Application Note

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Helium, Argon, Nitrogen, and Hydrocarbon Impurity Analysis in Hydrogen Using an Agilent 8890 GC and TCD/FID System

Author

Zhang Jie
Agilent Technologies
(Shanghai) Co. Ltd.

Abstract

In this application note, the analysis of helium (He), nitrogen (N_2), argon (Ar), and hydrocarbon (HC) impurities in hydrogen (H_2) was demonstrated on an Agilent 8890 gas chromatography (GC) system using gas sampling valve injection, capillary column separation, and flame ionization/thermal conductivity detectors (FID/TCD). The system repeatability, sensitivity, and linearity were evaluated. The excellent test results demonstrated that the 8890 GC can provide accurate and precise analysis of the target analytes. In addition, this system can be applied to the quality control of fuel cell vehicles that used hydrogen, according to different regulations such as ISO 14687-2019 and GB/T 37244-2018.

Introduction

As a desirable alternative energy source, hydrogen has caught increasing attention due to its zero emissions and high thermal value. Fuel cell vehicles (FCVs) powered by hydrogen are a key application area for hydrogen. Fuel cell performance and lifetime are closely related to hydrogen quality. Some impurities such as CO, sulfur-containing components, and ammonia will poison the catalyst in a fuel cell and degrade performance irreversibly. Other impurities such as CO_2, He, N_2, and Ar do not poison the fuel cell but dilute the hydrogen, thus reducing the cell potential and power output. To ensure optimal fuel cell performance and lifetime, hydrogen quality control that is based on accurate and precise analysis of hydrogen impurities from the manufacturing site to the gas refueling station is critical. The quality of FCVs that used hydrogen is regulated by international or regional standards in different countries and areas. European countries generally follow ISO 14687-2019[1], and China complies with GB/T 37244-2018[2] for FCV-grade hydrogen quality control.

Multiple analytical techniques are applied to the comprehensive analysis of hydrogen impurities. Among them, GC coupled with different types of sampling devices and detectors is the essential tool for certain types of impurity analysis. For example, gas chromatography/sulfur chemiluminescent detector/mass selective detector (GC/SCD/MSD) in tandem with preconcentration devices such as thermal desorption can quantify several-hundred ppt to single-digit ppb levels of sulfur compounds and 1 to 100 ppb organic halides. Injected through a purged gas sampling valve, 50 ppb CO and CO_2 in hydrogen can be analyzed by gas chromatography/pulsed discharge helium ionization detector (GC/PDHID).[3] He, Ar, and N_2 impurities at dozens of ppm can be detected by TCD and ppm-level hydrocarbons (HCs) can be determined by FID.[4]

In this application note, He, Ar, N_2, and HC analysis in hydrogen was demonstrated on an 8890 GC configured with gas sampling/switching valves and TCD/FID detectors. System performance was evaluated in terms of qualification/quantitation precision, limit of detection (LOD), and linearity.

Experimental

Chemicals and standards

Six cylinders of gas standards were purchased from Zhongce standards technology (Chengdu) Co. Ltd. Each sample contained He, Ar, N_2 and HCs at different concentrations. These samples were used for linearity and repeatability tests. He, Ar, N_2 and methane (CH_4) had six calibration levels and the other seven HCs had five calibration levels. Standard 1 (S1) to Standard 6 (S6) are sample names and the number in the name did not correspond to the calibration levels. For HCs (except methane), samples S2, S3, S4, S6 and S5 corresponded to calibration levels 1 to 5. For methane, S2, S3, S5, S1, S4 and S6 corresponded to calibration levels 1 to 6. And For He, Ar, N_2, samples 1 to 6 corresponded to calibration levels 1 to 6. The sample details are shown in Table 1.

Table 1. Composition of standard gases.

