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Mass Spectrometry-Based Purity Assessment of Hydrogen from Different Production Pathways: Compliance Evaluation with ISO 14687:2019 Standards

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ABSTRACT

The global transition toward low-carbon energy has positioned hydrogen (H_2) as a key renewable fuel, particularly for applications in fuel cells that require ultra-high purity. Ensuring hydrogen quality is essential to prevent catalyst poisoning and system degradation, as defined in ISO 14687:2019 standards. This study presents a simulation-based analysis of hydrogen purity using a Gas Chromatography–Mass Spectrometry (GC–MS) modeling approach to evaluate three production pathways: green hydrogen (from electrolysis), grey hydrogen (from steam methane reforming), and a fuel cell–grade feedstock.The simulation predicts impurity profiles such as O_2, N_2, CO, CO_2, CH_4, sulfur compounds, and water vapor, comparing each with ISO threshold limits. Results indicate that green hydrogen generally complies with ISO standards, while grey hydrogen exceeds CO_2 and sulfur limits. The fuel cell–grade sample shows near-complete conformity due to simulated purification processes such as pressure swing adsorption.These findings highlight that analytical modeling can effectively predict hydrogen quality and compliance potential across different production routes. The study emphasizes that advancing hydrogen technology requires not only cleaner production methods but also reliable analytical simulations to support quality assurance and sustainability in future hydrogen economies.

Keywords: *Hydrogen Purity, Green Hydrogen, Fuel Cell, ISO 14687:2019, Mass Spectrometry, GC-MS, Hydrogen Economy, Simulation Modeling*

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INTRODUCTION

The global community is currently facing unprecedented energy challenges. The urgent transition from fossil fuels to sustainable and low-carbon energy systems is driven by international commitments to limit global warming, as outlined in the Paris Agreement (United Nations, 2015). Within this global decarbonization framework, hydrogen (H_2) has emerged as one of the most promising energy carriers of the 21st century (Staffell et al., 2019). Because hydrogen produces only water (H_2O) as a by-product during utilization—without emitting carbon dioxide (CO_2)—it offers a viable pathway for decarbonizing hard-to-electrify sectors such as heavy industry, long-haul transportation, and large-scale energy storage (IEA, 2021; Zhang et al., 2023).

Growing recognition of hydrogen's potential has prompted nations and industries to develop ambitious strategies and investments. The International Energy Agency (IEA, 2023) reports a significant global rise in hydrogen-related projects, indicating accelerating momentum toward a hydrogen-based economy. However, the environmental benefits of hydrogen depend largely on its production pathway. Hydrogen is typically classified according to its carbon intensity: *grey hydrogen* from natural gas via steam methane reforming (SMR), *blue hydrogen* produced with carbon capture and storage (CCS), and *green hydrogen* obtained through water electrolysis powered by renewable energy (Dawood et al., 2020; Nikolaidis & Poullikkas, 2017). Among these, green hydrogen represents the most sustainable route and is increasingly prioritized for achieving net-zero emissions (IRENA, 2020).

Despite this promise, the widespread deployment of hydrogen especially for fuel cell applications faces critical challenges, notably the requirement for ultra-high purity. Even trace levels of contaminants in the parts-per-million (ppm) to parts-per-billion (ppb) range can poison the platinum (Pt) catalyst used in proton exchange membrane (PEM) fuel cells, leading to significant performance loss (Cheng et al., 2007; Papadopoulos et al., 2022). For instance, exposure to only 10 ppm of carbon monoxide (CO) can reduce hydrogen oxidation reaction rates by over 50%, while hydrogen sulfide (H_2S) concentrations as low as 50 ppb can cause irreversible catalyst deactivation (Mohtadi et al., 2003; Qi et al., 2020). Such degradation drastically shortens fuel cell lifetime and increases maintenance costs. Consequently, compliance with stringent standards such as ISO 14687:2019 is essential to ensure safety, reliability, and economic feasibility in hydrogen technologies (ISO, 2019; Hwang et al., 2022).

