trichlorofluoromethane	7113.5709	0.9999	9.47
Dichloromethane	3651.4566	0.9998	3.12
Cis-1,2-dichloroethylene	4852.2261	0.9999	3.22
Trichloromethane	6486.5905	0.9999	3.48
Tetrachlorethylene	4114.8094	0.9985	10.73
Chlorobenzene	8018.8238	0.9991	9.18

Limits of detection (LODs)

The peak-to-peak signal-to-noise ratio (S/N) for formaldehyde was assessed on a TIC chromatogram by analyzing a gas standard mix at a concentration of 0.1 nmol/mol, with a pre-concentrator injection volume of 8 mL (Figure 8A). In the case of organic halides, the peak-to-peak S/N were evaluated on a TIC chromatogram by using a mix at 0.5 nmol/mol, with a pre-concentrator injection volume of 800 mL (Figure 8B). The LODs for formaldehyde and organic halides were calculated on a SIM chromatogram as $3.143 \times$ standard deviation (S_0) over $n=7$ samples at a mole fraction of 1 nmol/mol, as reported in Table 8.

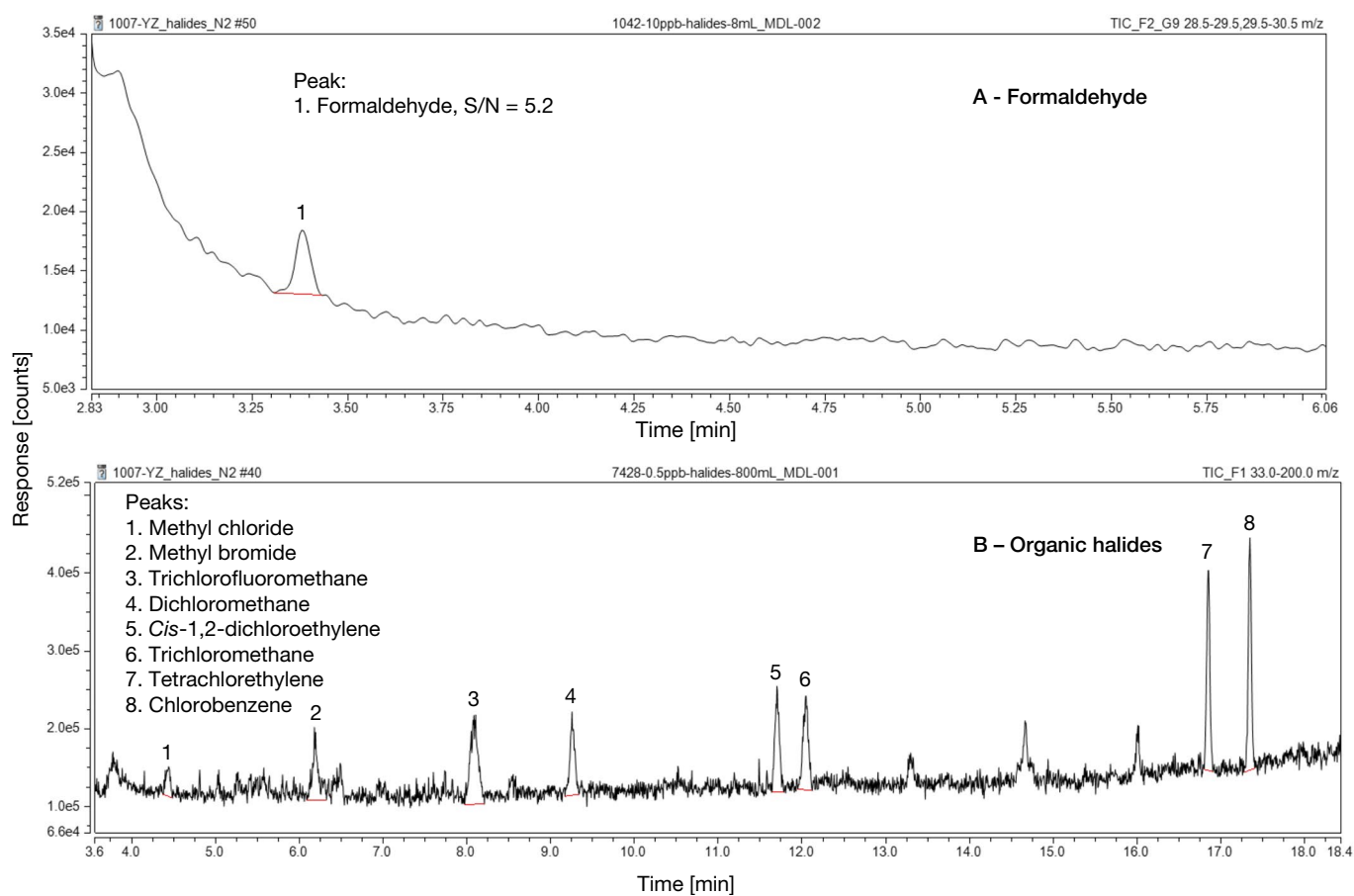


Figure 8. Examples of TIC chromatograms obtained for formaldehyde at a concentration level of 0.1 nmol/mol (A) and for organic halides at a concentration level of 0.5 nmol/mol (B)

Table 8. Calculated S/N for formaldehyde on the TIC chromatogram at a concentration level of 0.1 nmol/mol, S/N for organic halides on the TIC chromatogram at a concentration level of 0.5 nmol/mol, and LODs calculated on SIM chromatogram as $3.143 \times S_0$ using the standard at 1 nmol/mol (n=7)

