

EXPERT PAPER

A comparison of Gas Chromatography with Plasma Emission Detectors and Atmospheric Pressure Ionization Mass Spectrometry for UHP gas analysis in the semiconductor industry.

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GC-PED VS APIMS EXECUTIVE SUMMARY

Mass Spectrometry and Gas Chromatography (GC) both offer analytical solutions for the quality assurance of gases used in the semiconductor manufacturing industry. They have long been used for gas analysis, and each technique has its own advantages and disadvantages when applied to process environments.

When selecting a gas analyzer for the purpose of continuous quality control, these positive and negative factors must be taken into account. It is important to consider a variety of performance factors, alongside the uptime, reliability, and complexity of the product.

For example, GC enables analysis in background gases not achievable with Atmospheric Pressure Ionization Mass Spectrometry (APIMS), since it physically separates the molecules from the matrix gas, and is not dependent on ionization reactions. This ensures that only the species of interest is being analyzed, not an interferant isomer or other impurity.

The APIMS cannot cover the full range of background gases and impurities. It is also affected by inherent errors introduced by the calibration process and vacuum degradation.

Theoretically, the APIMS technology should deliver a lower detection limit. However, it needs frequent servicing to consistently achieve this theoretical performance, and is both difficult and expensive to maintain.

A GC with Plasma Emission Detector (PED) does not need regular maintenance, nor does it require supporting utilities. This prevents it from being affected by the same issues which cause the APIMS to show a deterioration in performance over time.

Despite the headline specifications of the APIMS making it appear, on the surface, to be the superior technology for the ultra-high purity gas market, the many benefits of the GC-PED technology proves it to be a better choice for continuous process analysis overall.

INTRODUCTION

This paper seeks to explain and compare the differences in Gas Chromatography with Plasma Emission Detectors (GC-PED) and Atmospheric Pressure Ionization Mass Spectrometry (APIMS) currently utilized in the Ultra High Purity (UHP) gas market for quality assurance of gases used in the semiconductor industry. It provides a brief history and description of the technologies, along with the benefits, limitations and practical aspects for each technology which should be considered when making purchasing decisions.

GC-PED	VS	APIMS
EVOLUTION (MILESTONE) TO GC-PED		EVOLUTION (MILESTONE) TO APIMS
1901 First Chromatography		1898 First Mass Spectrometer
1930s Normal phase (LC)		1930s EI ionization
1940s Paper Chromatography		1940s Isotope separation
1950s Reverse Phase Chromatography Gas Chromatography development Detectors (TCD, FID, ECD)		1950s GC-MS
1960s Reverse Phase Chromatography HPLC		1960s Quadrupole Chemical ionization Electrospray ionization
1970s GC-MS (tandem)		1970s Triple Quadrupole (tandem)
1990s GC-PED		1990s APIMS
GC-PED is a well-established and robust technique which combines the advantage of isolating the impurities from the background gas (GC) and the use of a very selective and sensitive detector (PED) suitable for semiconductor and electronics industries application to monitoring impurities at trace level analysis (ppt) in bulk gases (among other different applications in different industries or research labs).		APIMS is an adaptation of LC-APCI-MS (tandem) specifically developed for semiconductor and electronics industries application to monitoring impurities at trace level analysis (ppt) in bulk gases. Due to their specific limitations, it is not possible for it to be applied in other applications or fields. Atmospheric Pressure Ionization (API) is the specificity of this technique to be incorporated to the Mass Spectrometer, which is a more generic detector.

GC-PED

TECHNOLOGY:
GAS CHROMATOGRAPHY (GC)

Analytical chemistry technique for separating impurities by passing them through a column (stationary phase) which the components interact at different ration with the carrier gas (mobile phase). Impurities will be separated, identified and quantified depending on the retention time to reach detector.

PED is Plasma Emission Detector. Plasma excitation with spectral emission line for controlled (stable) and selective electromagnetic field. The advantage of PED to other detectors (i.e. RGD, FID and DID) is the high sensitivity, specificity, selectivity, maintenance-free, robustness, safety and no additional requirements (i.e. H₂ or make up gases) to perform. These qualities are highly appreciated to be required in CQC & IQC environments for industrial on-line GC.

VS APIMS

TECHNOLOGY:
MASS SPECTROMETRY (MS)

Analytical technique that identify the type and amount of chemical present in a sample by measuring mass to charge ratio (m/z) in a gas phase ion.