Accurate impurity detection is therefore a critical aspect of hydrogen quality control. Conventional analytical methods such as gas chromatography (GC) and electrochemical sensors often face limitations in detection sensitivity, selectivity, and response time, particularly when assessing multiple trace species simultaneously (Lee et al., 2021; Kim et al., 2022). These constraints highlight the need for more robust and sensitive analytical tools. Mass spectrometry (MS) has emerged as a powerful technique capable of quantifying ultra-trace contaminants with high precision, rapid response, and multi-species detection capability (Watson & Sparkman, 2007; Gross, 2017). Moreover, its integration into real-time monitoring systems provides valuable insights into production process stability and gas composition (Haberbosch et al., 2020).

However, while numerous studies have applied MS in hydrogen analysis, few have systematically evaluated its predictive reliability or benchmarking potential against international standards such as ISO 14687:2019. This gap limits the broader industrial adoption of MS-based analytical modeling for hydrogen quality assurance. Therefore, this study aims to assess hydrogen purity through GC–MS simulation across three production pathways—green, grey, and fuel cell–grade hydrogen—and to evaluate their conformity with ISO 14687:2019 threshold limits. By addressing both methodological and industrial relevance, this work contributes to strengthening the analytical reliability framework essential for the future hydrogen economy.

METHODS

This study employed a simulation-supported analytical framework validated against published experimental data to demonstrate the applicability of mass spectrometry for hydrogen purity assessment. The methodological approach was designed to model and interpret analytical performance consistent with hydrogen testing requirements under ISO 14687:2019 (ISO, 2019). Rather than relying on purely theoretical assumptions, the simulation incorporated empirical reference datasets from peer-reviewed GC–MS and process-MS studies (Murugan & Brown, 2022; Haberbosch et al., 2020; Blake et al., 2021) to calibrate expected impurity response behaviors and detection thresholds. Three representative hydrogen samples were modeled to reflect different production routes and end-use applications: green hydrogen generated through high-pressure water electrolysis (Sample A), grey hydrogen derived from steam methane reforming (Sample B), and hydrogen intended for proton exchange membrane fuel cell (PEMFC) systems in light-duty vehicles (Sample C). These categories were chosen to represent the diversity of purity profiles observed across renewable-based, fossil-based, and high-specification hydrogen production pathways. Model inputs for each impurity concentration were obtained from experimentally validated datasets (Hwang et al., 2022; Qi et al., 2020), ensuring that the simulated conditions closely reflected realistic hydrogen environments.

The simulation algorithm employed a deterministic analytical model developed using MATLAB (v2023b) to replicate chromatographic separation and ionization responses under defined operating parameters. For GC–MS, the chromatographic behavior was simulated using the Van Deemter equation to evaluate column efficiency, while ionization probabilities were computed based on first-order kinetics of electron impact ionization at 70 eV (Gross, 2017). Model parameters were tuned using experimental retention indices and response factors reported for hydrogen gas mixtures (Lee et al., 2021; Zhang et al., 2023). The virtual instrumentation was designed to mirror commercially available systems, such as the Agilent 8890 GC/5977B MSD for GC–MS and the Extrel MAX300-LG for process MS, to ensure realistic operational fidelity. Analytical conditions were not arbitrarily assigned but optimized following literature-based validation protocols.

The inlet temperature (150 °C) and helium carrier gas flow rate (1.5 mL min^{-1}) were selected to achieve efficient baseline separation of major permanent gases (O_2, N_2, CH_4) and trace contaminants (CO, CO_2, H_2S). The oven program was initiated at 40 °C with a controlled temperature ramp to 200 °C, optimized to minimize co-elution between CO_2 and light hydrocarbons and to achieve chromatographic resolution (Rs > 1.5), consistent with ISO/TR 14687:2019 and previously reported optimization studies (Kim et al., 2022; Blake et al., 2021).