Compound	Concentration (µmol/mol)					
	S6	S5	S4	S3	S2	S1
He	610	299	98.9	52	30.4	10.2
Ar	300	99.2	49.2	20.2	10.1	5.11
N_2	304	100	49.7	20.5	10.2	5.17
CH_4	200	2.00	99.3	1	0.101	10.0
C_2H_6	1.03	2.05	0.52	0.206	0.105	NA
C_3H_8	0.981	1.95	0.495	0.196	0.1	NA
C_4H_{10}	1	1.99	0.505	0.2	0.1	NA
C_5H_{12}	0.974	1.94	0.491	0.195	0.102	NA
C_6H_{14}	0.970	1.93	0.489	0.194	0.099	NA
C_6H_6	0.970	1.93	0.489	0.194	0.099	NA
C_7H_8	0.972	1.93	0.490	0.194	0.0992	NA
H_2	Balance	Balance	Balance	Balance	Balance	Balance

Instrumentation and analytical conditions

The Agilent 8890 GC, configured with a split/splitless inlet, one 6-port valve, one 10-port valve, a TCD, and an FID, was used for target analysis. The system schematic is shown in Figure 1. Sample injection was conducted by the gas valves. Columns 1 and 2 were used for He, Ar, and N_2 analysis. The "heavier" components (> C1) were backflushed from column 1 before entering column 2. He, Ar, and N_2 separations were carried out on column 2. HC separation was performed on column 3.

Hydrogen was chosen as the carrier gas due to its high thermal conductivity, which increases the sensitivity of other components on TCD. Hydrogen carrier gas was supplied by a hydrogen generator (Peak Scientific), because hydrogen produced from other types of feedstocks and processes may contain targeted analytes as contaminants. The separations of He, Ar, N_2, and HCs were performed simultaneously in one run after the gas sampling. Detailed instrument parameters and column information are shown in Tables 2 and 3.

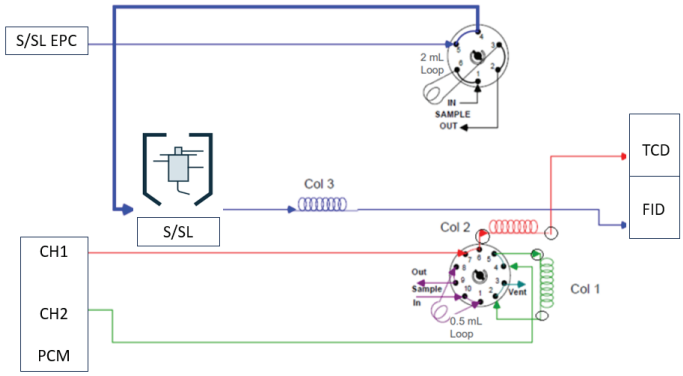


Figure 1. System schematic for He, Ar, N_2, and HC analysis.

Table 2. Analytical parameters of the Agilent 8890 GC with TCD/FID system.

Parameter	Value
He, Ar, and N_2 Analysis	
PCM CH_1/H_2	12.5 psi
PCM CH_2/H_2	10.0 psi
TCD Reference/H_2	18 mL/min
TCD Temperature	180 °C
TCD Make Up/H_2	Column + make up = 17 mL/min, constant
Valve 2 On	0.05 min
Valve 2 Off	2.2 min
HC Analysis	
Inlet Temperature	220 °C
Split Ratio	10:1
Column 3	8 mL/min (H_2)
FID Temperature	220 °C
Air	400 mL/min
Fuel Gas/H_2	30 mL/min
Make Up Gas/N_2	10 mL/min
Valve 1 On	0.01 min
Valve 1 Off	1.8 min
Oven Program	30 °C (4 min), 25 °C/min to 190 °C, hold 6.6 min

Table 3. Consumables of the Agilent 8890 GC with TCD/FID system.

Consumables	
He, Ar, and N_2 Analysis	**HC Analysis**
Column 1: Agilent J&W HP-PLOT Q, 30 m × 0.53 mm, 40 µm (p/n 19095P-QO4E)	**Column 3:** Agilent J&W GS-Alumina, 30 m, 0.53 mm (p/n 115-3532)
Column 2: Agilent J&W CP-Molsieve 5 Å, 50 m × 0.53 mm, 50 µm, with two particle traps (p/n CP7539PT)	**Inlet septa:** Agilent Nonstick Advanced Green (p/n 5183-4759) **Inlet liner:** Agilent Ultra Inert, low pressure drop split liner with glass wool (p/n 5190-2295)

