

APPLICATION NOTE

LD25-01

PST
PROCESS SENSING
TECHNOLOGIES



Analysis of trace impurities in UHP hydrogen chloride (HCl)



▲ MultiDetek3

▲ PlasmaDetek2
patent US 9,310,308 B2

The HCl is used at different functions in the industrial gas market. It is used for manufacturing silicones, pyrogenic silica and polysilicon for the solar.

The colorless, water-soluble gas is also an important processing aid for the semiconductor industry. Hydrogen chloride is used for etching hyper pure silicon wafers and for cleaning plant components. However, the media used must be extremely pure to prevent contamination and by the way is very difficult to be produced and controlled by gas producers.

The analysis of purity hydrogen chloride is a very complex application that requires a strong knowhow in the gas chromatography along with a solid platform using the proper hardware materials.

The demand of the UHP HCL in the semiconductor being stronger every year, then required LDetek to work and develop the proper gas analysis solution align with the industry.

LDETEK SOLUTION

The purity of HCL can be qualified with the use of the MultiDetek3 gas chromatograph configured with PED.

The unit is configured with a measuring range of 0-10ppm with Idl of 10ppb for impurities O₂-N₂-CH₄-CO₂-CO and another measuring range of 0-5ppm with Idl of 5ppb for impurities C₂H₆-C₃H₈-C₄H₁₀ and a third measuring range of 0-200ppm with Idl of 45ppb for impurity H₂ in a sample gas UHP hydrogen chloride (HCL)). The PED (plasma emission detector) has been mounted in the GC to measure the ppb impurities in UHP HCL using Helium as carrier gas. All previously listed impurities are measured within one single analyser.

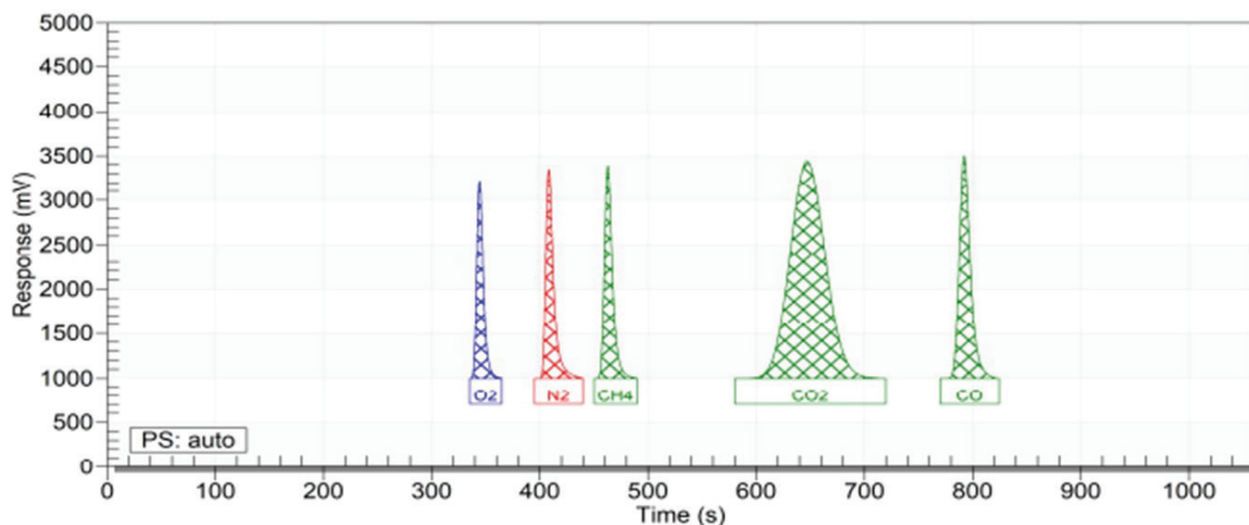
As the hydrogen chloride is listed as a very toxic and corrosive (aggressive) gas, our GC configuration offers here a specific configuration of the sample flow path. A multiport selection valve mounted in a purged box which is purged with the helium carrier gas ensures the sample is not in contact with its surrounding air. The selection valve ensures to minimize the period which the HCL is going into the injection's valves and the sample loops. A specific sequence is configured to have mostly helium in the GC sample flow path with a small period having the HCL sample filling the sampling loops for proper analysis. The sequence is built in consequence to properly purged the loops prior to fill with HCL sample gas. This solution offers the GC to have an improved safety level and have an extended lifetime due to the limited time of the analytical flow path in contact with the HCL.

