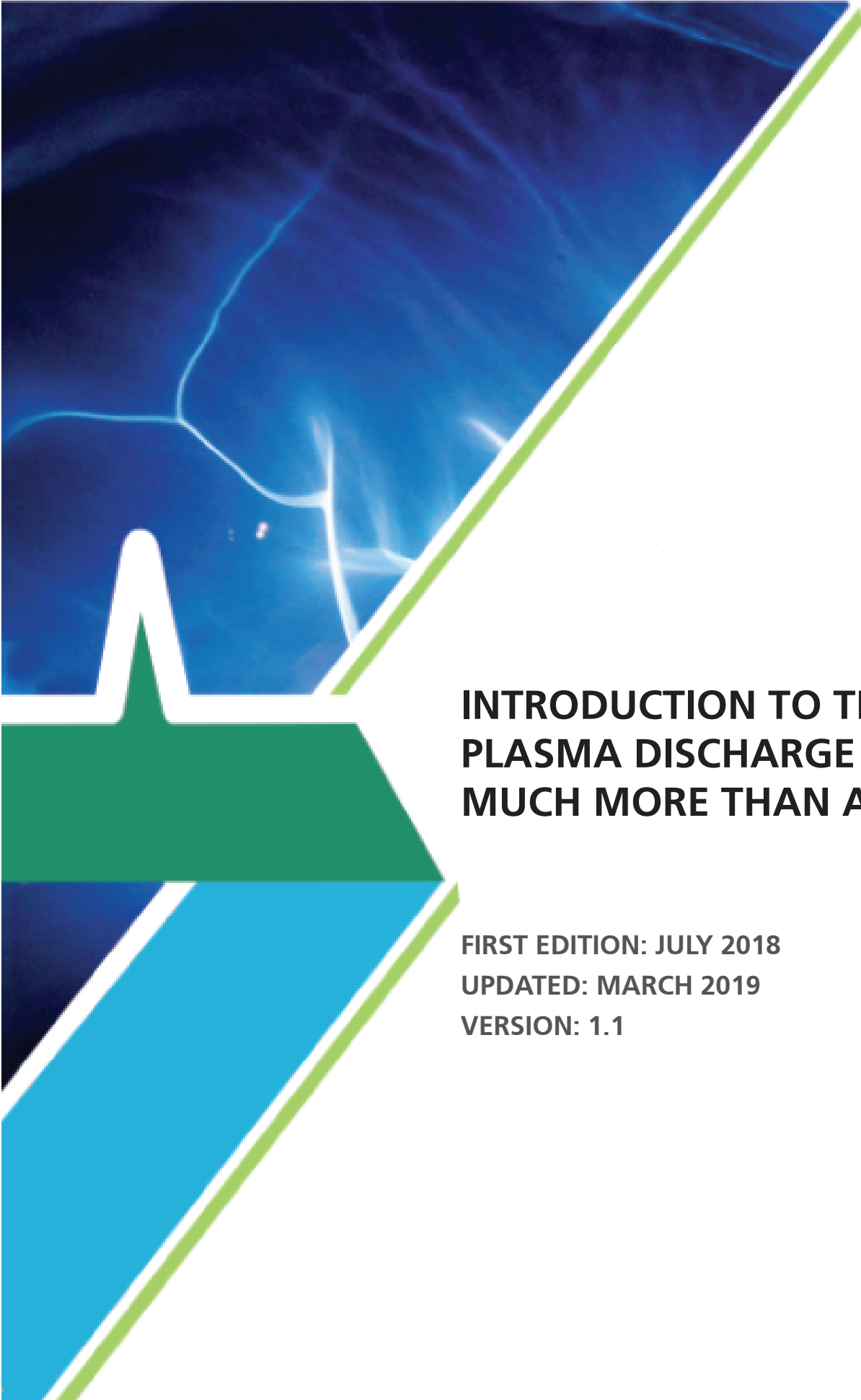
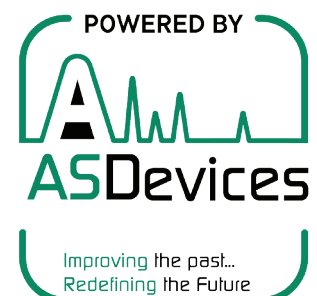




INTRODUCTION TO THE ENHANCED PLASMA DISCHARGE DETECTOR MUCH MORE THAN A DETECTOR...

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Introduction to the Enhanced Plasma Discharge Detector for Analytical Application. Much more than a detector...

A New development tool for OEMs and system integrators

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Foreword

Most papers talking about gas chromatographic detectors are done by scientists, researchers or highly focussed developers. They are most of the time highly academic and reserved for a specific audience. A good example of this can be seen in ref [33]. Generally such papers have a detailed theoretical approach of the subject. However most of time they lack of practical guide lines that would ease their integration into real world applications. Our system is based on a plasma discharge and this complex topic is well explained in many textbooks, scientific articles and publications. At the end of this paper, there are many references listed that cover in detail the plasma discharge physics. We don't want to repeat them, so only a little will be explained here about this topic, just enough to give you a good idea of what is happening into this detector. Most individual does not need an in-depth understanding of the complex physics and chemistry behind a dielectric barrier discharge system, but they would benefit significantly from an understanding of the basic concepts and processes that occur in a gas discharge. This paper is not intended to be an exhaustive treatise. Our goal is to focus on the practical side and explain how this new tool can make life easier for chromatographers; in other words, how to be creative and quickly productive. The system is intended to be simple to use and understand. It opens the door to creative solutions, moving away from the traditional paths and allowing new ones for innovators.

Reader Notice: Some mechanical design variations may occur in the production units, to ease and reduce production cost, without moving away of the basic concepts described in this document and performance.



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GLOSSARY AND DEFINITION

ASD: Atomic spectrometry detector

Colision Cross Section: Is an effective area related to molecular diameter, larger cross section, higher the probability of colision, excitation and ionisation

DA: Direct absorption spectroscopy, without the use of WMS, Fourier transform. Work well for high level of impurities measurement

DBD: Dielectric Barrier Discharge, refer to a plasma or a gas discharge where the power coupling is done by at least having one electrode isolated by a dielectric

DID: Discharge Ionisation Detector. Generally refer to the one manufacture by GOWMAC. First base on an electrical discharge.

ECD: Electron capture detector. Originally developed by LOVELOCK. See [16].

Electron Mean Free Path: Average distance that an electron travels before to collide with another particle. Higher mean free path, higher the energy the electron will gain. Mean free path depends upon the temperature and pressure as well as the molecular diameter and the colision cross section.

Epd: Enhanced Plasma Discharge, technology that uses not only spectral emission, but also other modes for impurities measurement. Dramatic performance improvement over the former PED.

FID: Flame ionization detector

FPD: Flame photometric detector

GC: Gas chromatography / Gas Chromatograph

HECD: Hall Electrolytic Conductivity Detector

ICP: Inductively coupled plasma

LDL: Lower detection limit

Methaniser: Accessory use with an FID to measure CO and CO₂, by transforming them in CH₄, Base on a nickel catalyst heated around 400°C. Not require with the Epd.

MIP: Microwave induced plasma

MMPD: Multi Mode Plasma Detector, former version of Epd.

MS: Mass Spectrometer

OES: Optical Emission Spectrscopy

PDID: Pulse discharge Ionisation detectors. Generally refer to the one manufactured by VALCO

PED: Plasma emission detector, most of the time base on a dielectric barrier discharge. First developped in 1947 by russian, made commercially by Fay and All, 1958. In chromatography introduced by orthodyne in the 60's. Improve version by Contrôle Analytique in 1992, sold to servomex in 2007, second source produced by LDetek. In all above cases, the system is based on a low power gas dichage driven by an open loop frequency generator.

TCD: Thermal Conductivity detector

TDLAS: Tunable Diode Laser Absorption Spectroscopy

VOC: Volatile Organic Compounds

WMS: Wavelength Modulation Spectroscopy



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1.0

INTRODUCTION

There are several GC detectors on the market. Some of them have a universal response while the others are more specific to a family of compounds. Some are mass dependent other are concentration dependent. Here is a description of the most popular ones. There is the FID, which requires H_2 and hydrocarbon free air to detect most of organic compounds. It is also used for CO and CO_2 , but then a methaniser is needed for the conversion of these into CH_4 . The ECD [16] is mainly used to detect halides, nitrides, organometallics. It is a very sensitive detector. However, it requires a radioactive source which comes with specific regulations to follow, permit and paper work for the disposal of a used detector [38]. The FPD detects sulfur, phosphorus, tin, boron, arsenic, germanium, selenium, chromium. It requires also H_2 and clean air for its operation. PID detects aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organo-sulfur and some organometallics. . It is also a powerful tool for VOC measurement depending on the lamp energy level, it requires frequent lamp replacement. See [17]. The DID and PDID could be classified as universal response detectors but most of the time they are used for permanent gases. Generally, helium is used as carrier gas and this requires more complex chromatographic configurations in order to eliminate the sample background. Otherwise it will result in a dramatic baseline upset and unresolved peaks. In some cases with the PDID, doped carrier gas is used to reduce its sensitivity to a specific background. See ref [34]. However this solution suffers of some drawbacks as reported in ref [18] and [19]. The TCD is a universal response detector too but with a relatively low sensitivity and in some case, exhibiting response inversion. It can also be damaged by reactive impurities, depending on the design used, as shown in ref [36].