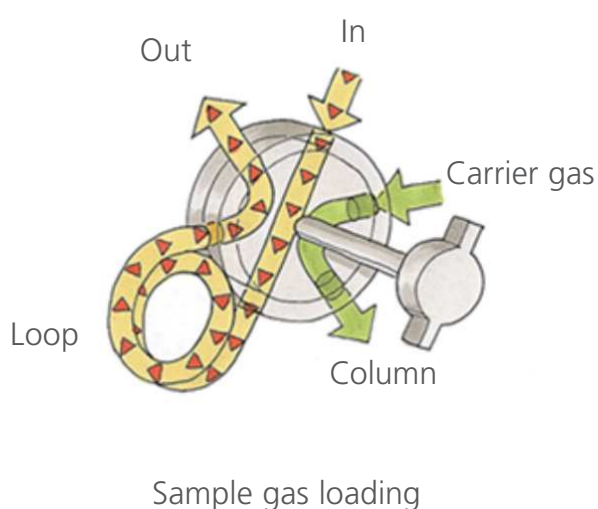
APIMS is referring to a Mass Spectrometer which is embedded with turbo pump and rough (rotary) pump to keep the system at vacuum. It has an orifice (controlled leak) to regulate high pressure sample inlet, generally above atmospheric pressure, which allows the pass of ions produced during the ionization process outside the MS (API).

MAJOR COMPONENTS STEPS

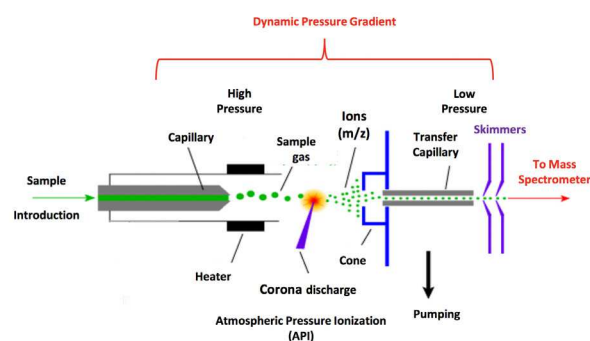
1. Sample introduction
2. Physical separation of impurities from the background gas
3. Detection

1. Sample introduction – ionization process
2. Ion separation/selection – quadrupole
3. Detection

1. Sample introduction step

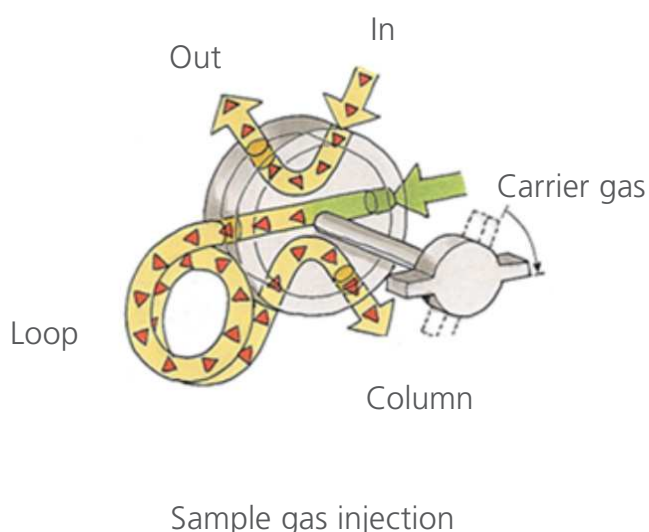


1. Sample introduction – ionization process step



The process gas (sample) is flowed onto the ion source at slightly higher than atmospheric pressure. A corona discharge is produced by a needle maintained at a high voltage which is located close to an orifice plate that forms the entrance to the lens stack to generate ions.

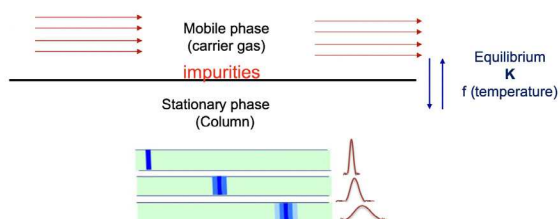
GC-PED



A portion of the process gas (sample) is introduced at high pressure (i.e. 30 psig) into the separation system at room temperature (i.e. 24°C) and mixed with an inert carrier gas (i.e. helium/argon). The system keeps a constant pressure (i.e. flow rate) during the determination.