The valves, fittings, columns and piping are all properly configured with Hastelloy as long as proper coating to ensure the durability of the system over the years.

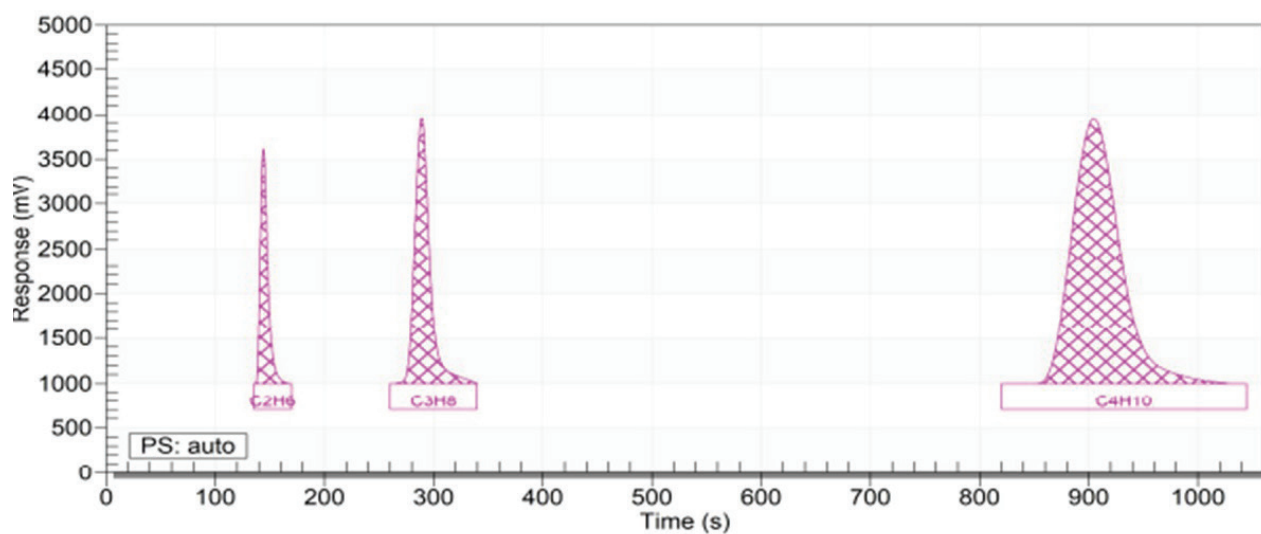
Other configurations and ranges/Idls are also available on demand. The parameters mostly depend on the site production requirements and process.