The MS (Mass Spectrometer) detector has a universal response and, for many applications, requires a GC front end to improve separation or to eliminate negative impact from a reactive sample background in the ionization section of the MS, see ref [20], [21] . The front end GC used with a mass spec will also ease the spectrum analysis by reducing the number of fragments in the spectrum, eliminating interference. A good example of this is when the sample comprises CO and N_2 at the same time, since the m/z ratio is the

same, i.e. 28. This is frequent in gas analysis.

Except for the MS detector system, the other detectors referenced above can almost be seen as sensors, giving the users a raw electric signal that is related to the impurity level. There is no, if any, mean for noise discrimination or more advance data processing. However MS detector used in a GC has a minimum of data processing algorithm and may also include a mass spectrum database easing data interpretation. Generally this is not the case for the other detectors we are referencing here.

Most of the time when the impurity level is low and chromatographic peaks are weak or not having a Gaussian shape, the users have the burden to treat the information embedded in noise and baseline drift, resulting most of the time in limited performance in term of LOD and repeatability. This becomes apparent at very low level measurement. See Table 1 for detector performance comparison.

Here, we are introducing a multi-element sensitive detector, which can be used from ppt range to percentage, capable to work with different carrier gases, that could be made selective or having a universal response, totally user configurable with the open architecture philosophy. A detector also capable to resolve co-eluting peaks, as it will be demonstrated later in this paper. All this at low cost compared to the other system.

This is a modified and improved detector based on a technology that was developed in 1992, by the author. This former technology has been the heart of several process GCs focused on air separation and co-generation plants. It has been widely used for refinery gas analysers and for less friendly applications in the electronic industry for silane and other electronic gases. This was a close architecture system and was never made available for third party users or lab GC community. This technology became a worldwide standard for the measurement of trace N_2 in Argon or Helium, with the online configuration i.e. without GC separation front end. In almost (for not say all...) air separation plants today, there is at least one gas analyser based on this technology for bulk gas impurity measurement and/or trace N_2 in Argon for process and quality control, see ref [1] for more detail. The operation of the detector was based on the optical emission of a low power plasma, maintained by a dielectric barrier discharge at atmospheric pressure. Our former version of this technology has been used by the CERN atomic particle accelerator project for controlling the quality of helium used to cool down the mega-magnets, as it was also used to qualify cryogenic Hydrogen to be used as fuel for the space shuttle. This specific system was delivered in 1999 and at the beginning of 2000.

This technology, developed by the author, is still in use today in process GC, with a LOD down to 100ppt, see ref [2], while still capable to measure in the high range value, like percentage.

Here, we will cover basic working theory and concept of the new detector while having in mind the practical side of the system. The main aim of this paper is introducing the readers to this new detector in a clear manner which avoids deep theory treatment, this being beyond the scope of this paper. However some references are provided for those interested in digging deeper in the field of plasma discharge. The target is to make it simple and point out the multiple possibilities of this new system, in order for the practionner to have enough understanding to quickly configure and assemble system for standard and demanding GC applications in various field. All this with a minimum learning curve.

Detectors	Type	Application	LOD (g/s)	Linear range	Carrier Gas
ASD	Universal/ Selective	Multi-element	10^{-13}	10^5	N ₂ , Ar, He, O ₂
HECD	Selective	Halogen, S and N	x: 10^{-13} y: 10^{-12} P: 10^{-12}	10^4	Air, H ₂
NPD	Selective	N and P	N: 10^{-13} P: 10^{-14}	10^5	N ₂ , He
FPD	Selective	S and P	S: 10^{-11} P: 10^{-12}	10^4	N ₂ , He, H ₂
ECD	Selective	Halogen, S and N and other electron capturing groups	10^{-15}	10^4	N ₂ , Ar, He, H ₂
FID	Universal	Organic carbon compounds	10^{-12}	10^7	N ₂ , Ar, He, H ₂
PID	Universal	All compounds	10^{-13}	10^7	N ₂ , Ar, He
MSD	Universal	All compounds	10^{-14}	10^6	He
SCD/NCD	Selective	Sulfur Nitrogen	10^{-12}	10^4	He
AED	Universal/ Selective	Atomic Emission	10^{-12}	10^4	He
IPC-MS	Selective	Ionized Atoms	10^{-14}	10^6	Ar, He
ELCD	Selective	Halogens	10^{-15}	10^5	He
IR	Universal/ Selective	Molecular vibration	10^{-9}	10^4	N/A
TCD	Universal	All compounds	10^{-10}	10^5	He, H ₂

■ TABLE 1: PERFORMANCE COMPARISON, REF [49],[55]

2.0

BASIC INTRODUCTION, A LITTLE BIT OF THEORY ABOUT PHYSIC OF DIELECTRIC BARRIER GAS DISCHARGE

This section gives a brief description of a plasma maintained through a dielectric barrier. Such system is called a dielectric barrier discharge or DBD. In what follows, the characteristics of the discharge for different operating conditions are described. However, for using our system, it is not necessary to understand all the ins and outs of gas discharge physic. This section is giving a minimum of information about which parameters guide our design choices. Non-technical users can skip this section. But a minimum of understanding of gas discharge is a plus. It will help to understand the features offer by this system and the resulting benefits.

Basically, the impurities measurement are achieved by exploiting various characteristics or behaviors of a gas discharge system. Some of these characteristics or behaviors could be directly or indirectly used as the source of chemical or physical information for impurities measurement. Actually, most of emission gas discharge detectors specifically use the optical emission characteristic as a measurement parameter and rely on specific emission wavelengths. Such detectors are categorized as OES. A more specific member of this family related to gas chromatography is known as the Plasma Emission Detector, or the PED, that we introduced in 1992. In our system we have investigated the optical Direct impurities emission, Tracer emission and the Constant Power Mode of a plasma discharge. The later is an all new mode of operation for such detector. There are other specific possibilities offered by the gas discharge that can be used to identify and measure specific impurities that are at the time of printing this paper, under investigation by ASDevices team at the Innovation Centre in Canada.. These are; afterglow ionisation mode, plasma conductivity or impedance measurement mode, excimers measurement through the use of fluorescence window or specific window coating material, the thermo-ionic assisted mode, harmonic mode, catalyst enhanced configuration and the use of the discharge capacitance variation related to the change of impurities level. Those are open fields of investigation and development offer by the Epd technology system and specific architecture. These various modes will be the topic of other papers describing applications and performance. The specific target of these on going investigation is to reduce the size and cost, while improving performance of detector based on dielectric discharge.

2.1 BACK TO THE BASIC, GENERAL CONCEPT

As we already said, our detector is based on a gas discharge, call plasma, maintained through a dielectric barrier, or more precisely a capacitive barrier. This is a partially ionized medium, which is defined as the fourth state of matter. Partially ionized means that not all molecules are ionized.

The ionization degree is defined as $\alpha = N_i / (N_i + N_n)$.

where N_i is the number of density of ions and N_n the number of density of the neutrals.

A plasma of a pure mono atomic gas like He or Ar is composed of electrons, positive ions, neutral particles, and metastable species, radicals, excimers and high energy photons. When there is more than one gas into the plasma, by-products are generated and other phenomena take place, like by-products generation due to chemical reaction and in some case the creation of unstable compounds not normally found in nature, like ArO . The plasma is also very reactive to electric or magnetic field. We will use this characteristic to improve the stability, it will be shown later in this paper. This is a highly chemically reactive medium that is used to fragment and excite the analytes of interest. See Figure 1.