2. Impurity (as a molecule) separation step

Physical Separation of impurities from the background gas is achieved through a simple single stage through Chromatographic separation process.



The impurities establish a unique interaction between the mobile phase (carrier gas) and stationary phase located in the column. This equilibrium is a function of the temperature controlled in the oven, where the column is located. Some impurities exhibit more affinity to the stationary phase, so they will be more retained in comparison to others, which elute faster to reach the detector at the end of the column. Impurities are separated from the background gas following the same principle.

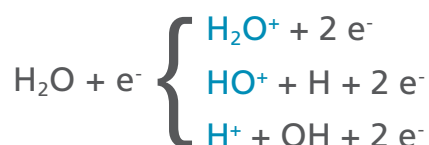
VS APIMS

Within APIMS a dynamic pressure gradient (high pressure during the ionization/low pressure into the MS) is maintained. Fluctuations in the dynamic pressure gradient would affect determination (see Appendix A).

This carries a significant risk of alteration of the sample composition when impurities are at very low concentration due to:

- High energy involved
- Hot metallic surface (active sites)
- Reactive backgrounds (i.e. H_2)
- Reactive impurities (i.e. H_2O , CO , CO_2 , O_2 & H_2)

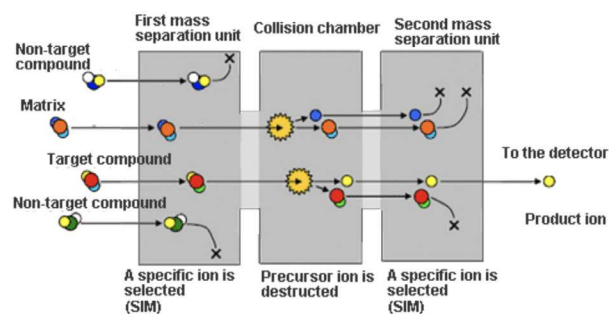
On the molecule ionization, there will be parallel ionization processes which might interfere with other target ions. As an example (below), H_2O will produce different ions which can interact with the other species.



See appendix A for more information.

2. Impurity (as an ion) separation step

Ion separation/selection (mass separation)

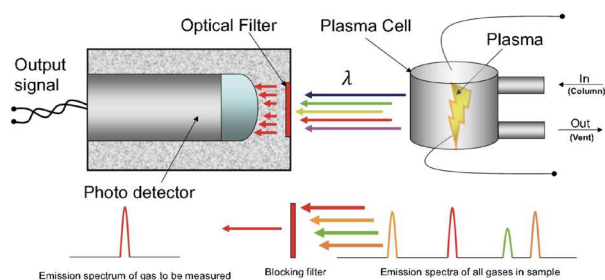


Q1	Q2	Q3
Mass Filter	Collision cell/ chamber	Mass Filter
Precursor ion selection	Fragmentation	Fragment ion selection

A Tandem mass spectrometry (i.e. triple quadrupole or Q3) is designed to quantified targets compounds in a matrix where only a specific ion related with the target compounds is detected removing other interferences (i.e. noise, matrix).

GC-PED

3) Detection: Plasma Emission Detector (PED)



Impurities reach the plasma cell (quartz) where an electric field of 1.2 KV/mm is applied to create the plasma conditions, where partially ions are present in gas phase, interact with the impurity (among other species, such as moisture, carrier gas, etc.) to produce different wavelengths (reaction chamber).

The intensity of this signal associated to the impurity will be monitored by the photodetector and a selectivity of the signal is increased with an optical filter located before the detection.

The intensity of the signal is proportional to the impurity concentration. After the detection, the impurity is vented.

Range: 0-250 ppb

LDL: 50 – 250 ppt, tested and corroborated for every analyzer produced.