RESULTS

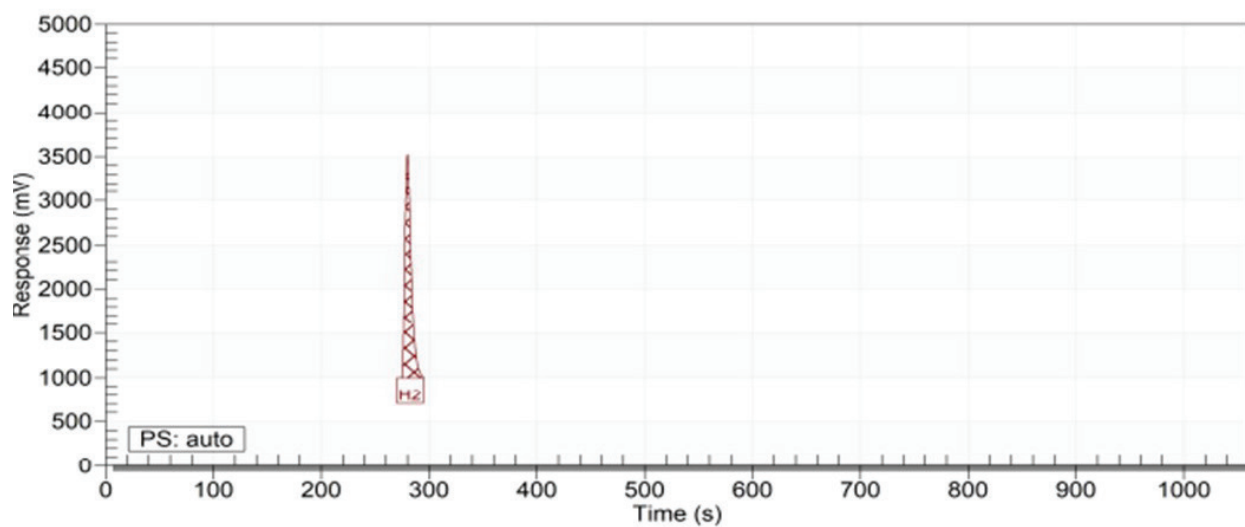
A series of chromatograms (Span calibration) of trace impurities O₂-N₂-CH₄-CO₂-CO-C₂H₆-C₃H₈-C₄H₁₀-H₂ in balance gas UHP hydrogen chloride (HCL)



Peak	Unit	Calibration Value	_Area Counts
O ₂	ppm	9.02	4426
N ₂	ppm	9.62	21085
CH ₄	ppm	9.55	5961
CO ₂	ppm	9.84	7982
CO	ppm	10.00	7018



Peak	Unit	Calibration Value	_Area Counts
C ₂ H ₆	ppm	5.06	8017
C ₃ H ₈	ppm	5.06	13025
C ₄ H ₁₀	ppm	4.98	16111



Peak	Unit	Calibration Value	_Area Counts
H ₂	ppm	200.00	7686

Limit of detection (based on 3 times the noise level from a blank)

COMPONENTS	CONCENTRATION (ppm)	PEAK HEIGHT	NOISE	LDL (3X NOISE)
O2	9.02	2250mV	0.74mV	9ppb
N2	9.62	2350mV	0.76mV	9ppb
CH4	9.55	2400mV	0.76mV	9ppb
CO2	9.84	2500mV	0.74mV	9ppb
CO	10.0	2500mV	0.74mV	9ppb
C2H6	5.06	2600mV	0.96mV	6ppb
C3H8	5.06	3000mV	0.91mV	5ppb
C4H10	4.98	3000mV	0.87mV	5ppb
H2	200.0	2500mV	0.19mV	46ppb

Note: other LDL could be obtained with different injection volume and chromatographic condition

Repeatability: Based on the GC standards. Using 6 of 10 consecutive runs, being lower than 5% of 3*CV%

Peak	Average	Standard Deviation	Coef. Variation (%)	3 * CV (%)	Status
CH4	0.97917500 ppm	0.00213700	0.22	0.65	Accepted
CO	1.10246500 ppm	0.00243217	0.22	0.66	Accepted
CO2	1.24331167 ppm	0.00208388	0.17	0.50	Accepted
H2	1.35396000 ppm	0.01140990	0.84	2.53	Accepted
N2	1.25846333 ppm	0.00197153	0.16	0.47	Accepted
O2	0.86366167 ppm	0.00320417	0.37	1.11	Accepted

Peak	Average	Standard Deviation	Coef. Variation (%)	3 * CV (%)	Status
C2H6	0.58640000 ppm	0.00185257	0.32	0.95	Accepted
C3H8	0.55372833 ppm	0.00216130	0.39	1.17	Accepted
C4H10	0.55271833 ppm	0.00051949	0.09	0.28	Accepted
THC	2.26975333 ppm	0.00591391	0.26	0.78	Accepted