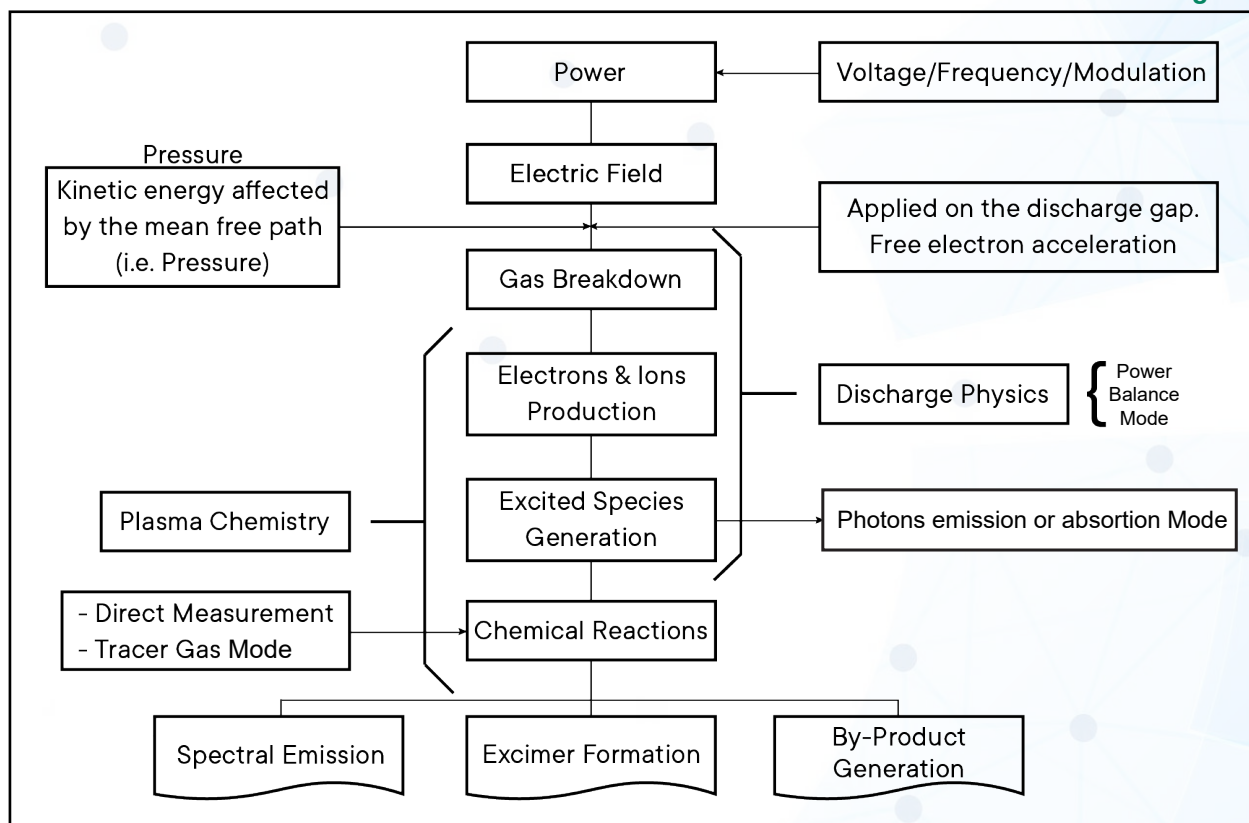


FIGURE 1: DISCHARGE PROCESS

In our specific case, i.e. the use of a dielectric barrier to generate a plasma, the discharge is classified as weakly ionized, i.e. $10^{-6} < \alpha_i < 10^{-1}$. It is also referred as low temperature plasma. For comparison purpose, plasma with degree of ionization close to 1 are characterized as highly or fully ionized, i.e. fusion plasma like the Sun. Our plasma is being said to be in the non-local thermodynamic equilibrium [3]. This means that the various particles in the plasma zone don't have all the same temperature. The discharge is started and maintained by applying an alternating electric field to a neutral gas, here a carrier gas. Any volume of neutral gas always contains a few electrons and ions that are formed as a result of interaction with cosmic ray or radioactive radiation with the gas. However, under specific condition, the number of free charge may be quite low making the starting process harder. We will show later how with the help of our electron injection electrodes, we can improve this issue. These free charges are accelerated by the electric field and new particles may be created when they collide with atoms and molecules in the gas or with the surface of floating electrodes like electron injection electrodes that may be also coated with a catalyst to improve by product generation or conversion. This leads to an avalanche of charged particles that are eventually balanced by charge carrier losses, so a steady-state plasma is developed [4].

We chose a dielectric barrier concept to create our new stabilised plasma cell. Other configurations are possible if a specific application calls for it. A planar configuration with the applied driving alternating voltage and resulting wall charges are shown in Figure 2.

NOTE: Here, we are talking of a typical plasma discharge with cell made of quartz wall as dielectric. This is more easy to visualize the idea. However, our design is not based on quartz cell, like in traditionnal PED, but it is based on an encapsulated electrode in a cylindral quartz. So in practice, the wall are in fact, the surface of the compound electrode made of quartz.

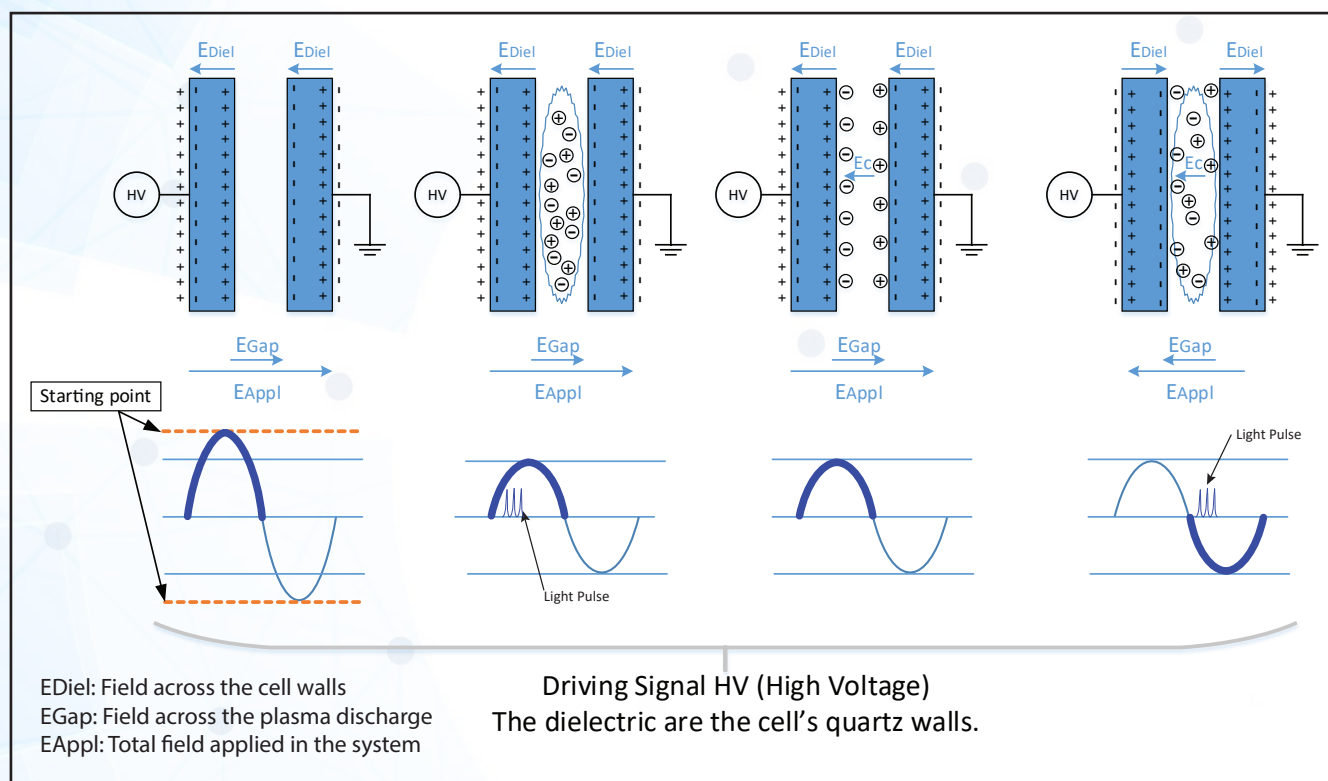


FIGURE 2: PLANAR DIELECTRIC BARRIER DISCHARGE

The dielectric barrier isolates the discharge electrodes from the gas, avoiding sputtering, cell inner wall coating and analyte interference. As shown in Figure 2, the cell discharge voltage is applied to the gas through a dielectric barrier. The first ignition breakdown in a homogeneous electrical field is governed by the same Paschen law that is known from the breakdown between metal electrodes in DC discharge. This is true only for the first half cycle of the applied field. One fundamental difference is, of course, that DBD cannot be operated with DC voltage. See Annex C for some typical Paschen curves of various gases. This imposes the use of a time varying signal, because the capacitive effect of the dielectric barrier, here the cell walls, will block a DC signal used as power source. The discharge could be a pulse, square wave or having a sinusoidal form. We are using a medium frequency sinusoidal shape driving signal. This reduces spurious harmonics generated by the system, compared to a pulse or square wave driving. See ref [37]. Lower frequency limits the power dissipated by the system. It is also possible to use only a dielectric barrier and one electrode, generally a small iridium alloy-based wire, in contact with the gas introduced into the discharge zone. This electrode wire is not into the discharge zone but acts as an electron generator. This configuration also allow the pre-ionisation of the gas to be introduce into the plasma zone improving a lot the ionisation process and resulting emission, call hollow electrode configuration.

The dielectric constant of the quartz cell wall in combination with the time derivate of the applied voltage, du/dt , determine the amount of displacement current that can be passed through the dielectric to transport current (other than simply capacitive) in the discharge gap. The electric field has to be high enough to cause breakdown in the gas. In most applications, the dielectric barrier limits the average current density in the gas space due to its intrinsic capacity and equivalent capacitive reactance. To increase that current, voltage and/or frequency can be increased. The dielectric barrier, here the two (2) quartz wall, acts as a ballast, limiting the maximum value of the transport current. This is most of the time the configuration we are using. When pre-ionisation of the discharge gas is desired, a configuration of an hollow discharge electrode combine with a flat compound electrode is use. More of this specific configuration later.

