Measurement of Gaseous Impurities in Hydrogen Fuel

Randall Bramston-Cook, Edward Bramston-Cook
Lotus Consulting, 5781 Campo Walk, Long Beach, California 90803

David Blekhman, PhD
California State University, Los Angeles, California 90032

INTRODUCTION

Hydrogen is on the cusp of being a major source of fuel for fuel cells and internal combustion engines for both motor vehicles and stationary sources. A big advantage of fuel cells is the dramatic reduction in emissions in mobile vehicles, and leaving the making of hydrogen to localized production sites where effective emission controls can be effectively implemented In 2004, former California Governor Arnold Schwarzenegger launched the Hydrogen Superhighway and committed California to building infrastructure needed to support fuel cell automobiles, especially fueling locations and fuel dispenser certifications. Presently, California has more than 42 hydrogen stations, congregated mostly around Los Angeles and the Bay Area and well over 450 fuel cell vehicles are in use in the state.[2]

The quality of this fuel is critical for proper operations of fuel cells. Its purity must be monitored to ensure that consumers receive product that has not been adulterated and is free of critical contaminants that can degrade performance, effect serious degradation of the life of fuel cells, and generate unintended pollutants. In 2005, California enacted legislation (Senate Bill 76, 2005[1]) to mandate monitoring of trace impurities in hydrogen fuel that is commercially sold in California for vehicle use. The allowable contaminant levels are listed by SAE International J2719 "Hydrogen Fuel Quality for Fuel Cell Vehicles", finalized in September 2011[3] and are listed in Table I. Some of the target analytes can have severe impact on performance of fuel cells used to power vehicles. Other gases are included to ensure the fuel has not been contaminated with air or other diluents. California Department of Food and Agriculture, Division of Measurement Standards was assigned the task to develop test methods for measuring these impurities, and then certify compliance with these standards by fuel suppliers and vendors.

California State University, Los Angeles, through its Power, Energy and Transportation curriculum, has embarked on a long range effort to become a leader in the area of teaching about sustainable energy systems and to engage in relevant applied research to mitigate the chronic problems of fossil fuel energy dependence and air pollution.[4] The centerpiece of the University's effort is the construction and deployment of a sustainable hydrogen production and dispensing facility. California State University, Los Angeles, is actively erecting a fueling station for public access, and is using analytical methods similar to those at the Division of Measurement Standards for testing fuel purity.

The report summarizes the design of instrumentation to measure most of the gaseous constituents and performance achieved in meeting the mandated fuel specifications. This list requires use of multiple detectors to attain detection below the required action levels, thus allowing a comfortable margin to properly assess the fuel. Most are detectable with gas chromatographic processes and include:

- Flame ionization detector for Total Hydrocarbons
- Electron capture detector for Oxygen
- Thermal conductivity detector for Helium
- Pulsed discharge detector for Nitrogen and Argon
- Flame ionization detector with reduction catalyst for Carbon Monoxide and Carbon Dioxide
- Pulsed flame photometric detector for Total Sulfur Compounds
- Mass spectrometer for Total Halogenated Compounds
- Ring-down spectrometers for Water and Formaldehyde/Ammonia

Measurement of formic acid and particulate size/concentration are not discussed here.

Table I. Hydrogen Fuel Specifications.

Specification	Value
Hydrogen Fuel Index (minimum, mol%)	99.97
Total Trace Gases (maximum, μmol/mol)	300
Water (maximum, μmol/mol)	5
Total Hydrocarbons (maximum, μmol/mol)	2
Oxygen (maximum, μmol/mol)	5
Helium (maximum, μmol/mol)	300
Nitrogen and Argon (maximum, μmol/mol)	100
Carbon Dioxide (maximum, μmol/mol)	2
Carbon Monoxide (maximum, μmol/mol)	0.2
Total Sulfur (maximum, μmol/mol)	0.004
Formaldehyde (maximum, μmol/mol)	0.01
Formic Acid (maximum, μmol/mol)	0.2
Ammonia (maximum, μmol/mol)	0.1
Total Halogenated Compounds (maximum, μmol/mol)	0.05
Particulates Size (maximum, μm)	10
Particulate Concentration (maximum, μg/L @ NTP)	1