Results and discussion

Purging the sample loop with gas sample

The sample loop/connection tubing and the standard gas cylinder regulator were filled with air before connecting to the hydrogen sample. It is necessary to purge the air out to analyze the trace level N_2 in hydrogen. A high sample flow rate (approximately 80 mL/min) was used to purge the whole sample flow path prior to the test. In this work, the purging result was verified by analyzing the hydrogen sample produced from the hydrogen generator. An effective purging (meaning a flat baseline) was observed within the retention time window of the nitrogen peak. After the purge time was determined, the calibration samples were analyzed for linearity and precision performance evaluation. Each time a standard gas cylinder was connected, the purging procedure was repeated. The overlaid chromatograms of S1 and S5 are shown in Figure 2. The concentration ratios of Ar and N_2 in the two samples were 0.988:1 and 0.992:1, respectively. Their response ratios in the chromatograms were close to 1:1, which was a good proof of effective purging. If the purging had not been sufficient, the response ratio would be notably less than 1:1 due to the interference of residual N_2 from air. For real FCV-grade hydrogen analysis, the sample is probably collected in a sample bomb cylinder. Usually, there are needle valves connected to the inlet and outlet of the bomb cylinder, and sometimes there is a pressure gauge connected before its outlet port. The internal volume of the bomb cylinder needle valve, the pressure gauge, and the connection tubing to the GC sampling valve sample inlet port will determine how long a purge is needed under certain purge flow rates. The purge time is recommended to be predetermined and applied to the future test to avoid the contamination of residual air in the N_2 analysis of the hydrogen sample.

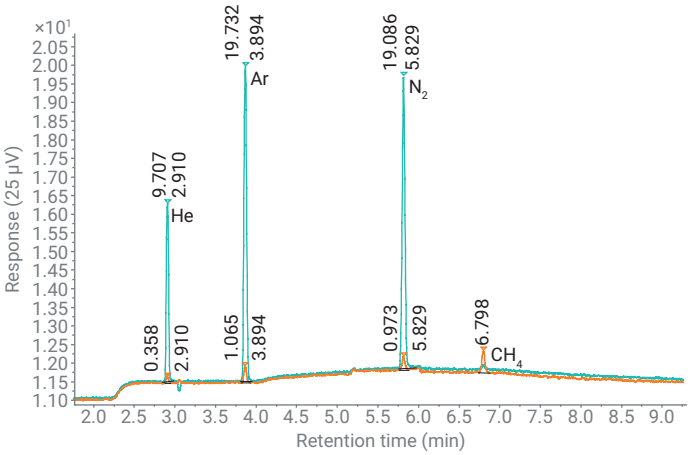


Figure 2. He, Ar, and N_2 in the chromatograms of S1 (orange) and S5 (blue). The RT and area are labeled at the tops of the peaks.

Argon and oxygen separation

Oxygen impurity also exists in hydrogen used in FCVs. Its analysis is usually recommended by using a non-GC technique because O_2 tends to be adsorbed onto the surface of the GC flow path through which the sample flows when using hydrogen carrier gas. This phenomenon can be observed especially for trace level O_2 analysis. Oxygen analysis in hydrogen was not the focus of this work, however, the good separation of O_2 and Ar on the selected Agilent CP-Molsieve column was necessary for accurate Ar quantitation without O_2 interference. The 50 m CP-Molsieve column was used for Ar and O_2 separation. The peaks of O_2 and Ar in the air sample are shown in Figure 3 (light blue). The enlarged peaks were for 300 ppm Ar and ~5 ppm O_2 in hydrogen matrix (blue). A baseline separation of Ar and O_2 was not achieved. However, the resolution obtained at the test concentration was good enough to ensure reproducible integration and accurate quantitation of the Ar peak, especially considering that the O_2 limit in FCV hydrogen required in both ISO 14687-2019 and GB/T 37244-2018 standards is only 5 ppm.