The principle of igniting (breakdown) and sustaining mechanism of the dielectric barrier discharge can be described as follow, (ref [5]and [6]), and referencing to Figure 2. As the AC driving signal is applied to the electrodes, the dielectric material, here quartz, polarizes and induces the electrical field in the gap between electrodes, EGap .

In other words, the power coupling to the gas is capacitive. This high ignition potential produces ionisation of the gas and the electrons and ions accumulated on the cell wall, i.e. the dielectric, charging them negatively and positively respectively, producing a decrease of the effective applied electrical potential that conducts to extinguish the plasma. So the light emission is pulsed, not continuous and there is corresponding current pulse at the same frequency of the light pulse rate. Light pulse are in the order of few nano second (10^{-9} sec.).

When the driving signal polarity is reversed, the applied potential and the memory potential due to the charge accumulation on the inner wall's surface are added and the discharge starts again. Therefore the potential required to sustain the plasma is lower than that for ignition that remember follow Paschen's curve. The memory potential is caused by the accumulated charge on the wall. The next half cycle of the driving signal will then have the same polarity of the accumulated charge, so both added together increase the effecting applied field.

NOTE: We are talking about charges accumulation on the inner wall's surface but the charge are accumulate on the internal surface of our quartz compound electrodes and also on the external surface of the compound electrodes. The quartz enclosure act as a dielectric barrier.

Then, the plasma ignites again automatically as a result of the charge dielectric. This memory potential formation by charge accumulation on the dielectric material represents an advantage of the dielectric barrier discharge in comparison with other electrodeless discharge, like ICP and MIP. Indeed, the memory potential increases the intensity of the effective applied field on the discharge gas. ICP and MIP will require a much higher voltage to operate in the same conditions, with the same spectral information output and more heat dissipation. Indeed ICP or MIP are operate at much higher excitation frequency. There is much more power loss. The impedance of the system, i.e. reactance X_c is much lower at high frequency.

NOTE: The above remark is true for static flow, i.e. no gas flow into the dielectric barrier, like a lamp. In this case, the discharge appears stable visually , i.e. the streamer or filament does not or oscillate only a little. However, in analytical application there must be a flow into the cell, like in a continuous gas analyser or a GC. The fluid dynamic will move some of the accumulated wall charge away, resulting in some loss of memory effect, and variation of the ignition potential or the net effecting field required to produce the next discharge. This, in analytical application, results in noise generation when measuring low level of impurity.

$$X_c = \frac{1}{2\pi f C_c} \quad (1)$$

Where f is the frequency and C_c the capacitance of the parallel plate cell. Between a system excited at 13.56 MHz and another at 40 KHz, there will be about 100 times energy loss at high frequency assuming the same peak voltage. This energy is dissipated as heat, and requires external cooling.

The power estimated by

$$P = 4f C_c^2 U_{DIS} [\hat{U} - C_c^{-1} (C_{DIS} + C_c) U_{DIS}] \quad (2)$$

where, P is the power, f is the frequency of excitation, U_{dis} is the voltage across the discharge gap.

$\hat{U}$: Peak Voltage

C_d : capacitance of the cell

C_g : capacitance of the discharge space

NOTE: Here we have taken only the capacitance of the DBD. Actually, the impedance is more complex.

Before the discharge start, the capacitive effect is dominant. Once the discharge start the plasma become a negative impedance, i.e. current increasing, while the voltage across the gap is decreasing. Furthermore the total impedance (resistive and complexe i.e. reactance) will change with the level of impurities flowing into it and the local pressure. This call for a more dedicated plasma generator to increase stability and noise performance, something not considered in previous and still existing PED.

See Ref [7] and [8].

Obviously, the power is directly related to the capacitance and frequency, these parameters that do rule our design approach for frequency selection and system feedback control.

In general, it can be stated than non-equilibrium low temperature plasma uses most of the discharge energy to produce and accelerate electrons, so little heat is generated.

The discharge type of a DBD operating at atmospheric pressure is a streamer type or also called filamentary type for Argon, Nitrogen, Air, Hydrogen or oxygen. In Helium or Neon, the discharge will be diffuse or glow type.

A streamer type discharge is composed of independent discharge filaments. The gas filling the space between discharge filaments is not ionized. However it contributes dissipating the heat. Between the streamers there is no plasma generated by the transport current. However the photon emission from the streamers will ionize some of the impurities located between them, some electrons will be liberated from this process. These will contribute to the discharge process and increase the overall ionisation efficiency. Indeed some of these electrons release by UV photon impact will enter into streamer and be accelerated by the transverse electrical field. The gas in the discharge cell has a high velocity so affecting also electron displacement. With our system these electrons are also deviated by the transverse auxiliary focusing field. A moderate power discharge of $.1W/cm^3$ at atmospheric pressure will have typically 10^6 microdischarges per second. Exposing the same discharge to UV coming from an external light source will result in more than 2 orders of magnitude of the number of microdischarges. So, as shown in Figure 3A, the UV radiation leaving one streamer, and these are emitted all around a discharge streamer or 360° around it, will ease the ionisation of the other streamer channels. It is like a UV assisted plasma. See ref [31] and [32]. A phenomenon that can be also exploited by the Epd system as it will be shown later in this paper. When there is some flow into the cell, or quick pressure/flow change into it, the streamer will move or oscillate, causing spatial movement that can generate noise. High flows have a tendency to sweep away some of the accumulate charges on the wall, affecting the plasma process. The same phenomenon may arrive if impurity level is high, by quenching the system [50], [51]. In this case we can say that the species in the discharge zone are in competition in regards to the energy available. As such, a compound having a lower ionisation or excitation potential, present in high quantity in a binary mixture will limit the electronic temperature or the energy level available into plasma. Steamer discharges are generally less stable and noisier, causing noise in measurement system and decreasing signal to noise ratio. We will see later how the focusing/stabilizing electrodes help to improve this issue.

EFFECT OF PRESSURE ON A DBD

Reducing the operating pressure will make the discharge to switch to a glow type. Reducing the plasma operating pressure has the effect of increasing the mean free path of electrons. The electrons temperature will be higher, or in other word its kinetic energy (speed) will be greater, allowing the ionisation of more difficult to ionize species. When operating at low pressure and having a relatively high intensity electric field, EGap, electrons gain enough energy to excite species having an higher excitation / ionization potential than the plasma background gas, here the carrier being used. Free electrons of the carrier gas are used as seeds for the discharge system. See [9]. However, in some specific case, for example a high concentration of electron negative gases, like O_2 , SF_6 , etc... it is beneficial to increase the number of seed electrons into the discharge zone. Higher number of free electrons increases the efficiency of the ionisation process, due to an increase probability of colisions with neutral atoms or molecules. In order to increase the number of seed electrons, extra electrodes are used to inject electrons into the system. This will be described in details later in this paper. Generally Helium produces glow type discharges which are less noisy. See Figure 3B.

