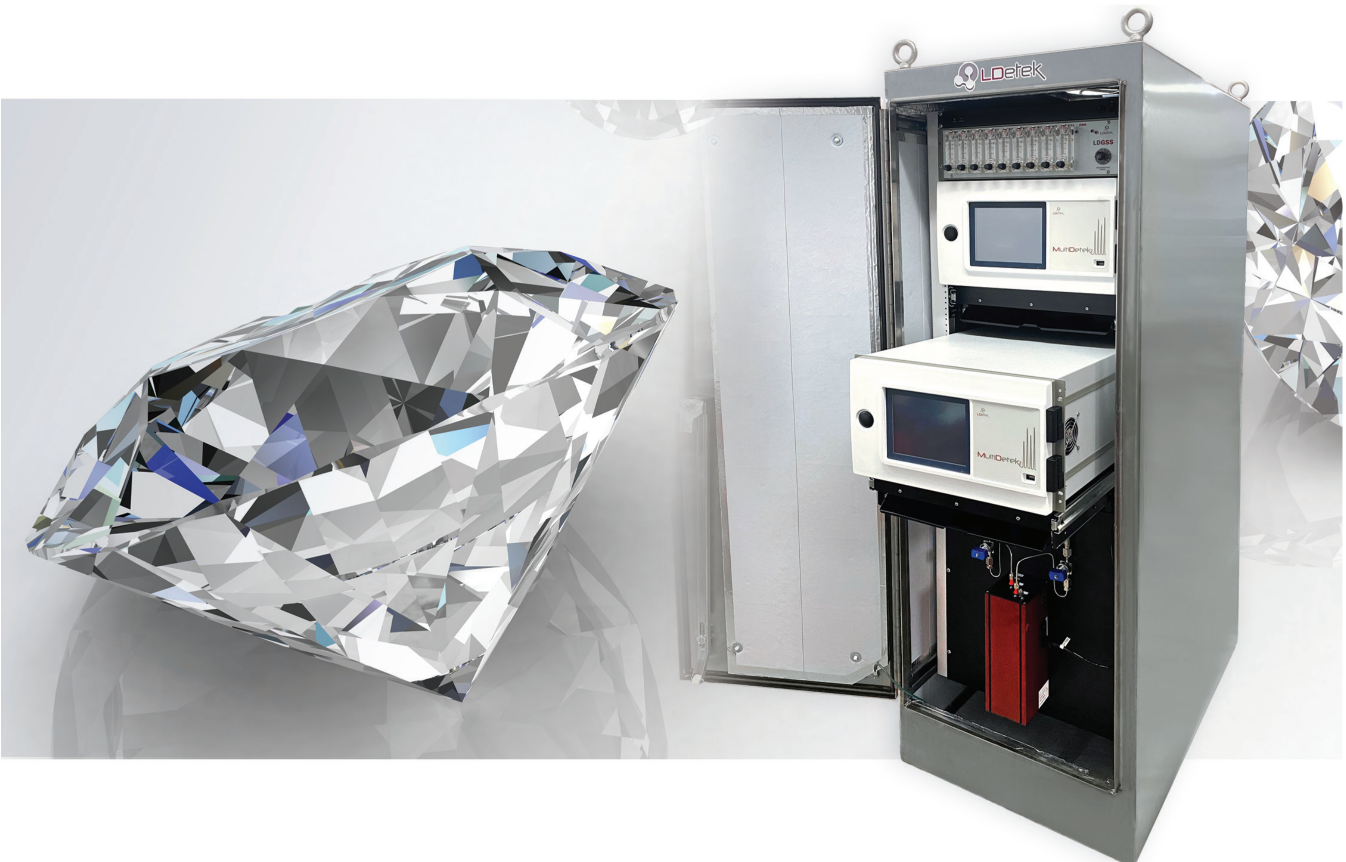
APPLICATION NOTE
LD21-01

Trace impurities measurement for synthetic diamond "grows" by chemical vapor deposition (CVD)



HOW DO YOU GROW A LAB DIAMOND?

By recreating the conditions underneath the Earth that result in diamond growth: pressure, heat, & carbon.