- see Appendix C for Limit of decision

Process gas (sample): H₂, N₂, O₂, He & Ar

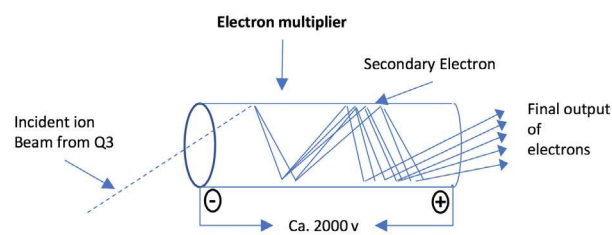
Impurities: H₂, N₂, Ar, CO, CO₂, CH₄ & NMHC

Batch process: one data point every 20 minutes

Method of Calibration: Span calibration dilution system is Integrated in the analyzer. **Lower cost \$.**

VS APIMS

3) Detection: Mass Spectrometer (MS)



The differences in masses of the fragments in Q3 allows the mass analyzer to sort the ions by their mass-to-charge ratio. The detector measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present.

The signal produced is amplified, which permits measurements up to 200 amu (atomic mass units) allowing the complete impurity spectrum to be measured at the detector.

A limitation of using a Triple Quadrupole system (Q3) is the low mass resolution (1 amu) achieved. Ions with same m/z ratio (i.e. N₂⁺ and CO⁺ $m/z=28$ or 15N⁺ and CH₃⁺ $m/z=15$) will not be possible to be discriminated. Although Selected Reaction Monitoring (SRM) is involved in Q3 (Precursor/Fragment ion selection) a high number of interferences at low atomic mass unit would be presented, then determination would be affected.

Range: 0-10 ppb

LDL: 10 - 150 ppt, not tested. No scientific data is available on how LDL is being calculated (see Appendix B for more discussion). Different ions produce different intensities, so different LDL would be expected.

Process gas (sample): H₂, N₂, He & Ar
Unable to determine O₂ background.

Impurities: N₂, Ar, CO, CO₂ & CH₄
Unable to determine N₂ in Ar, Ar in N₂, Ar in H₂
Inferior performance on low amu (atomic mass unit) impurities such as H₂ and He.

On-line detection: faster sampling rate

Method of Calibration: Span gas calibration dilution system to be provided separately by gas company or customer (not built-in). **Very high cost \$\$\$.**

GC-PED	VS APIMS
Single span calibration point, Span calibration gas: 5ppm containing impurities in Helium. The calibration gas is further diluted internally to reach 250 ppb. Dilution ratio 1/20 (calibrated in situ during the commissioning). Calibration conditions: Impurities in the calibration process and impurities in the process gas (quantification) are determined at the same experimental conditions, then the response factor would be the same (no matrix effect).	Single span calibration point, Span calibration gas: CH₄ (5ppm) CO₂ (5ppm) CO (50ppm) H₂ (50ppm) N₂ (20ppm) Ar (10ppm) balanced in helium. The calibration gas is further diluted in an external blender to reach around 1ppb. Dilution ratio 1/10,000 (the error associated to dilute a span gas 10,000-fold jeopardizes the accuracy and the precision of the calibration). Calibration conditions: The ionization process would be conditioned by the background gas (see Appendix A: Bulk gas). Thus, a different response factor would be expected for each impurity in the presence of different background gas (matrix effect).
Regular maintenance or interruption requirement: See Appendix C for Limit of decision.	Regular maintenance or interruption requirement: • Once a month for span calibration • Once a year for pump maintenance such as changing rotary pump oil and turbo pump bearing lubricator
Complexity of Corrective Maintenance: Relatively easier to repair, simpler parts.	Complexity of Corrective Maintenance: Mass spectrometer requires ultra-high vacuum to operate (10⁻⁶ mbar). Any unexpected circumstances such as power outage, component failure, or chamber contamination require significant effort to repair.
Parallel detectors to cover various impurities. Single failure will lose measurement on the respective detector.	One detector to measure all impurities, single failure will cause whole-system downtime.
Performance over time: PED detector offers long term stability against aging, temperature and humidity.	Performance over time: Mass spectrometer raw signal is electric current (eV), this electric current intensity is dependent on chamber vacuum pressure. Any degradation of vacuum pump performance will result in trending of analyzer reading.
Application and technology maturity: >40 years in UHP application.	Application and technology maturity: Mostly in lab environment, recent application on UHP application.

CONCLUSION

In choosing an analyzer for continuous quality control in purified gas and semiconductor applications there is a lot more to consider than just the brochure specifications of the technology.

Factors such as uptime, reliability, and complexity should be considered when choosing a technology. Though the front-end specifications of the APIMS appear to point to a superior technology for this application, the GC-PED proves to be a better overall continuous process analyzer choice.