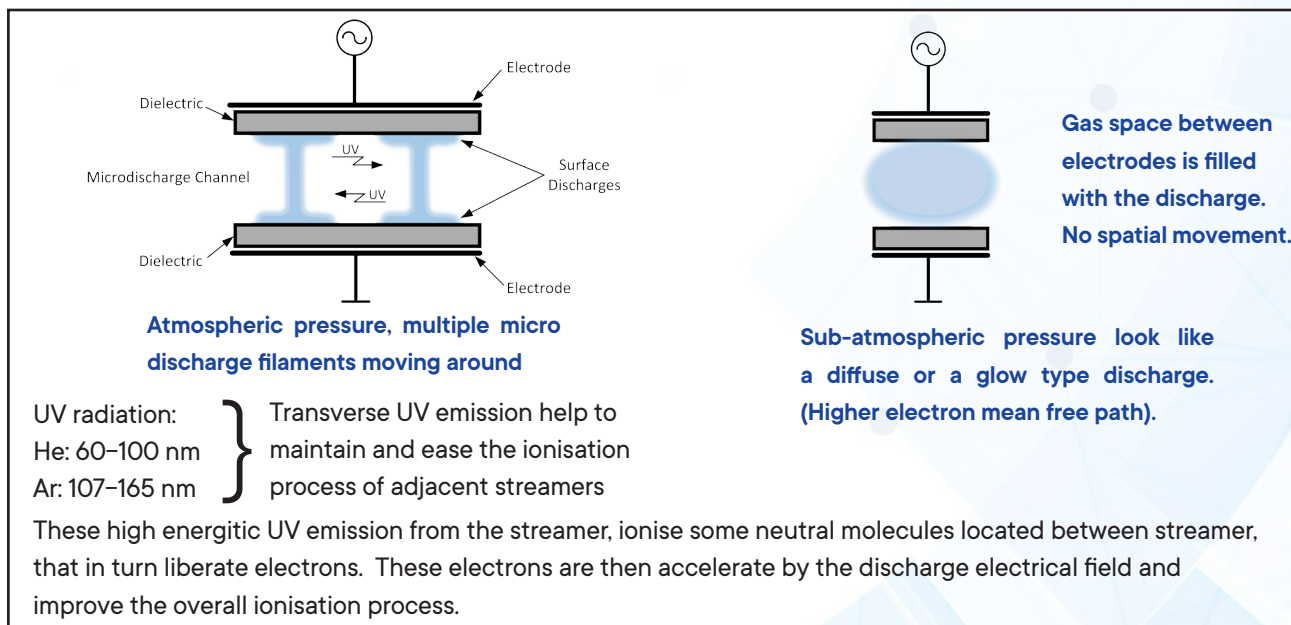


FIGURE 3A: STREAMER AND DIFFUSE DISCHARGE TYPE

Typical electrical waveform signal of our DBD can be seen in ANNEX E

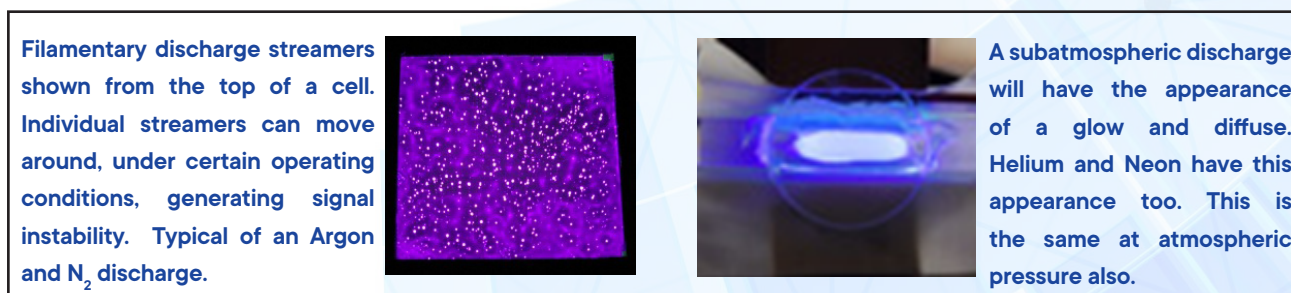


FIGURE 3B: STREAMER AND DIFFUSE DISCHARGE TYPE

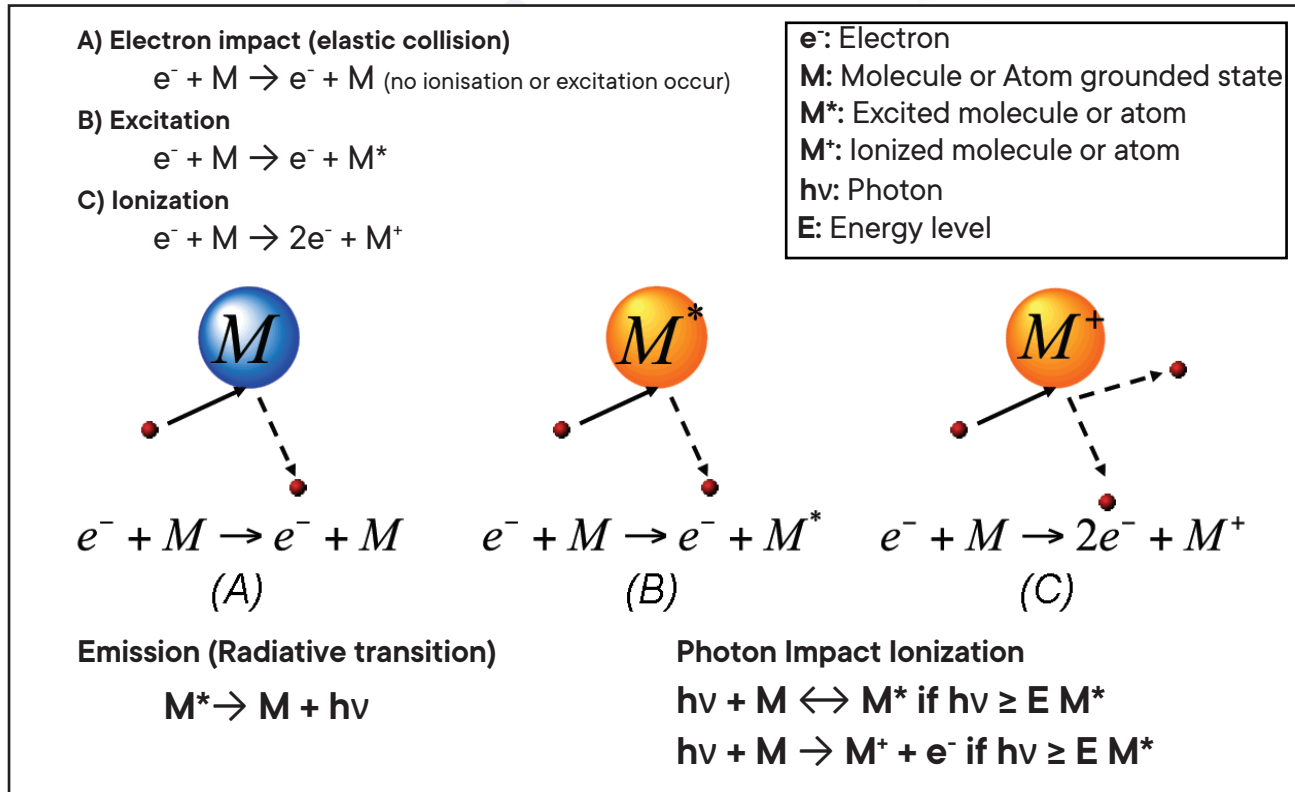
As we mentioned earlier, the ionisation process starts by an application of an electric field which transfers enough energy to a free electron in order to accelerate it, to ionise a particles through collision. From that point, an avalanche of collisions occurs and other ionisation mechanisms can take place.

Some are, but not limited to:

1. **Direct ionization by electron impact**, the first phenomenon to take place in our detector upon power up, while having a pure carrier gas blowing into it is ionization of neutral and previously an unexcited atom, radical, or molecule by an electron whose energy is high enough to provide the ionization act in one collision. These processes are the most important in cold or non-thermal discharges, where electric fields and therefore electron energies are quite high, but where the excitation level of neutral species is relatively moderate or low. However operating at low pressure and adding some seed electrons to the discharge system (with the help of proper mean, such as our electron injection electrodes or in a thermo-ionic assisted configuration) result in an electron cloud, that can gain enough energy transferred from the exciting field to ionize all species.
2. **Ionization by collision of heavy particles** takes place during ion-molecule or ion-atom collisions, as well as in collisions of electronically or vibrationally excited species, when the total energy of the collision partners exceeds the ionization potential. The chemical energy of colliding neutral species can also contribute to ionization in the so-called associative ionization processes.
3. **Photo-ionization** takes place in collisions of neutrals with photons, which result in the formation of an electron-ion pair. Photo-ionization is mostly important in thermal plasmas but it plays an important role in regard to the mechanisms of propagation of non-thermal discharges. Furthermore the photon-ionization mechanism could be also use here as the base for gas detector. (Photo-ionisation is the dominant mechanism in the helium ionisation detector and penning ionisation play also a role in such detector.)
4. **In a streamer discharge**, UV radiation emitted around one streamer contribute to ionise gas between streamer and other streamers, direct photon ionisation like explained in paragraph 3 above.
5. **Surface ionisation (electron emission)** is provided by electron, ion, and photon collisions with different surfaces or simply by surface heating. This will be the topic of the thermo-ionic mode, and floating electrodes and also as a secondary action of our election injection electrodes.
6. **Penning ionization** is a two (2) step ionisation involving a gas mixtures and not a pure gas along. The Epd operates with a doping gas or having He or Ar added to the detector entrance and mix to carrier gas flow, benefit of Penning type ionisation. Direct ionisation by electron impact is given by $e + M \rightarrow M^+ + 2e$ is in competition with $M^+ + A \rightarrow A^+ + e + M$. The Penning ionisation being a two-step process, is then a slower one than direct ionisation. This allow to slow down the ionisation process and prevent or reduce filamentary generation so resulting in a more stable discharge. Furthermore the energy spent to create a metastable state M^* is lower than the one need for a direct impact ionisation. Something that we will use at our advantage. For example, He ionisation potential is 24.6 eV and to create He^* we need about 19.6 eV. This process allow ionisation of impurities with a lower excitation field of lower intensity required to create a gas breakdown. We use the penning ionisation when working with a nitrogen gas as a carrier gas. Indeed the N_2 carrier is doped with He

or Ar. With He, the following occur; $\text{He}^* + \text{N}_2 \rightarrow \text{N}_2^+ + \text{He} + \text{e}$, since the ionisation potential of nitrogen is 15.78 eV is lower than energy of He^* i.e. 19.82 and 20.62 respectively. This is the dominant process when working with N_2 which is Paschen working function is less favorable to create stable discharge. Other gas mixtures could be use, He-Ar, He- N_2 , Ar- N_2 and others. See appendix C.