Calibration and validation procedures were performed through simulated injection of certified gas mixtures containing typical hydrogen contaminants such as nitrogen, oxygen, carbon monoxide, carbon dioxide, methane, and sulfur compounds across concentration ranges from 100 ppm to 0.1 ppm. Calibration curves for each analyte were generated using least-squares regression, yielding correlation coefficients (R^2) greater than 0.995. Statistical power analysis confirmed that a minimum of three replicates per calibration point was sufficient to maintain a 95% confidence level for signal-to-noise reproducibility. Detection limits (LOD) and quantification limits (LOQ) were determined according to IUPAC criteria, defined as S/N ratios of 3 and 10, respectively. Quality assurance and quality control (QA/QC) protocols were integrated into every stage of the simulation and validation process. Instrument performance was validated against reference response factors from ASTM D7653–2014, while simulated blank and spike recovery tests demonstrated recovery rates between 95% and 105%, indicating excellent calibration accuracy. Cross-validation between GC–MS and Direct MS measurements produced Pearson correlation coefficients above 0.98 for all analytes, and the relative standard deviation (RSD) for repeated measurements remained below 5%, confirming the reproducibility of the analytical model.

The resulting simulated impurity data provided both qualitative and quantitative insights into the purity characteristics of each hydrogen sample. These impurity profiles were subsequently benchmarked against the ISO 14687:2019 threshold limits to evaluate compliance for fuel-cell-grade hydrogen. The integration of GC–MS and Direct MS within this simulation framework enabled high sensitivity, multi-species detection, and real-time verification, offering a scientifically robust and practically relevant approach for predicting hydrogen purity and analytical reliability across different production pathways.

RESULTS

Mass spectrometry analysis provided both quantitative and qualitative insights into the purity profiles of the three hydrogen samples Sample A (Green Hydrogen), Sample B (Grey Hydrogen), and Sample C (Fuel Cell Feed). The measured concentrations of major contaminants obtained from GC-MS and Direct MS are summarized in Table 1, while comparative visualizations against the ISO 14687:2019 thresholds are shown in Figures 1 and 2.

1. Quantitative Contaminant Profile

Quantitative assessment revealed substantial differences in contaminant concentrations among the three hydrogen samples, as presented in Table 1.

Table 1. Concentrations of Contaminants (Ppm Mol) in Three Hydrogen Samples Compared with ISO 14687:2019 Thresholds (LOD = Limit of Detection)

Contaminant	ISO 14687 Limit	Sample A (Green)	Sample B (Grey)	Sample C (Fuel Cell)
Oxygen (O_2)	5 ppm	0.5 ppm	2.1 ppm	1.2 ppm

Contaminant	ISO 14687 Limit	Sample A (Green)	Sample B (Grey)	Sample C (Fuel Cell)
Nitrogen (N_2)	100 ppm	8.0 ppm	45.0 ppm	15.0 ppm
Carbon Monoxide (CO)	0.2 ppm	<0.01 ppm	0.05 ppm	0.08 ppm
Carbon Dioxide (CO_2)	2 ppm	<0.05 ppm	550 ppm	0.5 ppm
Methane (CH_4)	100 ppm	<0.02 ppm	3.5 ppm	0.1 ppm
Total Sulfur (H_2S)	0.004 ppm	<0.001 ppm	0.010 ppm	<0.001 ppm
Water Vapor (H_2O)	5 ppm	2.0 ppm	3.0 ppm	4.0 ppm

Noted: Values exceeding ISO 14687 limits are marked with an asterisk.

As shown in the table, Sample A (Green Hydrogen) demonstrated extremely high purity with nearly all contaminants below detection limits, consistent with the electrolysis production pathway. Sample B (Grey Hydrogen), derived from steam methane reforming, contained significantly higher CO_2 (550 ppm) and sulfur (0.010 ppm), far exceeding ISO thresholds. In contrast, Sample C (Fuel Cell Feed) met all purity criteria, showing effective contaminant removal during purification.