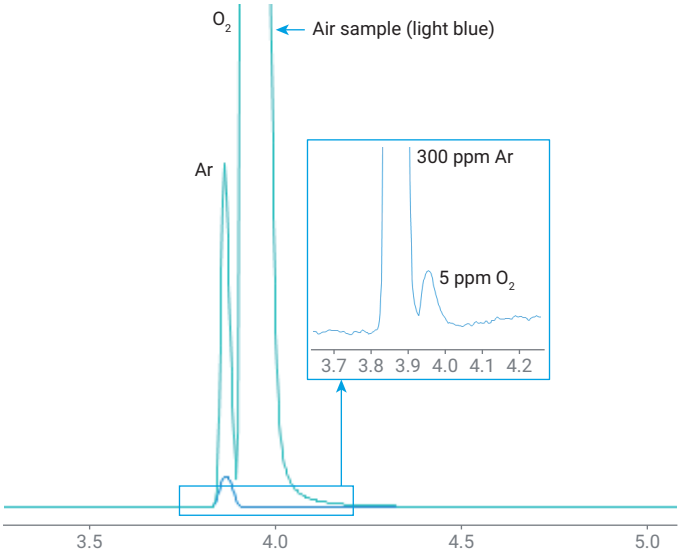


Figure 3. Ar and O_2 resolution on a 50 m Agilent J&W CP-Molsieve 5 Å column.

Helium, argon, and nitrogen analytical results

The analysis precision for He, Ar, and N_2 impurities was evaluated based on S2, S3, and S5 gases with six consecutive injections under each level. The retention time %RSD was from 0.008 to 0.087%. The area %RSD of the three components ranged from 0.2 to 3.0%, as shown in Figure 4. It is worth mentioning that the concentration of He, Ar, and N_2 in S2 was approximately one-tenth of their regulation limits in GB/T 37244. The response precision of He, Ar, and N_2 at such low concentration levels was less than 3.0%, which ensures the precise quality control of the target impurities in FCV hydrogen with a high level of confidence when using the described technique.

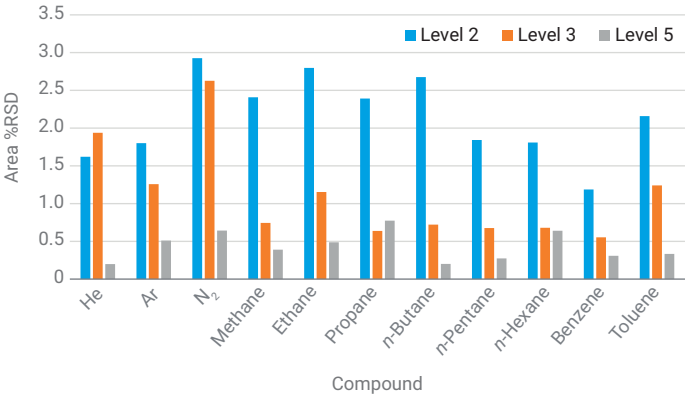


Figure 4. Response precision of He, Ar, N_2, and HCs at three concentration levels.

Linearity performance for the three compounds was evaluated using the six levels of calibration standards shown in Table 1. Each of the three linearity curves had a correlation coefficient (R^2) of no less than 0.9999. The quantitation accuracy across the calibration range was distributed from 92 to 113%. Ten injections of S1 were run for LOD calculation according to Equation 1. The calculated LODs of He, Ar, and N_2 were 2.6, 0.6, and 0.8 ppm, respectively (the detailed results are shown in the Appendix).

Equation 1.

$$LOD = 3 \times SD$$

SD: Standard deviation of analyte calculated concentrations.

Hydrocarbon results

There are two ways to analyze HC impurities in hydrogen. The HCs can be measured as one combined peak and reported as total hydrocarbons (THCs) based on FID response without separation and identification of individual HCs. The other way is to separate and detect each HC, then add their concentration to get the amount of THCs. In this work, the second approach was applied for the THCs impurity test.

Natural gas is the primary source of hydrogen production worldwide, followed by coal in China. In this study, the calibration gas included six normal HCs and two aromatic HCs. These eight compounds were analyzed as representative HCs because they are the main HC impurities that exist in natural gas and coal-based hydrogen manufacturing processes.