Laboratory grown diamonds can be referred to as lab created diamonds, grown diamonds, synthetic diamonds, man-made diamonds, cultivated diamonds, or cultured diamonds.

Diamonds are grown all over the world in high-tech facilities staffed by scientists, engineers, and technicians. West to East, here are locations of significant diamond production:

- United States
- United Kingdom
- France
- Belgium
- Netherlands
- Germany
- Ukraine
- Russia
- Israel
- India
- China
- Singapore
- Japan

APPLICATIONS

- **Jewelry**
- **Electronics**
- **Machining and cutting tools**
- **Thermal conductor**
- **Optical material**

MANUFACTURING TECHNOLOGIES

Today, there are two main methods used to produce synthetic diamonds. The uses of high pressure and high temperature (HPHT) is still widely used because of its relatively low cost. The process involves large presses that can weigh hundreds of tons to produce a pressure of 5 GPa at 1500 °C. This method is mostly uses for large industrial production. The second method, using chemical vapor deposition (CVD), creates a carbon plasma over a substrate onto which the carbon atoms deposit to form diamond. Other methods include explosive formation (forming detonation nano diamonds) and sonication of graphite solutions but are not so interesting.

The chemical vapor deposition by plasma is the method that allow the production of the best grade of synthetic diamond possible on earth in a relative short time. This method involves measuring the trace nitrogen in different high purity gases (mainly H2 and CH4) to accelerate the diamond growing and to improve the grade quality. For a proper trace N2 analysis, the PlasmaDetek2 detector with the MultiDetek2 gas analyser is the best solution available. Depending of the production process, the amount of N2 is critical and it is the reason why the analysis must be very accurate. Also, in some process, an additional trace O2 and trace H2O analysis are required to ensure the purity of the additive gases and the hydrogen/methane.

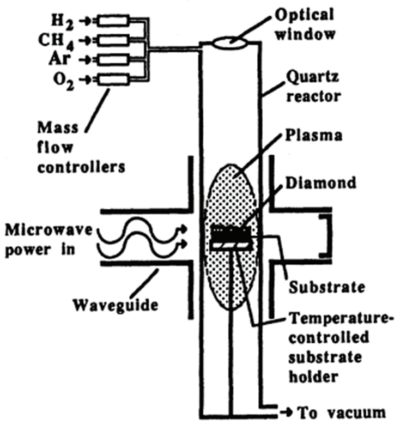
CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition is a method by which diamond can be grown from a hydrocarbon gas mixture. Since the early 1980s, this method has been the subject of intensive worldwide research. Whereas the mass-production of high-quality diamond crystals make the HPHT process the more suitable choice for industrial applications, the flexibility and simplicity of CVD setups explain the popularity of CVD growth in laboratory research. The advantages of CVD diamond growth include the ability to grow diamond over large areas and on various substrates, and the fine control over the chemical impurities and thus properties of the diamond produced. Unlike HPHT, CVD process does not require high pressures, as the growth typically occurs at pressures under 27 kPa.

The CVD growth involves substrate preparation, feeding varying amounts of gases into a chamber and energizing them. The substrate preparation includes choosing an appropriate material and its crystallographic orientation; cleaning it, often with a diamond powder to abrade a non-diamond substrate; and optimizing the substrate temperature (about 800 °C) during the growth through a series of test runs. The gases always include a carbon source, typically methane, and hydrogen with a typical ratio of 1:99. Hydrogen is essential because it selectively etches off non-diamond carbon. The gases are ionized into chemically active radicals in the growth chamber using microwave power, a hot filament, an arc discharge, a welding torch, a laser, an electron beam, or other means.

ANALYSIS SOLUTION FOR DIAMOND PRODUCTION USING CVD TECHNOLOGY

Diamond production diagram



Trace impurities analysis solution

Trace N2 from sub ppb to few hundreds' ppm is measured with the PlasmaDetek2 detector mounted in the MultiDetek2 analyzer. Optional H2O-NH3 and O2 analysis can be added in the same instrument when required by the process.

LDGSS stream selector system ensures the automatic switching sequence for analysis between H2/CH4 and the different additive gases. LDGDSA automatic dilution system can be added to accurately calibrate in ppb's.