Start Date	H2	O2	CH4	N2	CO2	CO
2024-11-21 23:41	1.339 ppm	0.866 ppm	0.981 ppm	1.255 ppm	1.245 ppm	1.099 ppm
2024-11-21 23:23	1.342 ppm	0.867 ppm	0.978 ppm	1.259 ppm	1.240 ppm	1.101 ppm
2024-11-21 23:05	1.361 ppm	0.865 ppm	0.976 ppm	1.258 ppm	1.243 ppm	1.105 ppm
2024-11-21 22:48	1.360 ppm	0.863 ppm	0.978 ppm	1.259 ppm	1.243 ppm	1.105 ppm
2024-11-21 22:30	1.353 ppm	0.863 ppm	0.981 ppm	1.258 ppm	1.244 ppm	1.104 ppm
2024-11-21 22:12	1.368 ppm	0.858 ppm	0.981 ppm	1.261 ppm	1.246 ppm	1.102 ppm

Model : MultiDetek3
TagName : MD3-0057824
Method : HCL

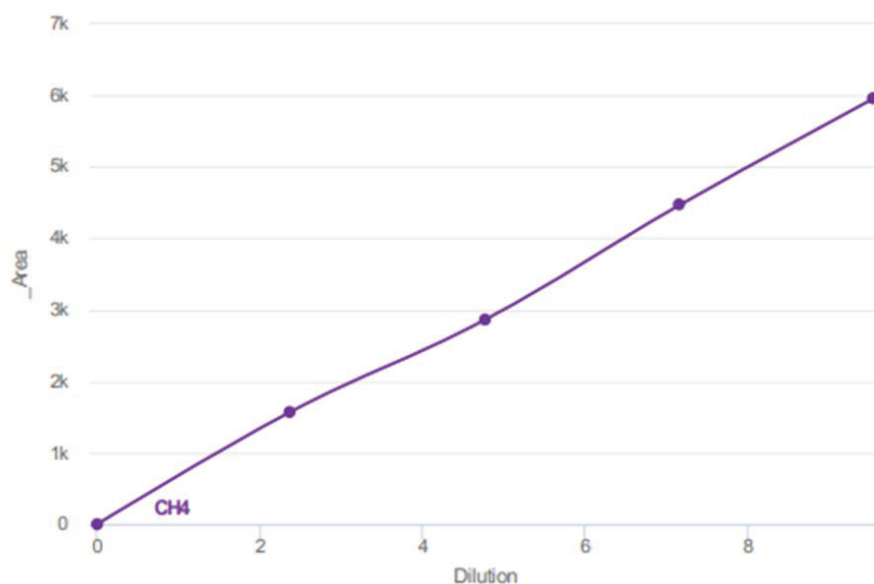
Start Date	THC	C2H6	C3H8	C4H10
2024-11-22 8:40	2.277 ppm	0.588 ppm	0.557 ppm	0.553 ppm
2024-11-22 8:23	2.274 ppm	0.587 ppm	0.555 ppm	0.553 ppm
2024-11-22 8:05	2.272 ppm	0.587 ppm	0.554 ppm	0.553 ppm
2024-11-22 7:47	2.270 ppm	0.587 ppm	0.553 ppm	0.553 ppm
2024-11-22 7:29	2.265 ppm	0.585 ppm	0.552 ppm	0.552 ppm
2024-11-22 7:12	2.261 ppm	0.583 ppm	0.551 ppm	0.552 ppm

Model : MultiDetek3
 TagName : MD3-0057824
 Method : HCL

Linearity: Based on the GC standards. A linear curve having its R2 at a value between 0.998 and 1.00.