So, in short, the mechanism could be explained as follow:



As it can be seen, a plasma or gas discharge can become very complex, and a better treatment of the subject can be found in ref [3], [10], [15]. See also Annex A, for a more complete list of some of the possible reactions into a dielectric barrier discharge. When a pure gas is flowing into the discharge, the reactions are different from when there is some impurities into it. The impurities can come from doping agent and from the sample itself. This give rise to many chemical reactions at various rate.

Here some interesting facts about our plasma discharge system. The system consumes very little power, and in this regards it could be embedded into battery operated system. It can be quickly turn on and off, limiting power consumption. Despite this fact, the system have the same power density of a 1 KW ICP see Ref [38]. The cell exhibit very little heat, just above the ambient by about 20 C, the internal electrons temperature can reach several thousand degree kelvin. The heat transfer is very low due the physical size of electron, so exhibiting weak heat transfer efficiency. A good treatment of the concept of temperature can be found in ref [48].

In the following section we will cover some phenomenon in a pratical way that are used to measure an impurity flowing into the detector. We also point out what we did to improve the discharge system and to ease system integration, compare to the previous technology, with the addition of stabilisation electrodes and electron injecton electrodes.

3.0

DETECTOR CELL AND COMPOUND ELECTRODES, PRATICAL DESCRIPTION

Figure 4 shows an example of a frequently used detector cell block. It consists of a metal body, i.e. stainless steel, having direct gas connection fitting on it for carrier and doping inlet and vent connection. When doping is not used, a plug is installed in the doping port inlet. The cell block has some opening to allow quartz window installation. These are the viewing ports.

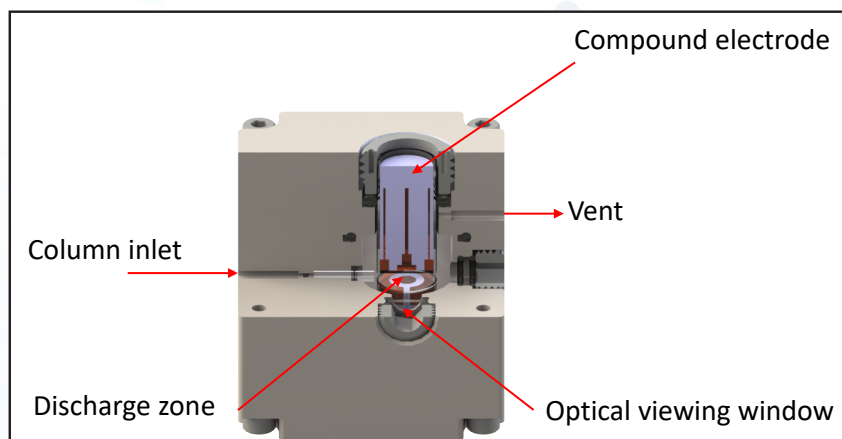


FIGURE 4: DETECTOR CELL BLOCK

The high temperature version of the detector cell is fitted with a rod heater and an RTD temperature sensor. These elements allow a tight temperature control of the system. Temperature could be set up to 350 °C, if necessary. The key of the system is the compound electrodes. The cell body has two large ports drilled face to face, allowing the compound electrodes to be installed.

It is possible to adjust the distance between these electrodes, to increase the electrical field intensity from 50 kV/cm to 400 kV/cm. A real benefit of working with gases other than argon or helium is to increase the ionisation efficiency.

Figure 5 shows the detail of compound electrodes concept. Each electrode assembly has 3 sets of electrodes. One for maintaining the discharge, this one is mounted in the center of the electrode wall. Their respective lead wires are connected to the plasma generator driving signal output. Then, partially surrounding the discharge electrode on each side, there is the stabilisation electrode. They consist of two, half circle-shaped electrodes. These are connected to the plasma controller module, stabilisation driving signal output.

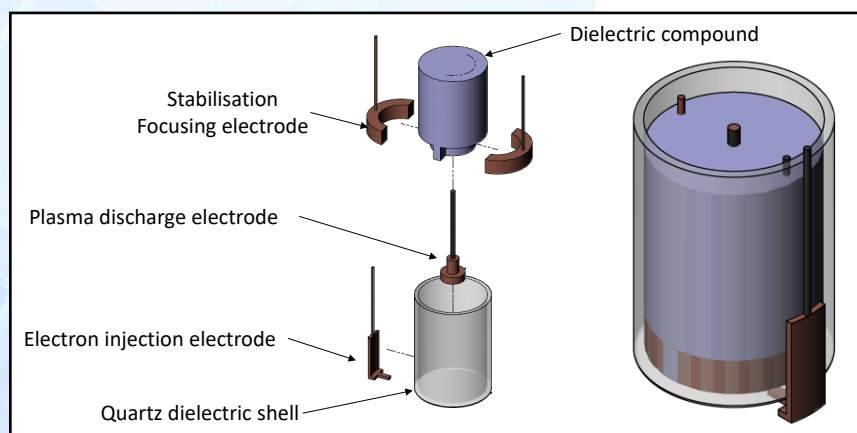


FIGURE 5: COMPOUND ELECTRODES VISUALISATION

Finally, externally mounted to the compound electrodes quartz wall, there is the electron injection electrodes. These are connected to the plasma controller module electron injection driving signal output.

These compound electrodes are the heart of our concept. They can be fit on any plasma discharge chamber, regardless of shape and material. Generally, two compound electrodes are used, but a cell body could be made to receive any number of these compound electrodes. For example, a cell body having 4 or 6 compound electrodes are feasible. This allows more viewing ports, and also allows using the first set of compound electrodes to trigger some chemical reactions generating by-products, that are monitored by the other compound electrodes action through their respective viewing windows.

One of the benefits of this design is the capability to operate the discharge system at high pressure. The block cell design body will resist and maintain plasma discharge at an operating pressure up to 150 PSIG. Figure 6 shows internal view of the cell block. There is a quartz tubing insert that brings the carrier gas and its doping gas, if any, directly into the discharge zone between the compound electrodes. The incoming carrier is released into the discharge zone, and no dilution phenomenon occurs, so, even with low carrier flow, like in a capillary column application, the internal value of the detector has no detrimental effect. Impurities peak dilution into the internal volume of the detector is avoid.

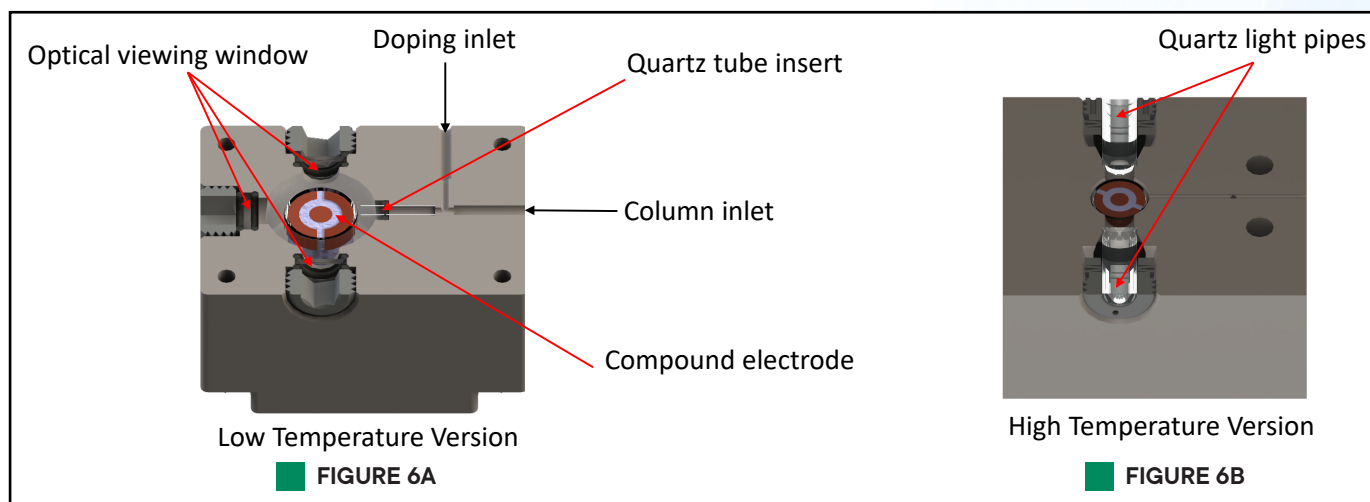


FIGURE 6: INTERNAL VIEW OF THE CELL BLOCK

3.1 SOURCE OF INSTABILITY FOR ANALYTICAL APPLICATION IN A DIELECTRIC BARRIER DISCHARGE

One of the drawbacks of a DBD is the discharge displacement or movement that occurs when operating at atmospheric pressure (streamer or filamentary type discharge), when the level of impurities substantially increases into the detector or when the plasma operating power is low. It is also happening when using a carrier gas giving more difficulties to maintain a stable plasma. In such conditions, the spatial distribution of the plasma changes or could become unstable (oscillation).