Figure shows a microwave plasma reactor in which diamond is grown on a silicon substrate. A gas mixture that is typically 99 volume percent hydrogen and 1 percent methane, often with additives such as oxygen and argon, is passed through a quartz tube inside a microwave waveguide. The microwave radiation partially dissociates the gas into a plasma containing hydrogen atoms, methyl radicals (CH3), high energy electrons [8] and other reactive species such as hydroxyl radicals (OH).

Diamond crystallites nucleate on the substrate and grow into a continuous polycrystalline mass. The outer diamond growth surface is rough, but the film face next to the substrate is as smooth as the original silicon surface. High quality Type 2a diamond with a thickness greater than 1 mm can be grown over areas greater than 100 cm2 with growth rates of approximately 0.1 mm/h by this technique.

HOW IS THE MULTIDETEK2 INSTRUMENT CONFIGURED

Channel 1: N2 (O2-NH3 optional)

IMPURITIES	RANGE (ppm)	LDL (ppb)	REPEATABILITY (%)	Detector
N_2	0-100	0.5	0.1	PED
O_2	0-100	10.0	0.5	PED

The first channel is configured with a PED, using Helium or Argon as carrier gas depending of the preference of the user. The plasma detector is mounted with a selective optical filter for measuring N2 and another filter for measuring O2. These two impurities can then be measured without to get affected by the background gas or other interference gas molecules. The sample is simply injected through a molecular sieve column and the O2-N2 impurities are measured by the plasma emission detector. Using this method, the impurities can be measured from low ppb up to ppm in the required gas mixtures containing He/Ar/H2/CH4.

The same plasma emission detector (PED) can also be used for measuring the ppb/ppm trace ammonia (NH3) in the different gas mixtures. A separate chromatographic flow path using the appropriacy capillary columns will be used.

Channel 2: H2O

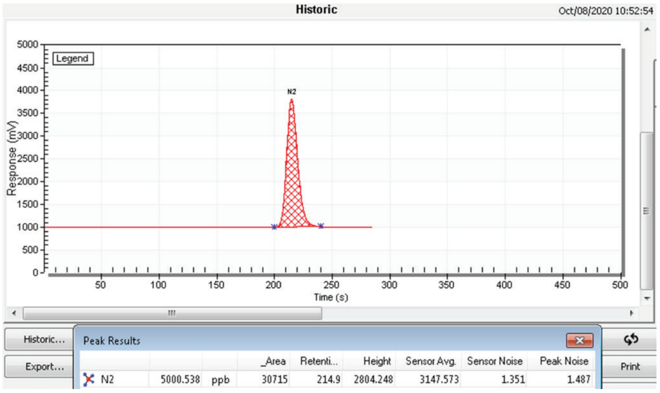
IMPURITIES	RANGE (ppm)	LDL (ppb)	REPEATABILITY (%)	Detector
H_2O	0-10	10.0	0.5	Quartz crystal

The second channel is mounted with a quartz crystal sensor capable to measure trace moisture from ppb to ppm in continuous. The sample gas is regulated with its mass flow controller and measured by the sensor. The MultiDetek2 GC has its built in moisture permeation span calibration device that allow to periodically validate the quartz crystal sensor.