EXPERIMENTAL

Analytes measureable by chromatographic techniques were determined by a Bruker SCION SQ Mass Spectrometer with two Bruker 456 Gas Chromatographs (Bruker, Fremont, Ca) configured in a master/slave setup so that a single sample was loaded up into multiple sample loops for each of the column and detector sets (Figure 1). With six detectors deployed for the chromatographic measurements, two chromatographs were set up by Lotus Consulting (Long Beach, Ca) to generate concentrations and special reporting generated a combined report with minimal operator interactions. To attain performance required for the very low levels of halogenates and sulfur compounds, large volume of sample was loaded (typically 300 ml) with mass flow controllers and focused with cryogenic traps and then desorbed for direct injection into the associated columns. The rest of the analytes were loaded into the system by fixed volume sample loops, with appropriate volumes for the target levels. All valves were actuated with micro-electric actuators and all column and detector flows were set through electronic flow controllers. A sixteen position automated sampler allowed unattended operations for multiple samples, pretested to withstand inlet pressures to 1,200 psiG. Typical incoming sample pressures were 1,000 psiG and had to be throttled down with a low-volume, high pressure regulator into a tolerable 20 psiG, to be within operating range of the remaining valves. When not in active use, this regulator was flushed with purge gas to eliminate possible component carry-over into the next sample.

Master Gas Chromatograph

Argon and Nitrogen
>	Sample Injection Volume: 2.0 ml
>	Columns - 6 feet, 1/8" OD, packed with Hayesep N plumbed in
>>		foreflush/backflush to vent and with Molecular Sieve 5A, plumbed in
>>		series/bypass
>	Column Temperature: 80 $^\circ$C
>	Carrier Gas: Helium, 10 ml/min with Electronic Flow Controller Type 23 and
>>		pressure regulator plumbed in parallel
>	Detector: Valco Pulsed Discharge Detector
>>		Detector Temperature: 100 $^\circ$C
>>		Detector Range: 10^{-11} amps/mv
>	Electrometer Scale: 1,000 volts

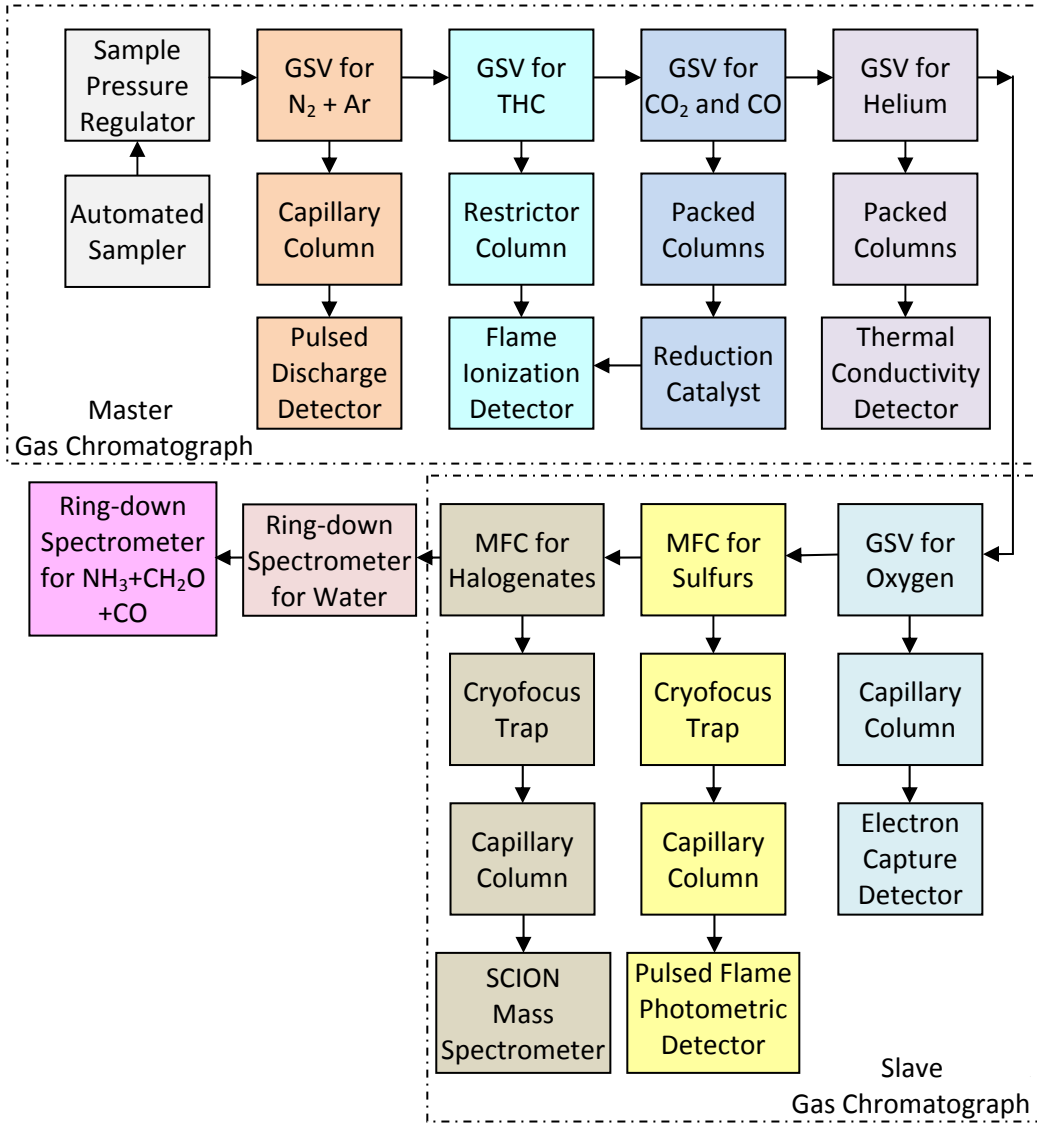Total Hydrocarbons (THC)
>	Sample Injection Volume: 0.25 ml
>	Detector: Flame Ionization Detector
>>		Detector Temperature: 120 $^\circ$C
>>		Detector Range: 10^{-12} amps/mv
>>		Electrometer Scale: 1,000 volts