Since this detector system is based on a dielectric barrier to transfer the power to the plasma zone (usually the dielectric barrier is provided by at least one of the cell's wall), it gives rise to wall charge build-up that eventually equals the charge applied to the external of the wall, cancelling the field applied to the gas resulting in the discharge interruption. This is typical of the dielectric barrier discharge, below 500 kHz of excitation frequency, with less than about 5 mm distance between the wall. At higher frequency, or in the RF range of excitation and also related to the width of the discharge volume, the charges into the plasma doesn't have the time to travel to the wall and accumulate on its surface, resulting in a glow or diffuse

discharge type. This gives a much stable discharge but have the serious drawback to require more complex electronic circuit and impedance matching network to get efficient power coupling. Furthermore, operating at such frequency results in much power lost and heat generation. This imposes limitation for miniature design and working lifetime.

The internal space between the walls cell play also a role in this matter since they have a direct impact on distance travel by particles, mostly electrons, since the frequency at the point this phenomenon may decrease or stop will be different. In our case during our experimentation we found that over 500 KHz the discharge begins to change from a streamer type to a glow type and this at atmospheric pressure. For a relatively wide range of frequency plasma driving signal, the spectral information is still the same, however the intensity is proportional to the driving signal frequency.

3.2 DISCHARGE STABILISATION AND ELECTRON INJECTION ELECTRODES

WORKING PRINCIPLE

3.2.1 DISCHARGE ELECTRODES

The discharge electrodes are responsible for the plasma ignition and of sustaining the mechanism as detailed in the section 2.1 of this document.

The electrodes consist of a circular metal disk fitted inside the flat disk-end quartz tube assembly as shown in figure 5. The quartz tube close end is the dielectric barrier.

3.2.2 STABILISATION ELECTRODES

Like previously mentioned, the source of instability is due to the wall charge build-up that causes discharge extinction. With the gas velocity into the system, the next discharge is not necessary at the same place causing spatial movement. The discharge appears to move, and streamers are moving around in the discharge zone.

In order to decrease the phenomenon substantially, a secondary field synchronised with the discharge field is applied to the system, moving or sweeping away the accumulation of charge on the inner surface of the dielectric, that causes discharge streamer extinction. The stabilisation field is a surface field as shown in figure 7. This field acts on the charge that naturally accumulated on the wall. It moves them and delays the accumulation. This results in a much more stable discharge, hence improving signal noise ratio (figure 8).

3.2.3 ELECTRON INJECTION ELECTRODES

As we have said earlier, the seed electrons start the discharge and avalanche process are supplied by the gas flowing into the cell or more precisely between the compound electrodes. Having more electrons improve the ionisation efficiency. In order to increase the electrons population in the discharge zone, two extra electrodes are added to the system. These are in close proximity of the discharge and not isolated by a dielectric barrier. Forcing a current between them allows some of the current electrons to be accelerate by the discharge field and these enter into collision with neutral particles, creating metastable and analyte excitation. All signal applied to these electrodes are automatically controlled by the plasma generator module.

The figure 12 shows the block diagram of the plasma controller module, while figure 9 shows various waveforms phase relationships. Notice the increase in signal stability when the stabilising field is applied,

see figure 8. Also notice the increase of signal intensity when the electron injection current is enabled. These improvements over previous PED design allows the detection to be used for measuring lower level of impurities.

The cell block body design and its control system allow various modes of use that were simply not possible with existing PED design.

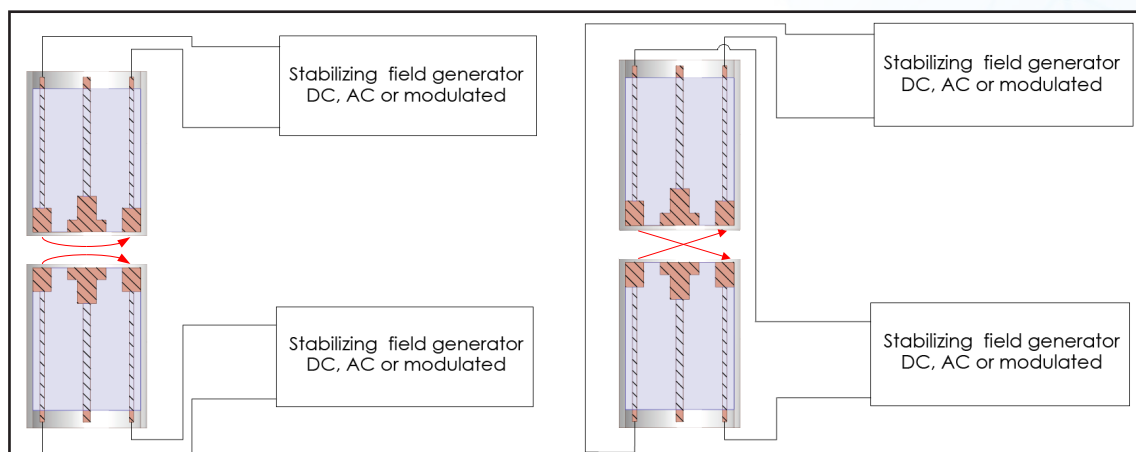


FIGURE 7: COMPOUND ELECTRODE

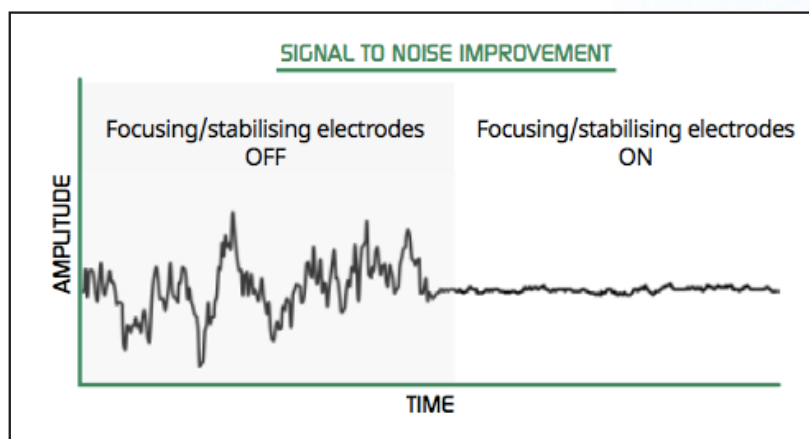


FIGURE 8: SIGNAL TO NOISE IMPROVEMENT

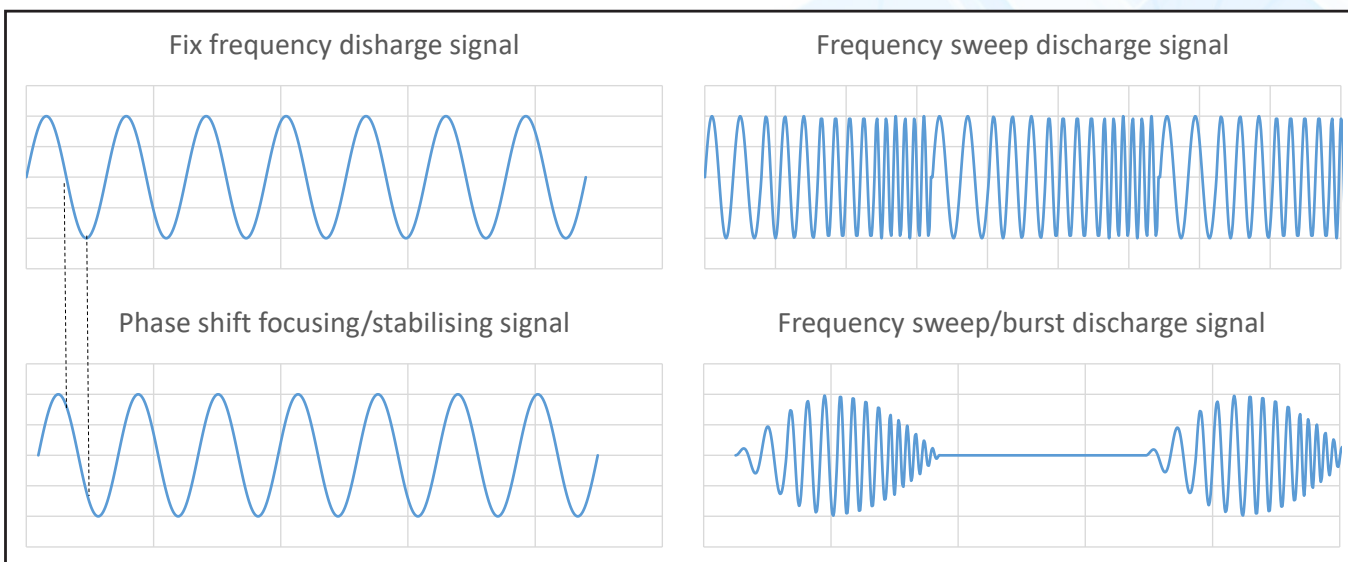


FIGURE 9: PLASMA CONTROLLER DRIVING SIGNAL

3.2.4 COMPARAISON WITH PREVIOUS PED DESIGN

FIRST, THE CELL DESIGN

Figure 10 shows some of the former and existing quartz cell used as plasma chamber. It is made of thin quartz plate and in some cases of rectangular shape quartz tube.