The elution order of HCs on the Agilent GS-Alumina column is shown in Figure 5. Their response precision was tested by consecutive analysis of S3, S4, and S5 with six replicate runs for each standard. S3, S4, and S5 corresponded to HC calibration levels of 2, 3, and 5. The HC area %RSD was distributed from 0.201 to 2.797%, as shown in Figure 4. The retention time %RSD was from 0.015 to 0.239%, which was not as good as the RT %RSD obtained on the CP-Molsieve 5 Å column. The RT shift on the GS-Alumina column was mainly caused by moisture in the carrier gas. To improve RT stability, a moisture trap can be used in the carrier gas supply line. In addition, it is recommended that the oven temperature is kept at 150 °C when no sample is running. These two measures can help reduce moisture accumulation on the GS-Alumina column and improve RT stability.

The control limits of methane and HCs (except methane) in FCV-grade hydrogen is 100 and 2 ppm, as required in ISO 14687-2019. In this work, methane linearity was evaluated across a concentration range of three orders of magnitude (from 0.1 to 200 ppm). The linearity of other HCs was evaluated from 0.1 to 2 ppm. All compounds generated outstanding linearity results with $R^2 > 0.9998$. The method LOD for HCs was calculated based on methane, with the assumption that all HCs have the same response as methane. Ten consecutive analyses of 0.1 ppm methane gave an LOD of 0.019 ppm (Equation 1). The quantitation accuracy across the linearity range was 98.7 to 116.1% for methane, and 96.4 to 111.9% for other HCs, demonstrating the accurate quantitation capability of the test system.

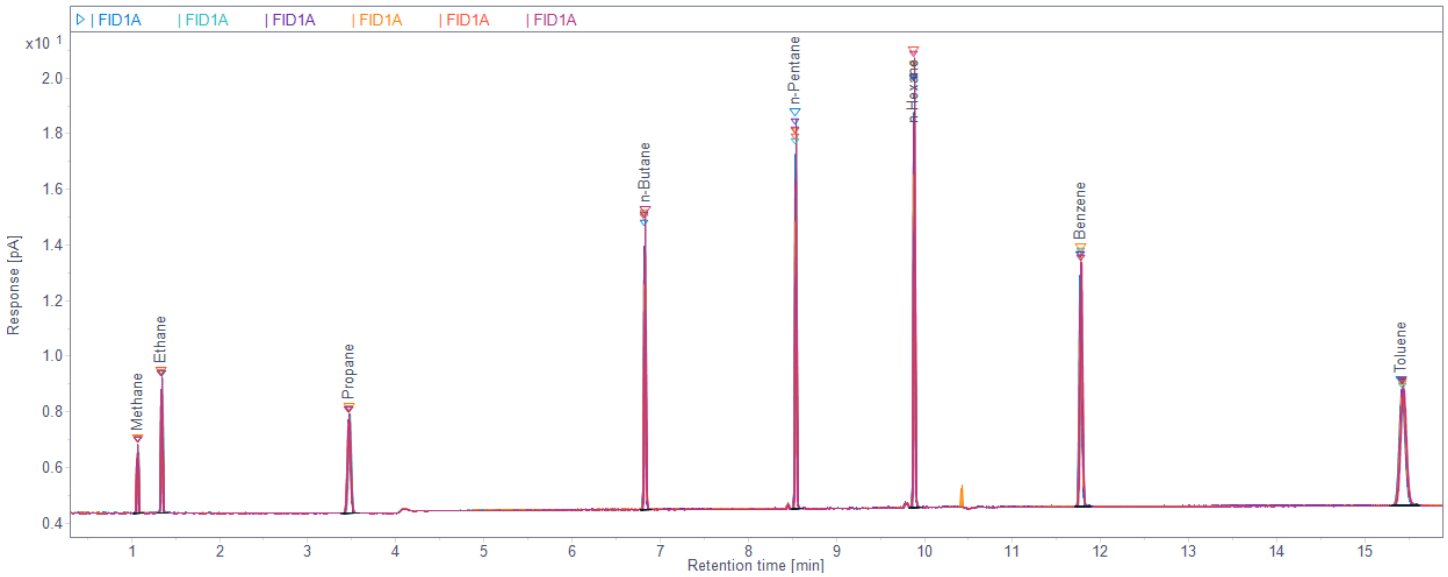


Figure 5. Overlaid chromatograms of HCs in gas standard S5 (n = 6).