Figure 1. Block Diagram for Hydrogen Fuel Analyzer.
GSV is Gas Sampling Valve and MFC is mass flow controller.

Carbon Dioxide and Carbon Monoxide

        Sample Injection Volume: 2.0 ml

        Columns - 6 feet, 1/8" OD, packed with Hayesep N plumbed in foreflush/backflush to vent and with Molecular Sieve 5A, plumbed in series/bypass

        Column Temperature: 80 ^{o}C

        Column Flow: Argon, 25.0 ml/min with Electronic Flow Controller Type 23 and pressure regulator plumbed in parallel

        Reduction Catalyst- 2" 10% Nickel Nitrate on Chromosorb PAW

        Reduction Catalyst Temperature: 380 ^{o}C

        Detector: Flame Ionization Detector

            Detector Temperature: 120 ^{o}C

            Detector Range: 10^{-12} amps/mv

            Electrometer Scale: 1,000 volts

Helium

        Sample Injection Volume: 0.25 ml

        Columns - 6 feet, 1/8" OD, packed with Hayesep N plumbed in foreflush/backflush to vent and 12 feet, 1/8" OD, packed with Molecular Sieve 5A

        Column Temperature: 80 ^{o}C

        Carrier Gas: Argon, 5.0 ml/min with Electronic Flow Controller Type 23 and pressure regulator plumbed in parallel

        Detector: Thermal Conductivity Detector

            Detector Temperature: 100 ^{o}C

            Filament Temperature: 250 ^{o}C

            Detector Range: 0.05

            Reference Flow: Argon 5.0 ml/min

Slave Gas Chromatograph

Oxygen

        Sample Injection Volume: 1.0 ml

        Columns – Hayesep N micro-packed column, 100/100 mesh, 1 meter, plumbed in series/bypass and Carboxene 1010, 0.53 mm ID, 30 m capillary column (Supelco, Bellefonte, Pa), with attached particle trap

        Micropacked Column Temperature: 65 ^{o}C

        Capillary Column Temperature: 50 ^{o}C

        Carrier Gas: Helium, 1 ml/min with Electronic Flow Controller Type 23

        Detector: Pulsed ^{63}Ni Electron Capture Detector

            Detector Temperature: 120 ^{o}C

            Detector Range: 10

            Detector Make-up: Nitrogen, 25 ml/min

Total Sulfur

    Cryofocus Parameters:

        Trap Cryogen: liquid nitrogen

        Trap: 90 µl empty tubing

            Initial Temperature: $-179\ ^{\circ}C$, hold 7.00 minutes

            Temperature Ramp: $+200\ ^{\circ}C/min$

            Temperature: $+140\ ^{\circ}C$, hold 69.27 minutes

    Mass Flow Controller setting: 50 ml/min, calibrated for hydrogen

    Sample Loading Volume: 300 ml

    Sample Processing Interval: 0.01 to 7.40 minutes

    On-column injection occurs at 7.40 minutes.