CH4 (ppm)

Dilution	_Area
9.550	5961.000
7.160	4467.000
4.770	2864.000
2.380	1575.000
0.000	0.000

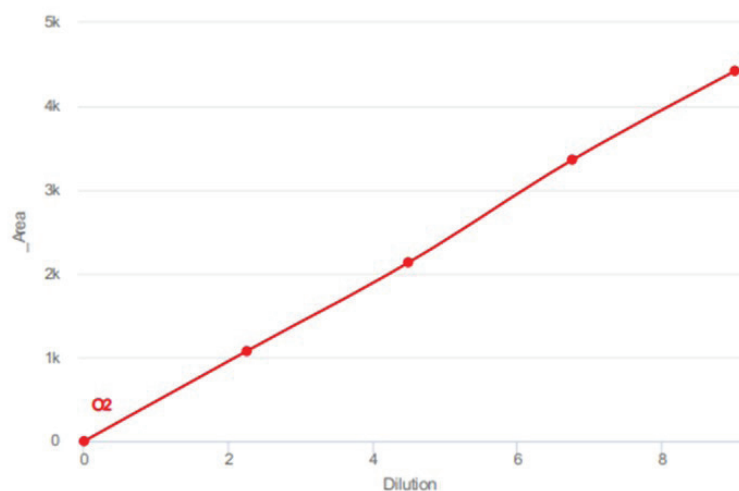


Coefficient correlation (R^2) = 0.9991

**Linearity Test
Accepted**

O2 (ppm)

Dilution	_Area
9.020	4426.000
6.760	3361.000
4.500	2140.000
2.250	1076.000
0.000	0.000

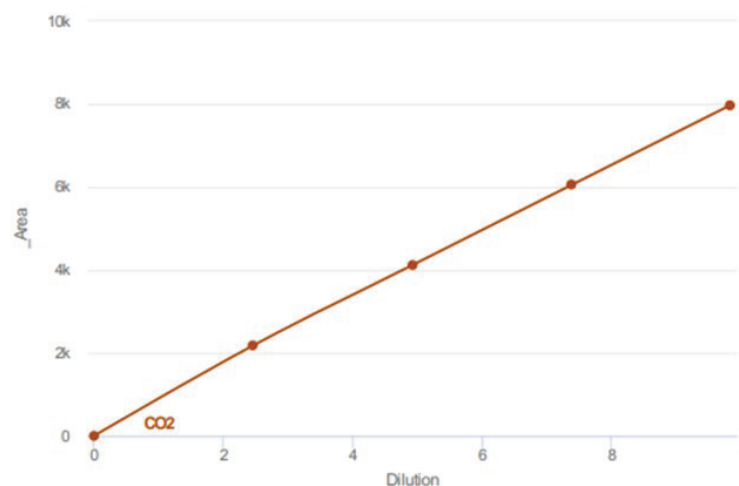


Coefficient correlation (R^2) = 0.9995

Linearity Test
Accepted

CO2 (ppm)

Dilution	_Area
9.840	7982.000
7.380	6053.000
4.920	4120.000
2.460	2180.000
0.000	0.000

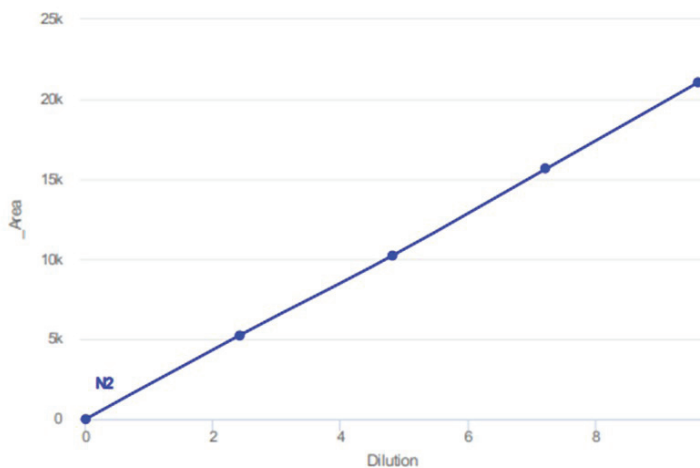


Coefficient correlation (R^2) = 0.9994

Linearity Test
Accepted

N2 (ppm)

Dilution	_Area
9.620	21085.000
7.220	15649.000
4.810	10225.000
2.420	5254.000
0.000	0.000