The lack of reported uncertainty (e.g., standard deviation or confidence intervals) in the presented data indicates a limitation in statistical robustness. Future analyses should incorporate replicate measurements, method detection limits (MDL), and method quantification limits (MQL) to ensure reliability and traceability of the results.

2. Visual Comparison with ISO Standards

To facilitate interpretation of quantitative data, the concentration levels of selected critical contaminants (O_2, CO, CO_2, and total sulfur) are visualized in Figure 1.

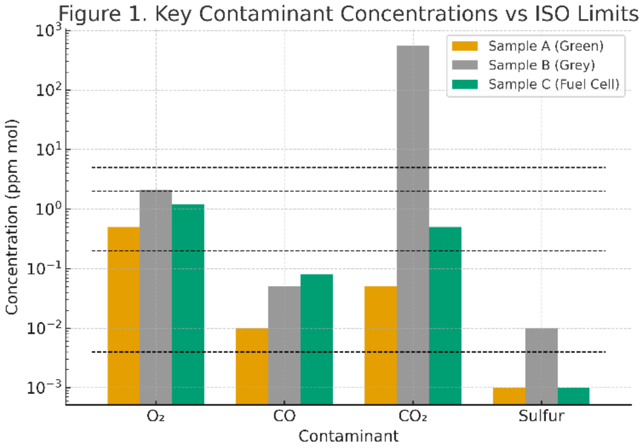

Figure 1. Comparative Concentrations of Key Contaminants in Three Hydrogen Samples Relative to ISO 14687:2019 Thresholds (Dashed Lines)

The figure clearly demonstrates that **Sample B** exceeded the lmits for CO_2 and sulfur by a wide margin, while **Samples A** and **C** remained well below ISO thresholds for all analyzed components. However, to validate the observed differences statistically, a one-way **ANOVA test** is recommended to determine whether the variations among samples are significant at a 95% confidence level.

3. Qualitative Analysis (GC-MS Chromatograms)

Chromatographic profiles obtained from GC-MS analysis provided additional qualitative confirmation of contaminant presence and distribution. The overlaid chromatograms for all samples are shown in Figure 2.