    Column: CP-Sil 5CB for Sulfur, 0.32 mm ID, 30 m, 4.0 µ film thickness (Agilent, Santa Clara, CA)

    Column Flow: 1.5 ml/min with Electronic Flow Controller Type 25

    Split State: Off

    Column Oven Cryogen: liquid nitrogen

    Column Temperature Program:

        Initial Temperature: $-40.0\ ^{\circ}C$, hold 15.00 minutes

        Temperature Ramp: $+3\ ^{\circ}C/min$

        Temperature: $+100.0\ ^{\circ}C$, hold 0.00 minutes

        Temperature Ramp: $+9\ ^{\circ}C/min$

        Final Temperature: $200.0\ ^{\circ}C$, hold 5.00 minutes

    Detector: Pulsed Flame Photometric Detector

    Detector Temperature: $120\ ^{\circ}C$

    Photomultiplier Voltage: 550 volts

    Gate Delay: 5.0 msec

    Gate Width: 10.0 msec

    Trigger Level: 200 mv

    Detector Range: 10^{-10} amps/mv

Sulfur compounds were individually identified and quantitated and then mathematically summed to get Total Sulfur.

Total Halogenates

    Cryofocus Parameters:

        Trap Cryogen: liquid nitrogen

        Trap: 90 µl empty tubing

            Initial Temperature: $-179\ ^{\circ}C$, hold 7.00 minutes

            Temperature Ramp: $+200\ ^{\circ}C/min$

            Temperature: $+140\ ^{\circ}C$, hold 69.27 minutes

    Mass Flow Controller setting: 50 ml/min, calibrated for hydrogen

    Sample Loading Volume: 300 ml

    Sample Processing Interval: 0.01 to 7.40 minutes

    On-column injection occurs at 7.40 minutes.

    Column: CP-Select 624, 0.32 mm ID, 30 m, 1.8 µ film thickness (Agilent, Santa Clara, CA)

    Column Flow: 2.0 ml/min with Electronic Flow Controller Type 25

    Split State: Off

Column Oven Cryogen: liquid nitrogen
Column Temperature Program:
      Initial Temperature: -40.0 ^{o}C, hold 15.00 minutes
      Temperature Ramp: +3 ^{o}C/min
      Temperature: +100.0 ^{o}C, hold 0.00 minutes
      Temperature Ramp: +9 ^{o}C/min
      Final Temperature: 200.0 ^{o}C, hold 5.00 minutes
Mass Spectrometer
      Scan Range for Full Scan: 45 to 300 m/z
      Mode: Single Quadrupole
      Source: EI
      Filament Emission Current: 80 μA
      Electron Energy: -70 eV
      Source Temperature: 150 ^{o}C
      Transfer Line Temperature: 150 ^{o}C
      Manifold Temperature: 40 ^{o}C
      Full Scan (for peak locating) and Selected Ions Monitoring (for monitoring)
      Extended Dynamic Range (EDR) activated
      Compound searches were conducted with NIST 11 Spectral Library.

Halogenates were individually identified and quantitated and then mathematically summed to get Total Halogenates.

Water content in hydrogen fuel was measured by cavity ring-down spectroscopy with Tiger Optics Halo Trace Level Moisture Analyzer (Warrington, Pa) without any pretreatment. Concentrations for formaldehyde and ammonia were determined with another cavity ring-down spectrometer, Tiger Optics Laser Trace Series (Warrington, Pa), specifically tuned for these two analytes. This technique measured concentrations directly from established absorbtivities at the target wavelength and did not require standards. The sample outlet from the chromatographs was plumbed directly to the spectrometers' inlet so that the sample could be analyzed by all techniques at the same time.