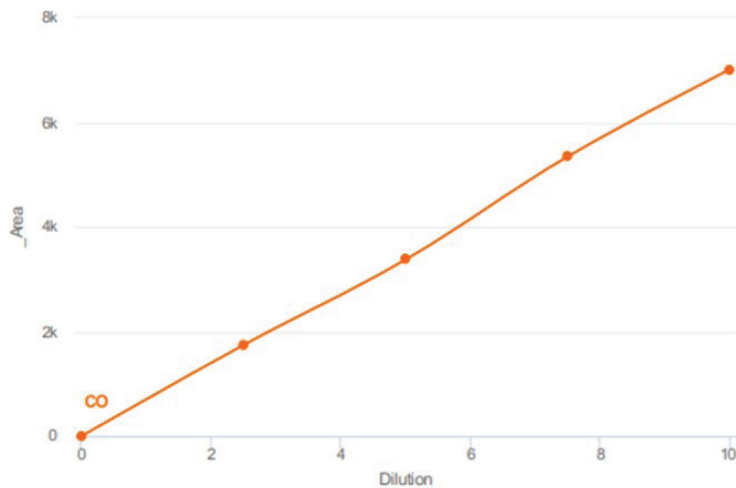


Coefficient correlation (R^2) = 0.9997

Linearity Test
Accepted

CO (ppm)

Dilution	_Area
10.000	7018.000
7.500	5352.000
5.000	3382.000
2.500	1744.000
0.000	0.000

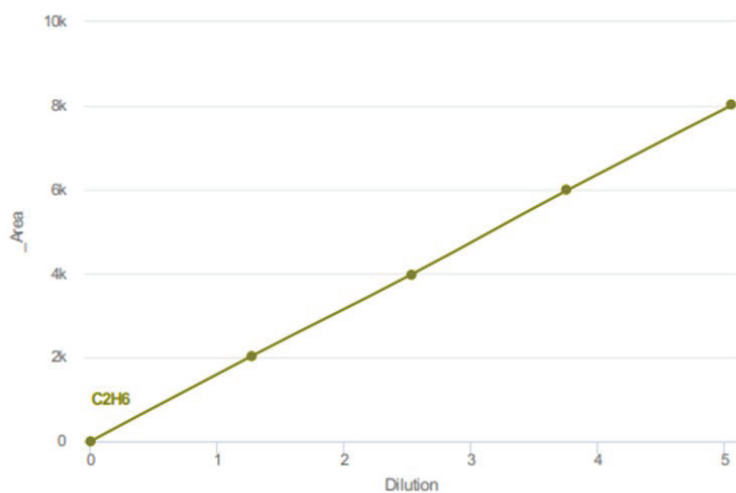


Coefficient correlation (R^2) = 0.9993

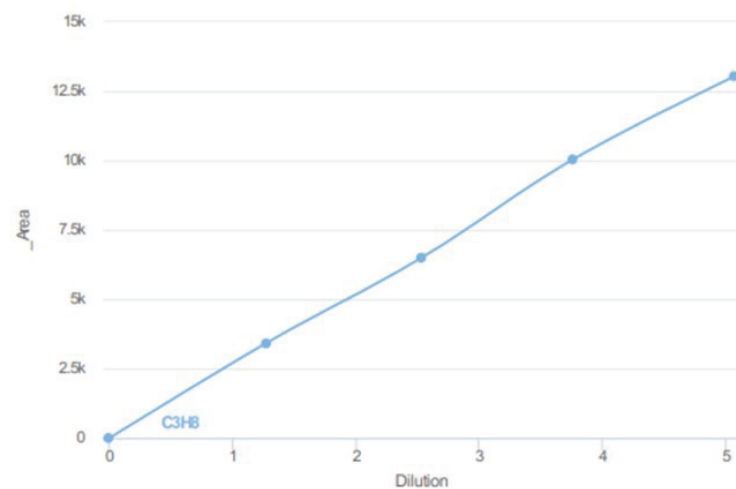
Linearity Test
Accepted

C2H6 (ppm)

Dilution	_Area
5.060	8017.000
3.760	5987.000
2.530	3978.000
1.270	2031.000
0.000	0.000