As outlined above, the APIMS has limitations in background gas and impurities as well as inherent errors introduced by the calibration process and vacuum degradation overtime. It is important to examine closely all performance factors when choosing the correct analyzer for the application.

APPENDIX A

The ionization process will be affected by:

- Pressure in the ionization chamber
- The energy associated in the Corona discharge needle
- The bulk gas analyzed
- The impurities present in the bulk gas

PRESSURE IN THE IONIZATION CHAMBER

API-MS encounters a difficult challenge to hyphenate two antagonist situations:

- a) Ionization process at high pressure (>1 atm or 760 torr)
- b) Detection at very low vacuum (<10⁻⁶ torr)

Therefore, it would be impossible to keep a constant pressure during the ionization. A pressure gradient variation in the ionization chamber would be unavoidable. Pressure is mass proportional, related with abundance signal (m/z^+) of the impurities monitored by the Mass Spectrometer. And this effect would jeopardize the LDL.

THE ENERGY ASSOCIATED IN THE CORONA DISCHARGE NEEDLE

The Corona energy is set at conditions (i.e. 2-5 KV) where, predominantly, the impurities present in the bulk gas are ionized (avoiding the ionization of the bulk gas). The ionized impurities (and their fragments produced during the ionization process) are transferred to the MS detector and separated by m/z^+ ratio, increasing the selectivity of the analyzer.

However, it is impossible to avoid an excess of the energy applied in the ionization process. The energy applied would have a gaussian distribution, where the mean value would be set at 2-5 KV, but a small proportion of this energy would have higher values (the proportion of energy higher than 2-5 KV would be defined by the standard deviation of the energy).

This excess of energy could produce that some molecules of the bulk gas cannot keep the excess of energy and then the ionization process of some bulk gases is produced. Even when this value could be extremely low, due to the high concentration of the bulk gas (100% concentration) the number of molecules of the bulk gas that potentially could be ionized (and therefore transfer to the detector) would not be ignored (specially at ppt levels). And this effect would be more evident in gases with lower ionization values, such as H₂ or N₂ (less evident in He or Ar).

This drawback would have consequences in the blank level, interference in the determination of some impurities, and would increase the LDL.

Also, variations of this energy during the ionization process would affect the mass proportion ratio related with abundance signal (m/z^+) of the impurities monitored by the Mass Spectrometer, and thus the reproducibility of the determination.

THE BULK GAS ANALYZED

The bulk gas plays an important role in the ionization process, where the bulk gas is an intermediate to transfer this energy to the impurities to determine which at the end produce the ionization. Some bulk gases would be more efficient in transferring the energy than others, producing a higher abundance of ions. This effect has an important role when the API-MS is calibrated. The response factor of the impurities in the presence of helium (as a bulk gas) would not have the same value in an H_2 or Ar environment (matrix effect).

Also, some bulk gases (i.e. H_2) can chemically react with impurities (i.e. alkenes, CO_2 or CO), so the ions associated to be monitored would be affected, misleading the determination.

The bulk gases have natural isotopes. The relative isotopic abundance of nitrogen is $m/z=14$ (99.63%) and $m/z=15$ (0.368%). Although 0.368% in proportion is despicable, when the N_2 bulk gas is analyzed, that means 3,680 ppm of ^{15}N $m/z=15$ is present in the bulk gas. Even if an extremely low proportion of this N_2 is ionized (i.e. 10^{-6}) and passed to the MS, then it would be detected at ppb-ppt levels.

However, $m/z=15$ is an ion characteristic of CH_4 when in the ionization process a proton is lost (M^+-H). So the alternative is to monitor the molecular ion of CH_4^+ ($m/z=16$) but then the fragment ion of oxygen O^+ ($m/z=16$) would cause interference (O_2 can be present as an impurity, but also the fragmentation of H_2O could generate O^+). So, the determination of methane in N_2 by API-MS is not trivial.

The background gas yields ions that potentially overlap with the impurity ions in the mass spectrum, so the effect would be a less accurate quantification (spectral interferences).

THE IMPURITIES PRESENT IN THE BULK GAS

As highlighted above, some impurities can react with the bulk gas during the ionization process due to the energy and high temperature involved. But also, some impurities can react between them (i.e. some hydrocarbons can be hydrolyzed in the presence of moisture, methane can react with moisture to produce MeOH). It is impossible to avoid this kind of reactions in the ionization process, because all impurities are co-existing at the same time (something avoided when a separation technique is involved with a MS).