Halogenate standards were prepared in 6 liter Summa canister that had been evacuated to below 10 mTorr with Lotus Consulting CC-1 Canister Cleaner, and then humidified with 150 μL purified liquid water prior to loading. Working standards were made from TO-14 stock gases (1 μmol/mol, Restek, Bellefonte, Pa) by serial dilutions with Lotus Consulting PS-1 Pressure Station. Multi-level calibrations were performed by varying the sample loading time with a fixed flow rate into the cryofocus trap into a mass flow controller.[5] Calibrations for helium, oxygen, argon, nitrogen, methane, carbon dioxide and carbon monoxide were performed using a gravimetric mixture at the target levels from Scott-Marin, Inc. (Riverside, Ca). Multi-point standards were prepared by serial dilutions.

Sulfur standards were generated from permeation tubes (VICI Metronics, Poulsbro, Wa) and a VICI Metronics Dynacalibrator 500. Multiple calibration points were created by altering dilution flows within the Dynacalibrator.

RESULTS AND DISCUSSION

Nitrogen was readily separated from the other gases with a molecular sieve column and very detectable at the target level of 100 µmol/mol (Figure 2). Possible detector interferents were stripped away with the Hayesep N precolumn.

Figure 2. Chromatogram of 100 µmol/mol each of Argon and Nitrogen in Hydrogen.
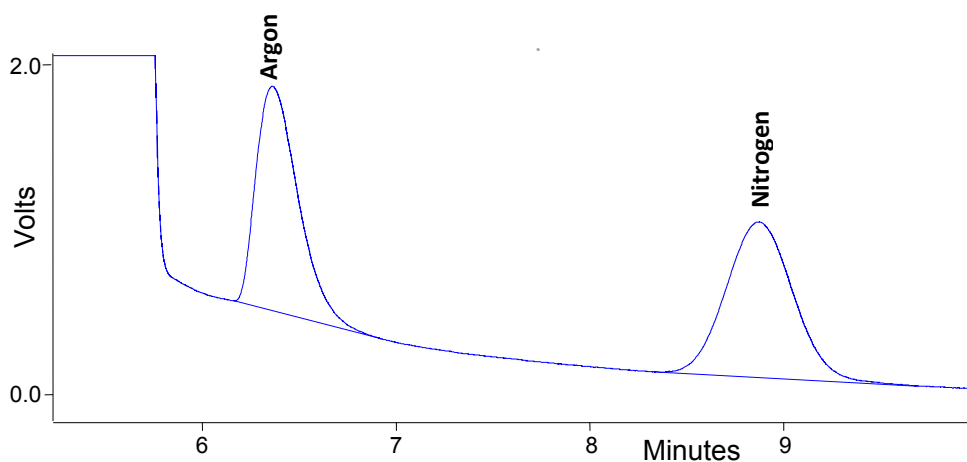
Argon and oxygen are extremely difficult to separate under reasonable conditions, and are often reported as a combined concentration. Since the action level for argon (100 µmol/mol) was dramatically above the target for oxygen (5 µmol/mol), argon dominated the eluting composite peak. The combined peak is reported here as "argon".

Oxygen concentrations were independently reported by electron capture detection that was sensitive to only this component and not to argon. Oxygen was very responsive to the electron capture detector and was readily identifiable and accurately measured at the 5 µmol/mol level (Figure 3). Possible detector interferents were stripped away with a micropacked Haysep N precolumn.