Conclusion

In this application note, an Agilent 8890 GC configured with two gas valves, two types of detectors (FID/TCD), and three capillary PLOT columns, was applied to He, Ar, N_2, and HC impurity analysis in hydrogen. The system performance was evaluated using certified gas standards. The comprehensive assessment covered RT and response repeatability, linearity, quantitation accuracy, and method LODs. The area precision of all test compounds was better than 3.0% at the low concentration level. The LODs for He, Ar, N_2, and methane were 2.6, 0.6, 0.8, and 0.019 ppm, which were far below their quality limits in the ISO 14687-2019 and GB/T 37244-2018 standards. The quantitation accuracy was 92 to 116% across the calibration range. These excellent results demonstrate that the 8890 GC, together with the selected Agilent GC columns, can provide accurate, precise, and sensitive analysis of target components. The test system can reliably be used for the quality control of He, Ar, N_2, CH_4, and other HCs in FCV-grade hydrogen, according to ISO 14687-2019 and GB/T 37244-2018 requirements.

References

1. ISO 14687-2019, Hydrogen Fuel Quality—Product Specification.
2. GB/T 37244-2018, Fuel Specification for Proton Exchange Membrane Fuel Cell Vehicles—Hydrogen.
3. Analysis of Trace Carbon Dioxide and Permanent Gas Impurities in Fuel Cell Hydrogen and High-Purity Hydrogen by GC, *Agilent Technologies application note*, publication number 5994-4415EN, **2021**.
4. T/CECA-G 0179-2022, Determination of Helium, Argon, Nitrogen and Total Hydrocarbons in Hydrogen—Gas Chromatography-Thermal Conductivity and Flame Ionization Detector Method.

Appendix

Table A1. Linearity performance of He, Ar, N_2, and HCs.

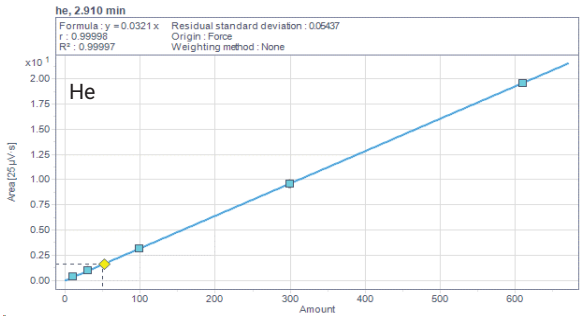
Compounds	CF Formula (Origin: Force)	R^2	Concentration Range (µmol/mol)
Helium	y = 0.0321x	0.99997	10 to 610
Argon	y = 0.1999x	0.99997	5 to 300
Nitrogen	y = 0.1928x	0.99993	5 to 300
Methane	y = 1.4756x	0.99999	0.1 to 200
Ethane	y = 2.9391x	0.99985	0.1 to 2
Propane	y = 4.3577x	0.99993	0.1 to 2
n-Butane	y = 5.7788x	0.99994	0.1 to 2
n-Pentane	y = 7.1043x	0.99998	0.1 to 2
n-Hexane	y = 8.6881x	0.99999	0.1 to 2
Benzene	y = 8.6418x	1.00000	0.1 to 2
Toluene	y = 10.0633x	0.99999	0.1 to 2

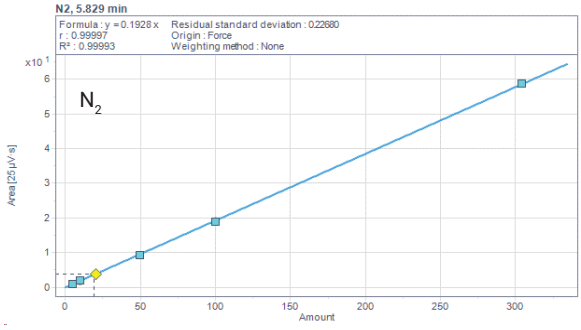
Table A2. Quantitation accuracy across tested calibration levels.