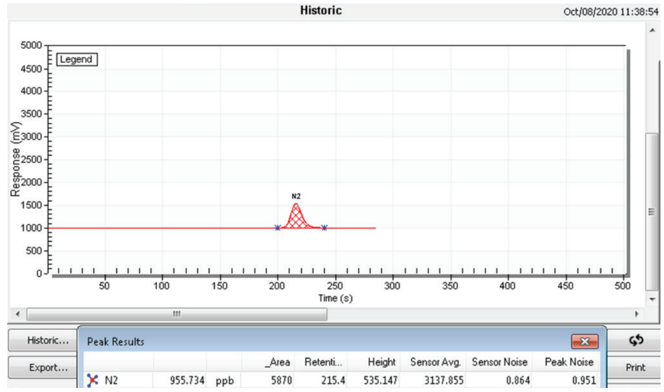
RESULTS

Chromatograms : Channel 1

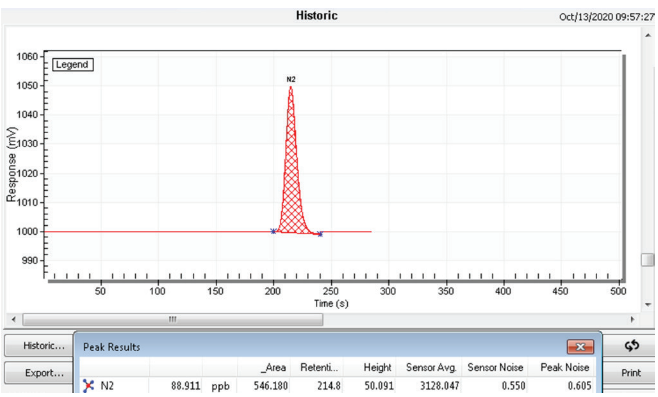
Sample : 5000ppb N2 Balance H2



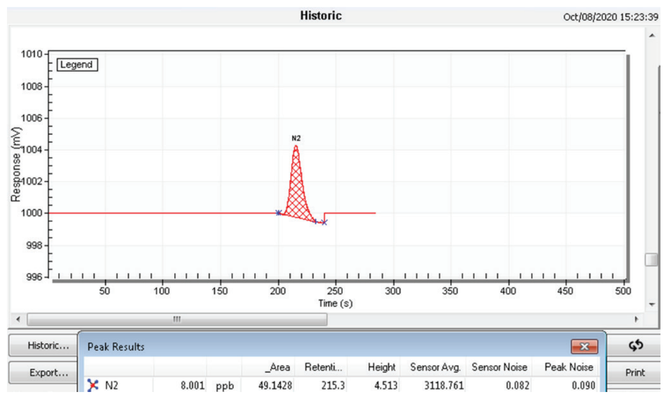
Sample : 1000ppb N2 Balance H2



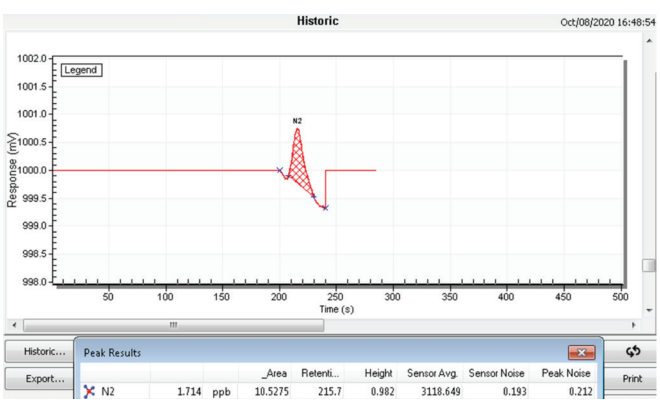
Sample : 100ppb N2 Balance H2



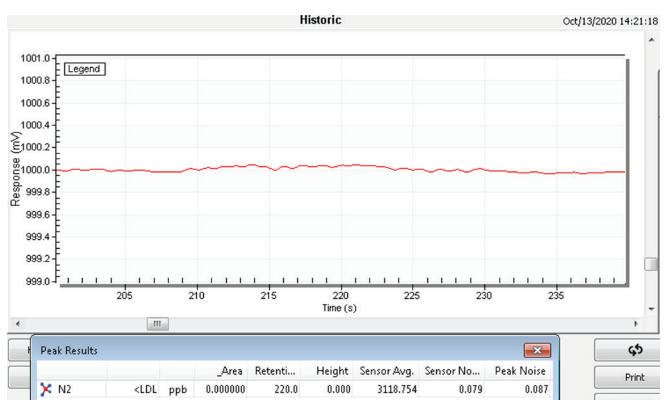
Sample : 8ppb N2 Balance H2



Sample : 1.5ppb N2 Balance H2



Sample : blank for noise analysis



LDL

COMPONENT	CONCENTRATION (ppb)	PEAK HEIGHT (mV)	NOISE (mV)	LDL (3X NOISE) (ppb)
N_2 (Nitrogen)	8	4.51	0.087	0.46