**Figure 3. Chromatogram of 5 μmol/mol Oxygen in Hydrogen.**
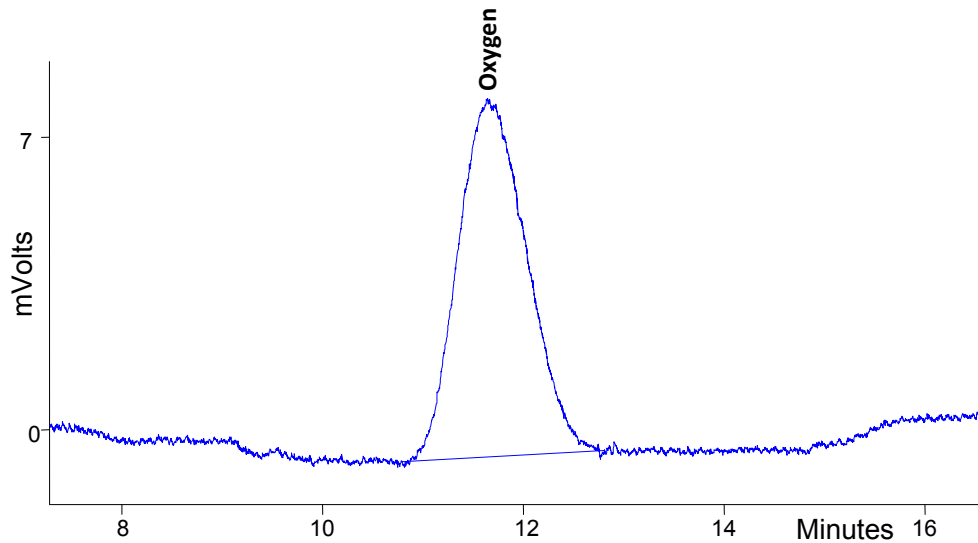
Total Hydrocarbons (THC) relied on the perfect carbon counter inherent in a high performance flame ionization detector to generate a measure of hydrocarbons in hydrogen reported as methane equivalent (Figure 4).[6] A fixed volume sample loop was directed to the detector without any chromatography. The square shape of the resulting peak was effectively the laminar transfer of the sample from the loop to the detector.

**Figure 4. Total Hydrocarbons measured at 2 μmol/mol.**
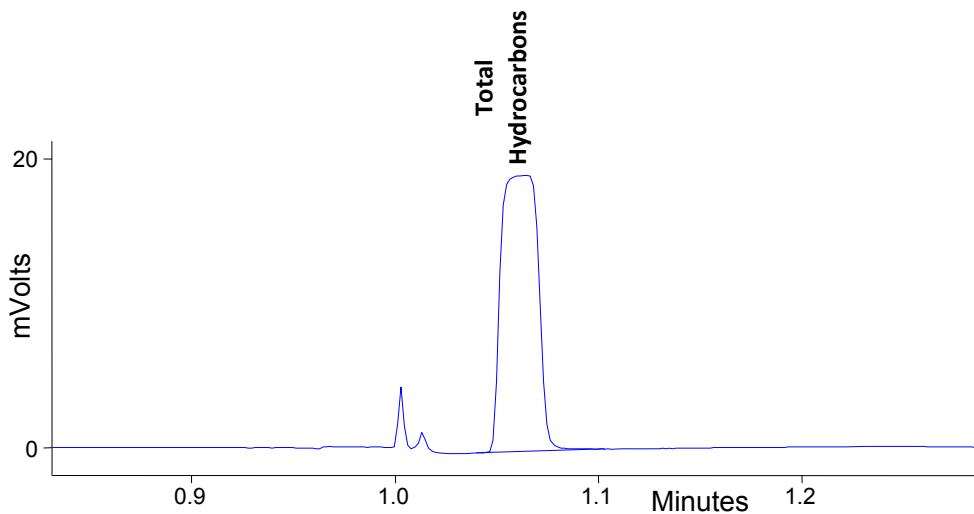
Helium could only be detected with a thermal conductivity detector using argon as the carrier and reference gases (Figure 5). Separation of helium from hydrogen was accomplished with a long molecular sieve column (12 feet) with a Hayesep N plumbed in to strip off possible interferents. Fortuitously, helium elutes prior to hydrogen to allow helium to be not overwhelmed by the major tail from the elution of hydrogen. Packed columns were used to allow larger sample injection volumes to be employed for enhanced sensitivity.