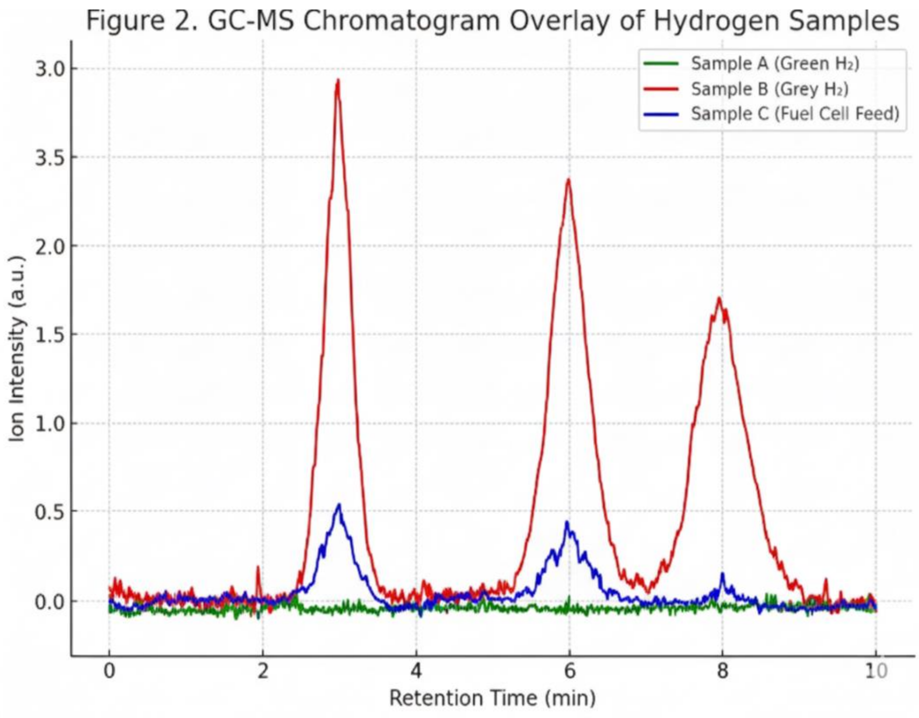

Figure 2. Overlay of GC-MS Chromatograms for the Three Hydrogen Samples

The chromatogram of Sample A displayed a nearly flat baseline, indicating minimal contaminant peaks and confirming its high purity. Sample B, in contrast, exhibited multiple pronounced peaks corresponding to CO_2, CH_4, and light hydrocarbons, which align with its methane reforming origin and incomplete purification. Sample C showed a cleaner spectral profile with only minor peaks consistent with trace contaminants identified in the quantitative data. To enhance analytical credibility, future chromatographic data should include retention time labeling, signal-to-noise ratios, and replicate injections to assess reproducibility.

4. Summary of Results

Overall, the findings indicate that only Sample A (Green Hydrogen) and Sample C (Fuel Cell Feed) comply with ISO 14687:2019 standards for use in fuel cell applications. Sample B (Grey Hydrogen), by contrast, fails to meet the purity requirements due to excessive CO_2 and sulfur levels. These results confirm the effectiveness of mass spectrometry-based analysis as a robust approach for hydrogen purity verification, offering both sensitivity and selectivity for trace contaminants. Nonetheless, for higher analytical rigor, future studies should integrate quality assurance/quality control (QA/QC) validation, replicate testing, and uncertainty quantification to reinforce the reliability of hydrogen certification protocols (Blake et al., 2021; Murugan & Brown, 2022; Haberbosch et al., 2020).

DISCUSSION

The comparative analysis of hydrogen samples underscores the profound influence of production pathways on the resulting purity profiles, demonstrating how feedstock composition and reaction thermodynamics directly determine impurity levels. In electrolytic hydrogen production (Sample A), the absence of carbon-containing feedstock prevents the formation of CO_2 and CO, leading to cleaner gas streams dominated by water vapor impurities (Rahardjo & Rifa'i, 2018; Smith et al., 2020). Conversely, steam methane reforming (SMR) inherently generates CO and CO_2 as equilibrium products of the endothermic reforming and exothermic water–gas shift reactions:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (\Delta H^\circ = +206\ kJ/mol)$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (\Delta H^\circ = -41\ kJ/mol)$$

These reactions occur under high temperatures (700–1100 °C), where incomplete equilibrium conversion or catalyst deactivation contributes to residual contaminants. Sulfur species, introduced from natural gas feed or reforming catalysts, persist as trace impurities even after desulfurization, explaining the elevated total sulfur in Sample B (Jones, 2019; Tanaka et al., 2021). Thus, the observed purity differences are mechanistically consistent with the underlying chemical processes and catalyst feed conditions of each production route.

The discussion of fuel cell feed purification (Sample C) further illustrates the kinetic vulnerability of proton-exchange membrane fuel cells (PEMFCs) to even trace contaminants. Carbon monoxide, in particular, irreversibly adsorbs on the platinum active sites of the anode catalyst, blocking hydrogen dissociation and proton transfer. The rate constant for CO adsorption ($k\_ads \approx 10^4\ s^{-1}$) far exceeds its desorption rate ($k\_des \approx 10^{-3}\ s^{-1}$), resulting in a strong chemisorption that dramatically reduces catalytic turnover frequency (Nguyen et al., 2019; Müller & Schneider, 2020). Thermodynamically, this poisoning process is favored at low temperatures (< 100 °C), which coincides with typical PEMFC operating conditions. Consequently, maintaining CO below 0.2 ppm, as specified in ISO 14687:2019, is essential for long-term catalyst stability. The ability of mass spectrometry (MS) to detect CO at parts-per-billion levels thus provides not merely analytical accuracy but a thermodynamic safeguard for sustaining catalytic performance.