Moreover, some impurities can generate the same fragmentations ions. All hydrocarbons above C_2 present in the bulk gas would generate $m/z=15$ because of their fragmentation process after their ionization, which is a typical monitoring ion for methane.

As a rule of thumb, Mass Spectrometry shows big drawbacks when low molecular ions (i.e. all the impurities of interest show less than 50 amu) are monitored, because many interferences can affect the determination.

The presence of one or more components in the sample may suppress or enhance the response of the impurity through a chemical process (chemical interference). It implies an effect on the accuracy of the qualitative analysis. Interferences may also change the spectrum qualitatively (i.e. adduction) and then the quantification itself.

APPENDIX B

API-MS uses a triple quadrupole (Q3), which avoids some problems related with interferences and increasing the selectivity when Selected Reaction Monitoring (SRM) is involved. In this configuration, selected analyte (impurity) precursor masses can be continuously introduced into the collision region by the first mass analyzer, and only selected product ions monitored through the second mass analyzer. This mode of MS/MS yields maximum sensitivity and selectivity for known target impurities. However, the matrix effect (i.e. bulk gas), as highlighted previously, would play a crucial role in the ionization process.

The assumption to achieve an LDL=10 ppt for all impurities in all background gases when APIMS is involved is not accurate. The first question to be addressed is how this value was obtained (experimental data?). The detection limit is intimately associated with the signal-to-noise ratio (S:N). How and when you measure the signal and the noise will affect the value of your detection limit.

The voltage measured from a given ion signal (V_{measured}) at a given mass should exceed the average base line signal (V_{baseline}) plus 3 times the standard deviation (SD) of the baseline as:

$$V_{\text{measured}} > V_{\text{baseline}} + 3SD_{\text{baseline}}$$

Each impurity would have different signal and noise level. Since noise is ultimately the primary limitation in terms of detection limits, the system should be operated to minimize all components of noise. Common sources of noise originate from electronic and mechanical components of the system (i.e. oil contamination originated from the rough (rotary) pumps). Other sources of noise are found in chemical background inherent in the ionization process and mass analyzer. Examples would be helium metastable neutrals that drift to the detector and ionize background gas after they pass through the analyzer.

LDL will be affected by the blank level of the system, so LDL would increase through the performance of the analyzer (time) until the maintenance is done.

APPENDIX C

Comparison of GC-PED vs APIM on the basis of impurities determination present in different bulk gases (red cell not possible to determine using APIMS):

GC-PED (Limit of decision) *

GC-PED		BULK GAS				
		N ₂	Ar	He	N ₂	O ₂
Impurities (ppt)	H ₂	250	250	250	x	250
	CH ₄	50	50	50	50	50
	CO	50	50	50	50	50
	CO ₂	50	50	50	50	50
	N ₂	x	50	50	50	150
	Ar	250	x	250	250	250
	NMHC	50	50	50	50	50

*Calculated as 1.65 *σ

		BULK GAS									
		N ₂		Ar		He		H ₂		O ₂	
		GC	APIMS	GC	APIMS	GC	APIMS	GC	APIMS	GC	APIMS
Impurities detected at ppt level	H ₂							NA	NA		
	CH ₄										
	CO										
	CO ₂										
	N ₂	NA	NA								
	Ar			NA	NA						
	NMHC										

SUMMARY

The techniques of Mass Spectrometry and Gas Chromatography both have a long history in laboratory analysis, and more recently for Mass Spectrometry in process analysis, and as has been shown in this paper have their specific benefits and drawbacks for use in process environments.

Physical separation of the molecules (no reliance on ionization reactions) from the background matrix gas in a GC enables analysis in backgrounds not possible with APIMS and ensures that the analysis taking place is of the species of interest and not an interferant ion/isomer generated at the corona discharge as a result of the background matrix gas or other impurities present.

Although APIMS technology offers a lower theoretical LDL, it is a more complex and expensive to maintain technology, reliant on regular servicing of the rough and turbo pumps to maintain this theoretical performance, conversely a GC with PED does not require regular maintenance or supporting utilities and does not suffer with the same issues with loss of performance over time.

The positives and negatives of these competing technologies must be considered when making a decision on suitability of gas analyzer.