**Figure 5. Chromatogram of 300 µmol/mol Helium in Hydrogen.**
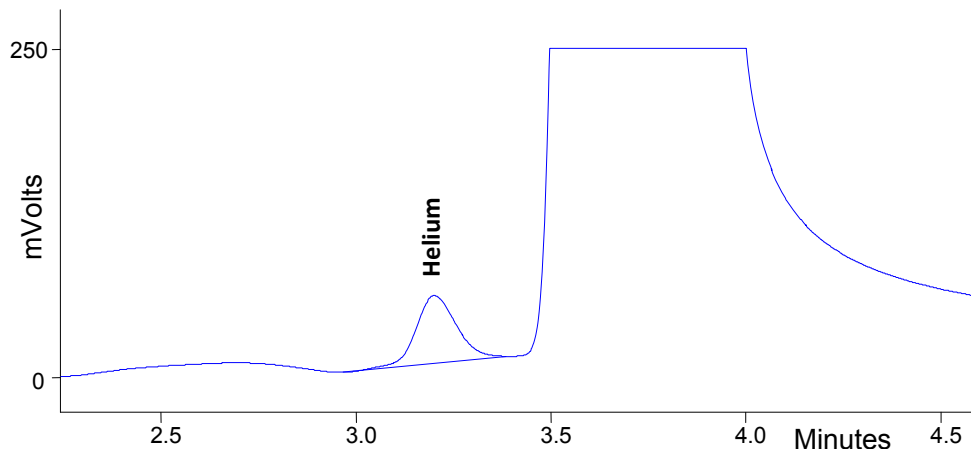
Carbon dioxide and carbon monoxide, at the mandated levels of 2 µmol/mol and 0.2 µmol/mol respectively, could not be monitored directly by common detectors.   To enhance detection, both were passed through a reduction catalyst for conversion to methane after chromatographic separation.   In both cases, possible interferents were stripped away with a Hayesep N precolumn. Carbon dioxide was eluted through the Hayesep N column prior to the backflush, but with the molecular sieve column bypassed (Figure 6). Carbon monoxide was separated from others with a molecular sieve column (Figure 7).   Both peaks were generated with the same injection.

**Figure 6. Chromatogram of 2 µmol/mol Carbon Dioxide in Hydrogen.**
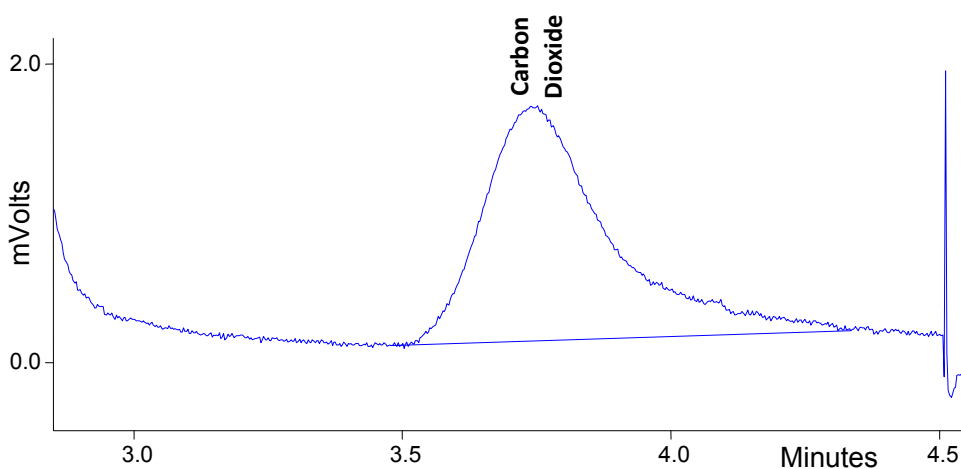
The mandated level of 0.2 µmol/mol for carbon monoxide approached the detection limit for the flame ionization after conversion to methane with a reduction catalyst. Larger injection volume had been attempted, but resulted severely distorted peak shapes due to the overloading of the column system.

Figure 7. Chromatogram of 0.4 µmol/mol Carbon Monoxide in Hydrogen.
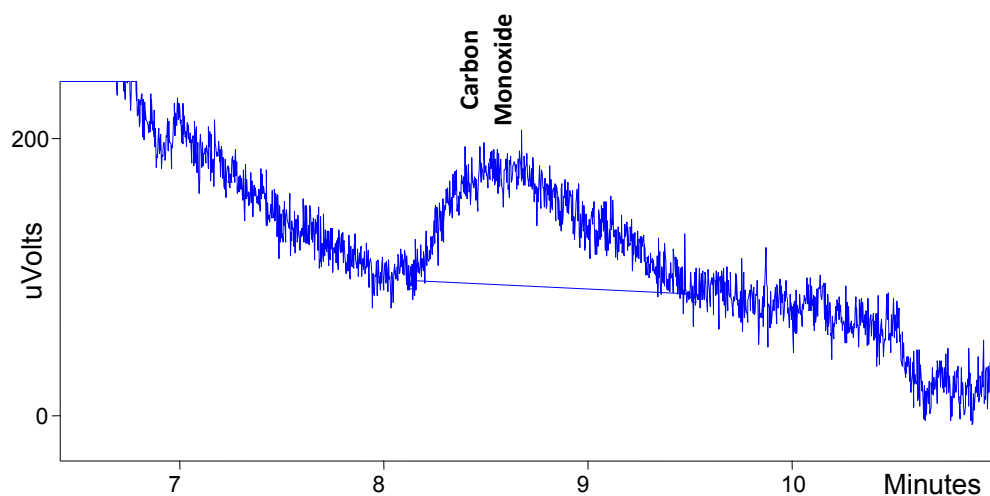
Sulfur compounds can have serious detrimental effects on the performance of fuel cells and must be individually measured at very low levels, especially as their concentrations are added together post-separation. A sample volume of 300 ml was loaded into a low volume cryo-focus trap and then injected into the column.