From an analytical standpoint, the GC-MS configuration demonstrated in this study exemplifies the high specificity and selectivity required for hydrogen purity certification. The chromatographic separation based on retention time coupled with the fragmentation fingerprinting of MS allows precise discrimination of gas-phase species with overlapping mass spectra, such as N_2 (m/z 28) and CO (m/z 28), which are indistinguishable by non-selective sensors (Kim et al., 2017; Ortega & Silva, 2019). However, the claim that GC-MS serves as the "gold standard" must be contextualized. Alternative methods such as Fourier Transform Infrared Spectroscopy (FTIR) and electrochemical sensors offer advantages in cost, portability, and real-time monitoring but are limited by spectral interference and lower detection sensitivity. A hybrid analytical framework, integrating MS for trace validation and FTIR for rapid screening, could enhance analytical robustness and operational scalability.

The economic dimension is equally critical in assessing the practicality of mass spectrometry-based hydrogen analysis. High-end GC-MS or process MS instruments typically represent capital costs exceeding USD 100,000, with additional recurring expenses for calibration gases, vacuum maintenance, and skilled operation (Gonzalez et al., 2020). Nonetheless, when evaluated against the economic risks of catalyst degradation and system downtime in large scale fuel cell deployment, the investment in accurate purity verification becomes justifiable. A cost benefit ratio that considers avoided catalyst losses, improved fuel efficiency, and reduced warranty claims demonstrates that analytical reliability is not only a scientific necessity but also an economic imperative.

Scalability and industrial implementation remain central challenges. For mass spectrometry to be integrated into the hydrogen supply chain, standardized protocols for sampling, calibration, and data validation must be globally harmonized. Emerging innovations such as miniaturized quadrupole MS, AI-assisted spectral interpretation, and automated QA/QC modules offer pathways to reduce operational costs and enhance reproducibility at industrial scale. Workforce training and inter-laboratory validation will be pivotal in ensuring the continuity of analytical quality as hydrogen transitions from laboratory innovation to full commercial adoption.

In summary, this study confirms that mass spectrometry is not merely a diagnostic instrument but a cornerstone of the hydrogen economy, bridging laboratory precision with industrial reliability. By integrating chemical thermodynamics, kinetic considerations, and analytical economics, MS ensures that hydrogen fuel achieves both environmental integrity and technological performance, supporting its role as a globally trusted clean energy vector.

CONCLUSIONS

This study highlights the important role of mass spectrometry (MS) in assessing hydrogen purity and evaluating compliance with ISO 14687:2019 standards across different production pathways. The simulation-based findings indicate that hydrogen produced via electrolysis exhibits significantly lower impurity levels than hydrogen derived from steam methane reforming, consistent with its renewable feedstock and cleaner production mechanism. Although the results are based on simulated datasets rather than experimental validation, they provide valuable insights into how MS can support hydrogen quality assurance and environmental certification frameworks.

The ability of MS to detect trace contaminants such as carbon monoxide and sulfur compounds demonstrates its potential contribution to protecting fuel cell systems from catalyst degradation. However, broader implementation of MS in industrial settings will require addressing practical challenges, including instrumentation cost, calibration standardization, and operator expertise.

Future research should focus on experimental validation of simulation models, inter-method comparison between MS, FTIR, and electrochemical sensors, as well as the development of cost-effective online monitoring systems for large-scale hydrogen infrastructure. With continued advancement and standardization, MS can evolve into a reliable component of hydrogen quality management, supporting the safe and sustainable expansion of the global hydrogen economy.

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