Component	Calculated concentration (nmol/mol)	S/N (0.01 nmol/mol)	Calculated LOD (nmol/mol)
Formaldehyde	0.0960	5.2	0.0407
Methyl chloride	0.4885	1.5	0.0952
Methyl bromide	0.5000	3.8	0.0637
Trichlorofluoromethane	0.4990	5.9	0.0868
Dichloromethane	0.4915	4.8	0.0763
Cis-1,2-dichloroethylene	0.5050	5.3	0.0910
Trichloromethane	0.4980	6.8	0.0798
Tetrachlorethylene	0.5050	15.7	0.0750
Chlorobenzene	0.5050	15.1	0.0614

Repeatability

The peak area repeatability was evaluated on the n=7 repetitions at a mole fraction of 1 nmol/mol. The pre-concentrator injection volume was 8 mL. Peak area RSD of all components were not higher than 3.17%. The overlaid chromatograms are shown in Figure 9, and the detailed repeatability test results are shown in Table 9.

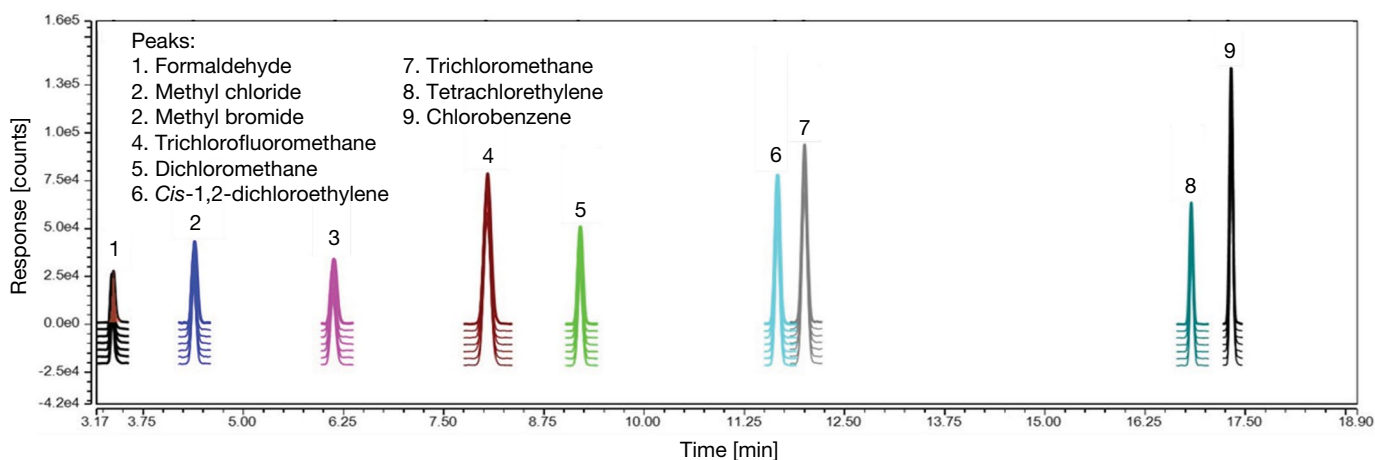


Figure 9. Overlaid SIM chromatograms showing the peak area repeatability for formaldehyde and organic halides obtained by analyzing n=7 standards at 1.0 nmol/mol

Table 9. Peak area (counts*min) as well as calculated %RSD for formaldehyde and organic halides obtained by analyzing n=7 standards at 1.0 nmol/mol

Component name	Peak area response value (mV*min)							RSD %
	1	2	3	4	5	6	7	
Formaldehyde	1115	1121	1108	1135	1136	1140	1105	1.27
Methyl chloride	2739	2729	2775	2816	2872	2890	2976	3.17
Methyl bromide	2713	2769	2690	2848	2766	2740	2820	2.03
Trichlorofluoromethane	7949	7861	7896	8160	7895	7982	8149	1.54
Dichloromethane	3450	3357	3469	3517	3497	3414	3525	1.74
Cis-1,2-dichloroethylene	5458	5293	5209	5491	5427	5459	5622	2.49
Trichloromethane	7130	6987	7114	7330	7160	7102	7304	1.67
Tetrachlorethylene	3163	3222	3180	3235	3206	3092	3272	1.82
Chlorobenzene	6401	6346	6449	6508	6564	6490	6584	1.32

Conclusion

The results obtained in this study demonstrated that the Markes UNITY-CIA *Advantage-xr* pre-concentrator combined with the TRACE 1610 GC equipped with the SCD detector and connected to an ISQ 7610 single quadrupole mass spectrometer provides a highly performing solution for selective and sensitive analysis of some critical hydrogen impurities in compliance with the requirements of the Chinese regulation.

- R^2 values were ≥ 0.995 for all the investigated compounds with linear ranges from 0.1 to 10 nmol/mol for sulfur-containing compounds, from 1 to 400 nmol/mol for formaldehyde, and from 1 to 100 nmol/mol for organic halides, with RSD of response factors well below the acceptance limit of 30%.
- LODs calculated as $3.143 \times S_0$ resulted close to 0.01 nmol/mol for sulfur-containing compounds, 0.04 nmol/mol for formaldehyde, and between 0.06 and 0.095 nmol/mol for organic halides.
- Peak area repeatability was $<12\%$ for all the target analytes.

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