**Figure 8. Chromatogram of typical sulfur species
at concentrations in the range of 0.0001 to 0.001 µmol/mol,
with 300 sample loading.**
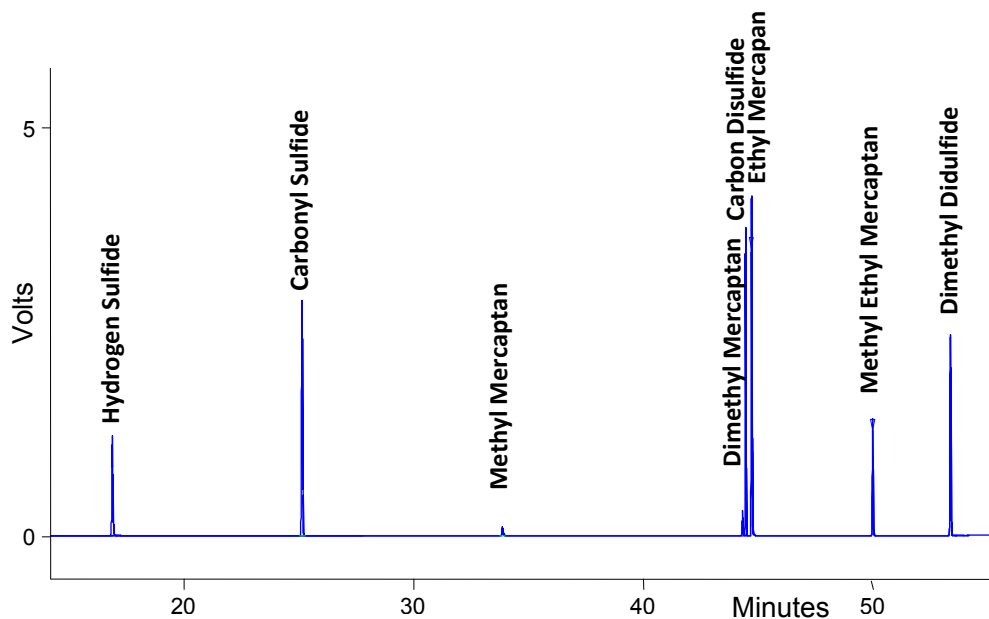
Well over 200 gaseous chemical species containing fluorine and chlorine atoms are possible, many labeled as Freons. They can only be properly identified and quantitated by mass spectrometry. The low levels require focusing a large volume into a cold trap and then injection into the column. Chromatogram of representative components is shown in Figure 9. The concentration for total halogenates was generated by summing up individual concentrations.

**Figure 9. Chromatogram of representative halogenates
at 0.01 µmol/mol each by mass spectrometry with 300 ml sample loading.**

SUMMARY

Maximum concentrations listed in specifications for hydrogen fuel are solely based on their effects on performance of a fuel cell, and are not related to capabilities of analytical equipment to measure them. Thus the design of the analyzer must conform to capabilities needed to measure these mandated levels with good precision and accuracy. A single detection approach is not feasible with the very low sensitivities required. Even with specifically tuned detectors, some target levels push intrinsic performance limits, especially carbon monoxide. And several others rely on separating individual species and then summing their concentrations to get a total, including total sulfurs and halogenated compounds. These very low action levels require large volumes focused down to a small injection volume in order to detect them.

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