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

REPEATABILITY

Sample : 1.5ppb N2 Balance H2

	Description	N2
Historic		
⊟ Thu, Oct-08-2020		
16:48:54		1.712
16:43:47		1.703
16:38:42		1.703
16:33:35		1.681
16:28:28		1.670
16:23:21		1.640
16:18:15		1.673
16:13:08		1.658
16:08:01		1.680
16:02:54		1.623

Sample : 100ppb N2 Balance H2

	Description	N2
Historic		
⊟ Tue, Oct-13-2020		
09:57:27		88.850
09:52:20		88.893
09:47:15		88.877
09:42:09		88.819
09:37:02		88.762
09:31:56		88.831
09:26:51		88.786
09:21:45		88.760
09:16:38		88.792
09:11:31		88.850

IMPURITIES	AVERAGE (ppb)	SIGMA σ (ppb)	CV (%)	CV x 3 (%)	STATUS	REPEATABILITY (%)
N_2	88.84	0.047	0.05	0.15	pass	0.05

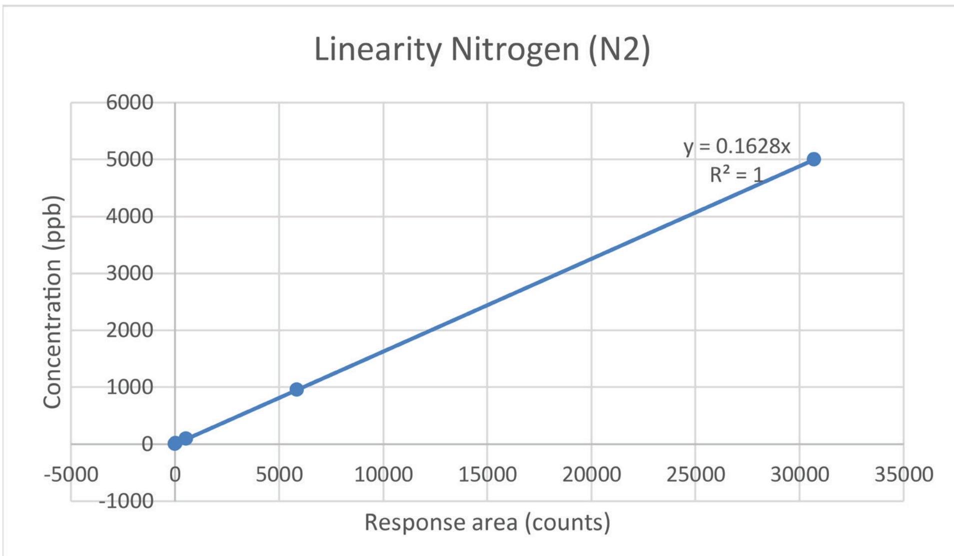
Using a series of 6 consecutive analysis, the repeatability conformity test must be below 5% considering a value of 3 times the coeficient of variation (CV) to be accepted.

The repeatability % is obtained by applying the sigma of the 6 consecutive analysis on the average of these 6 same analsysis.

LINEARITY

Impurity : N2

RESPONSE AREA (counts)	CONCENTRATION (ppb)
0	0
10.5	1.7
49	8
546	89
5870	955
30715	5000



Using a series of 5 points within the measuring scale, being approximativly 100%,75%, 50%, 10%, 0% of the scale of the instrument to be measured. The points have to be generated from a certified gas bottle diluted with the same gas as the carrier gas of the instrument. The 5 points have to achieve a linear curve having its R2 at a value between 0.998 and 1.00.

CONCLUSION

The MultiDetek2 process GC configured with a plasma emission detector (PED) for measuring trace N2 impurity in the different gas matrix used for the synthetic diamond grow is perfectly suitable. The same channel can be used for measuring trace O2 as well. By adding a channel with the quartz crystal technology inside the same unit, it becomes easy to have all the measurements accomplish together. The PED sensor can also be used for tracing ammonia (NH3) all in the same analyzer. The analyzer is used with the LDGSS stream selector system, that is used to switch from the different gas streams (H2-CH4-noble gases and others). In order to calibrate the analyzer in the ppb ranges, the LDGDS-A, our dilution system can be added to the solution. All the system is integrated in the LDrack cabinet series offering a turn key solution for the diamond production industry.