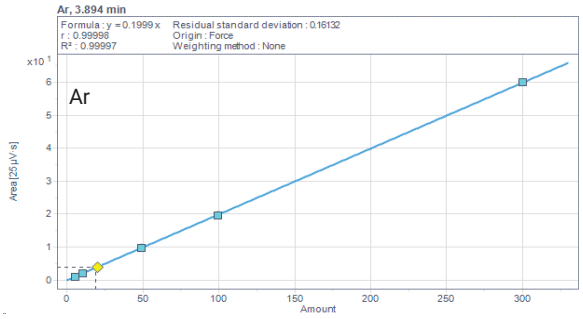
Compounds	Quantitation Accuracy (%)					
	L6	L5	L4	L3	L2	L1
Helium	102.7	99.9	97.8	99.8	104.9	112.9
Argon	100.1	98.2	98.6	93.8	103.1	104.7
Nitrogen	101.6	97.6	96.5	96.8	96.5	92.3
Methane	99.8	98.7	99.9	102.3	116.1	104.6
Ethane	103.0	102.1	105.5	104.9	108.2	
Propane	97.8	97.7	101.6	103.6	106.6	
n-Butane	99.7	99.3	101.9	101.1	111.9	
n-Pentane	97.7	97.1	98.0	99.3	104.4	
n-Hexane	96.5	96.6	97.5	99.3	101.9	
Benzene	97.3	96.4	97.6	97.4	101.4	
Toluene	96.8	96.5	98.5	100.2	100.0	

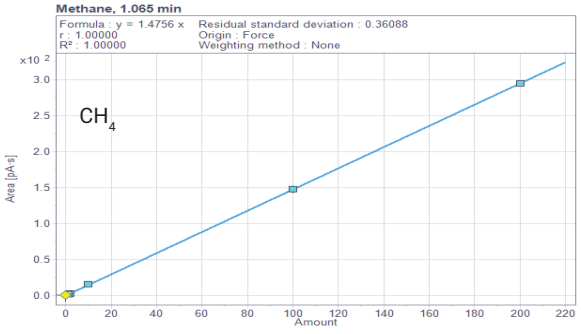
Table A3. LODs determination of He, Ar, N_2, and CH_4.

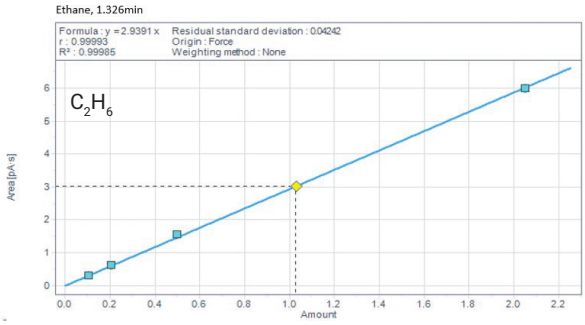
Compound	Calculated Concentration (ppm) of 10 Injections for LOD Measurement											
	Injection 1	Injection 2	Injection 3	Injection 4	Injection 5	Injection 6	Injection 7	Injection 8	Injection 9	Injection 10	SD (ppm)	LOD (ppm)
He	30.810	30.779	30.498	31.620	30.062	30.779	30.779	28.660	31.090	31.838	0.877549	2.633
Ar	10.335	10.040	10.445	10.240	10.205	10.005	10.475	10.570	10.045	10.140	0.199725	0.599
N_2	9.393	9.404	10.109	9.787	9.969	9.855	9.549	9.611	9.881	9.891	0.243362	0.730
CH_4	0.116	0.116	0.114	0.129	0.132	0.116	0.126	0.125	0.118	0.118	0.006462	0.019