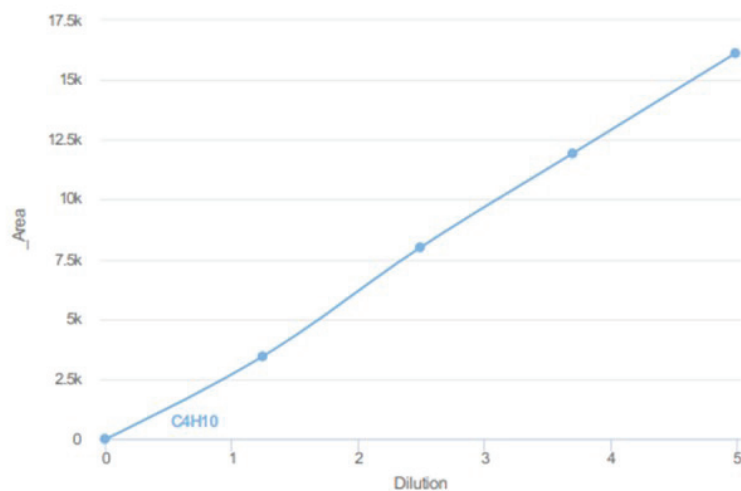
Coefficient correlation (R^2) = 0.9999**Linearity Test
Accepted****C3H8 (ppm)**

Dilution	_Area
5.060	13025.000
3.760	10053.000
2.530	6506.000
1.270	3421.000
0.000	0.000

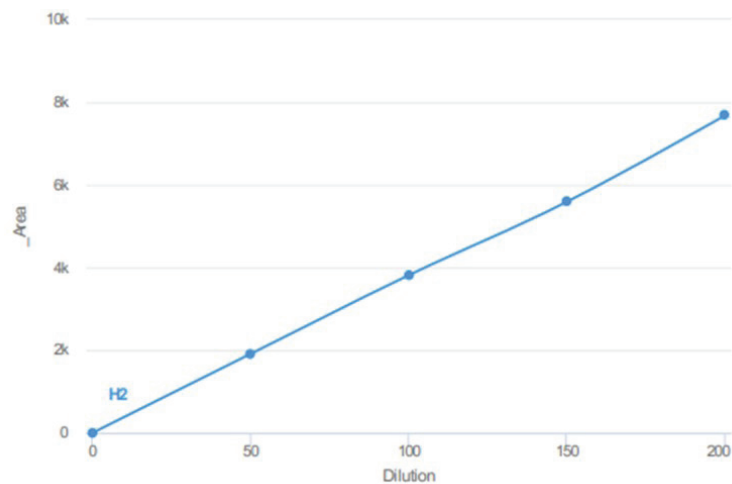
Coefficient correlation (R^2) = 0.9990**Linearity Test
Accepted**

C4H10 (ppm)

Dilution	_Area
4.980	16111.000
3.700	11952.000
2.490	8002.000
1.240	3447.000
0.000	0.000

Coefficient correlation (R^2) = 0.9987**Linearity Test
Accepted****H2 (ppm)**

Dilution	_Area
200.000	7686.000
150.000	5596.000
100.000	3816.000
50.000	1913.000
0.000	0.000

Coefficient correlation (R^2) = 0.9995**Linearity Test
Accepted**

Accuracy: Based on the GC standards. $\leq 1\%$ of error or 1σ whichever is higher

The MultiDetek3 detailed in this application note complies with the previously listed repeatability/linearity and accuracy standards.

CONCLUSION

The MultiDetek3 configured with the PED module offers a good analytical solution for trace ppb/ppm impurities for the validation of the quality and the production for semiconductor HCL. The gas chromatograph is configured with standard industrial communication protocols and a remote-control interface. Due to its high sensitivity plasma emission detector, the unit can measure trace impurities down to low ppb is perfectly suitable for the semiconductor and industrial gas industries. The MultiDetek3 is a very robust gas analyzer configured for industrial market to run 24/7. Combined with the other LDetek accessory modules, it fits the complete application requirements of the industry.



Where **innovation** leads to **success**

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