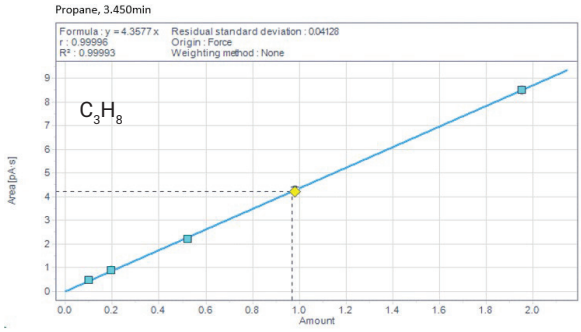












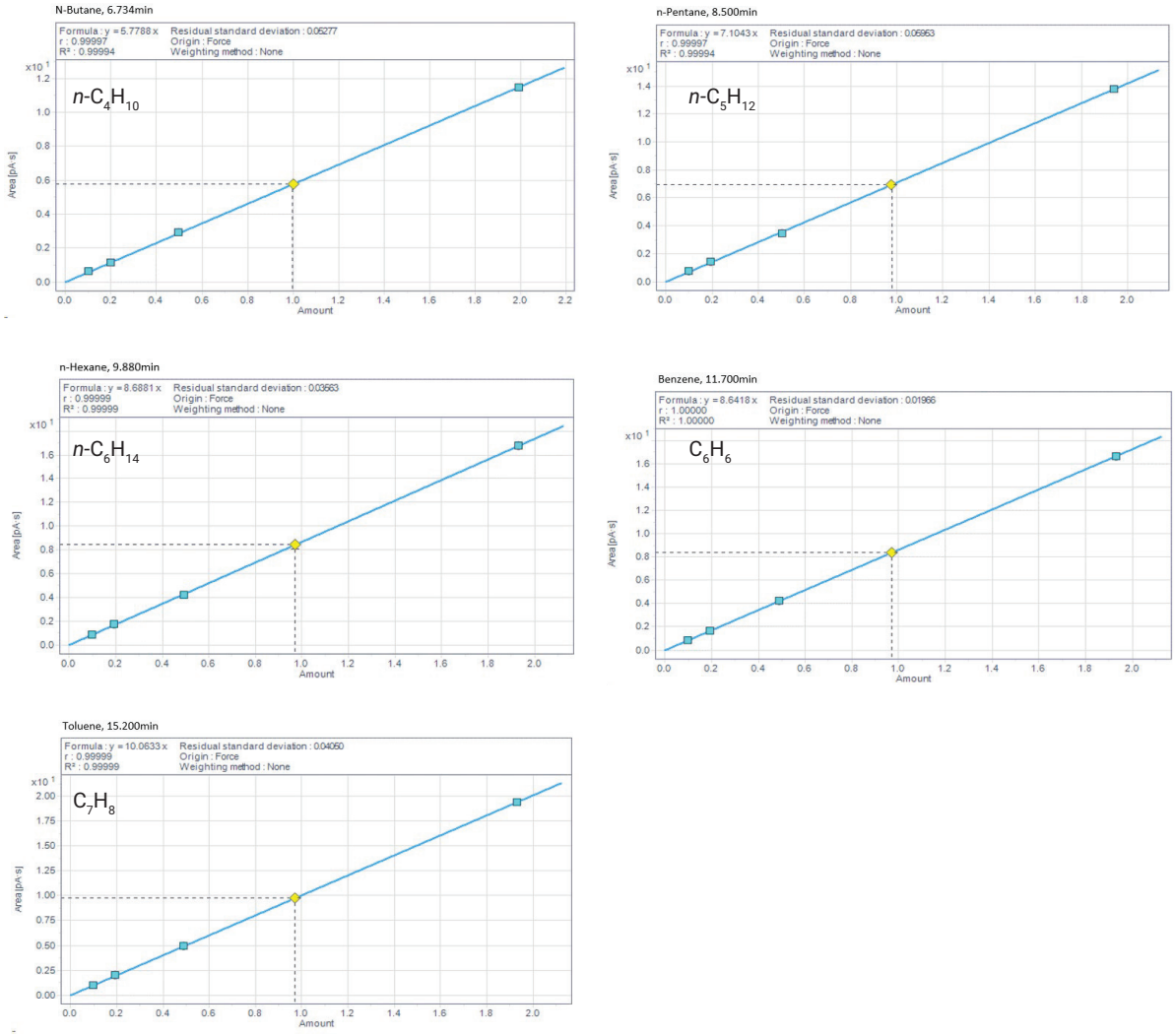


Figure A1. Calibration curves of He, Ar, N_2, and HC impurities.

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