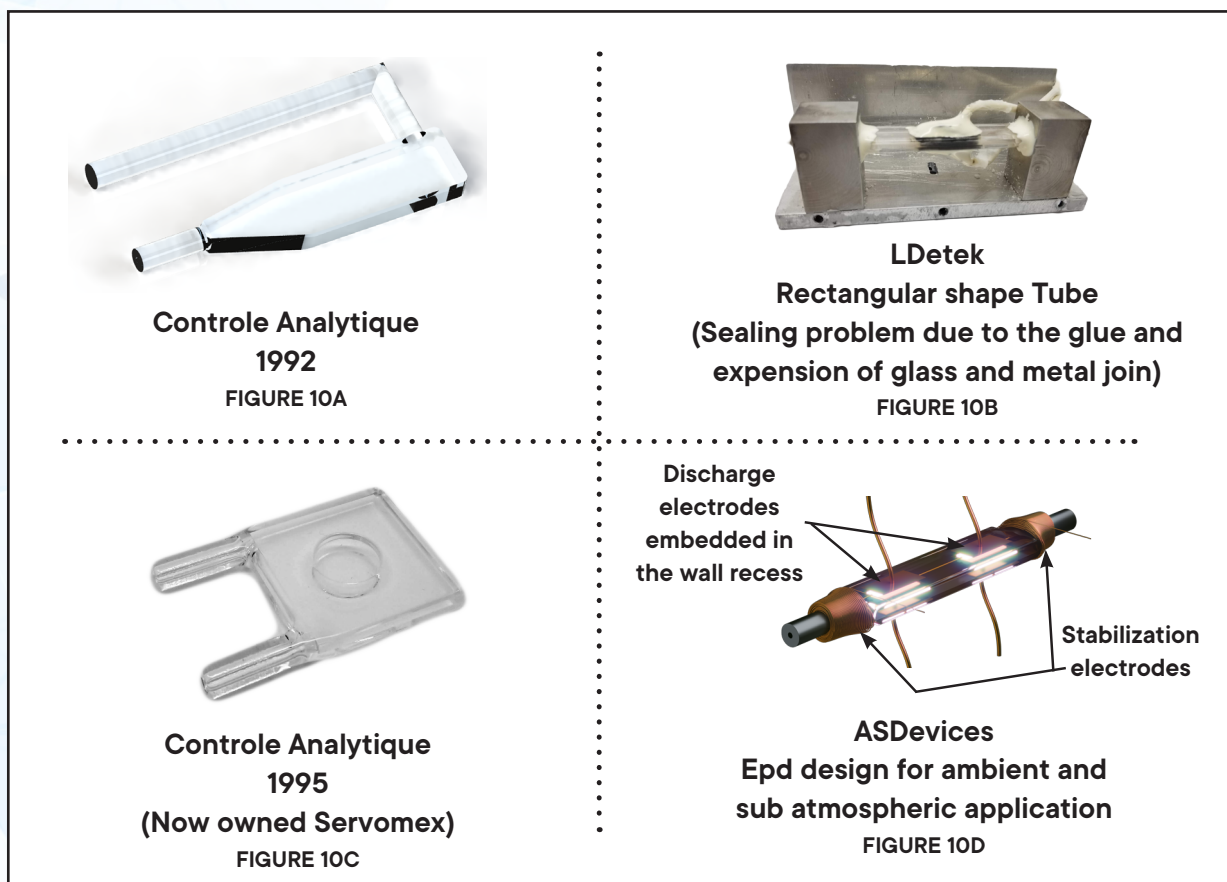


FIGURE 10: OLD CELL DESIGN COMPARE TO EPD DESIGN FOR AMBIENT PRESSURE

These various designs were fragile and can't resist to over pressure. It also had to be seal with some potting compound for thermal stability and also to avoid corona discharge around the electrode. It also help maintain the electrodes in place.

This design was subject to cell failure, i.e. cracking, it can't be heated. Maintenance of the cell, like cleaning is not possible, since the cell module can't be disassemble. Another drawback is the internal cell volume that require make up gas when using small diameter column, like Plot or capillary.

In case of failure, the detector have to be replaced. Furthermore for system integrators and OEMs, it was difficult or impossible to customize or experiment various configuration to develop specific methods.

Figure 10D, show our Quartz cell design for online operation at atmospheric and sub-atmospheric application that does not require the electron injection electrodes. Thicker quartz walls with discharge electrode embedded in wall recess result in a more robust design compare to former cell. Stabilization electrodes are mounted at the inlet and outlet of the cell. They are made of coiled wire, this is also a turbulence free and flow through design. However, the design show in Figure 6 will become our standard, since it reduce cost and it is resistant up to 150 psig (10Bar).

Figure 6, show one typical cell block configuration our new EPD technology. The cell block could be easily disassembled for inspection or maintenance. Compound electrode gap is adjustable, so giving the possibility to increase excitation field from 40Kv/cm to 400Kv/cm. View window could be remove for cleaning or replacement if necessary.

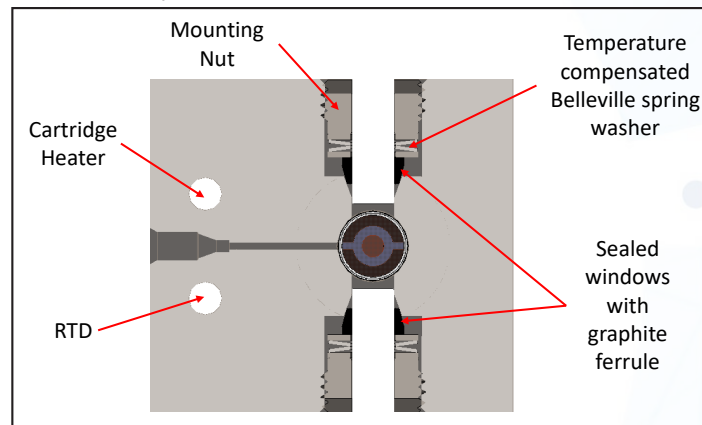


FIGURE 11: HIGH TEMPERATURE EPD VERSION

The user could easily select and change optical filter in less than 1 minute. Various material window could be install, like MgF_2 for infrared measurement, or fluorescence window for deep UV and excimer measurement.

The cell block, and associated compound electrodes are robust and will not break or crack if submitted to an over pressure. In fact, the system will resist to pressure up to 150 psig.

Figure 11, shows the high temperature version. A rod heater and RTD is fitted into the cell block. The compound electrodes are mounted with graphite ferrules backed by a metal plate compressed by proper Belleville spring and mounting nut. Another benefit of our design is that the internal volume have no effect. Indeed, the gas is directly release into discharge zone, to be instantaneously ionised before subjected to expansion.

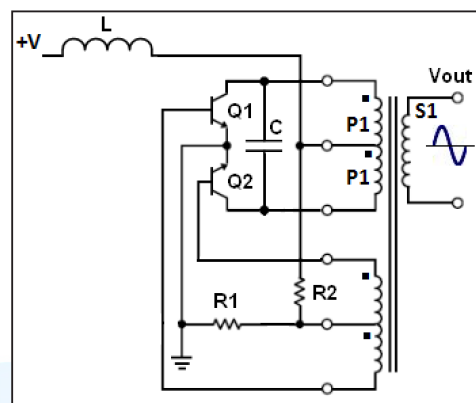


FIGURE 12A: SIMPLE OPEN LOOP FREE RUNNING PLASMA GENERATOR

SECONDLY, THE PLASMA GENERATOR

The plasma generator of the former and still commercialise today are based on a simple oscillator operating in free running mode. This generator configuration in figure 12A. This is based on the Royer converter developed in the fifties. However this modified version provides a sinewave at the ouput and the frequency is fixed by the standard LC resonant circuit.

The transformer step up the voltage and their secondary are connected to the discharge electrodes bonded on the quartz cell.

This design was simple and low cost, but was plagued by major drawback. Indeed it subject to temperature drift, frequency shift, noise and depend in the level of impurities flowing into it, its response factor change. The change in response factor is cause by the change into the plasma (load of the transformer) when flow pressure and impurities level change into cell. In short, the load impedance (plasma load) change and this change in reflected back at the primary of the transformer, and appearing in parallel of the capacitor of the LC resonant circuit. This will cause a shift in frequency and voltage that change power of the plasma. See annex E, that show change in electrical characteristic when impurities level change in a plasma. Finally, there is no mean to control charge build up on wall surface and spatial movement of the plasma streamer, that are the cause of substantial noise mostly at low level measurement.

Our new plasma generator resolve all these issues as explained in section 4.0

4.0 EPD PLASMA CONTROLLER / DRIVER

The level of performance achieved by the EPD could not be reached without a close control of various parameters affecting discharge power distribution. Figure 12B, shows a block diagram of the new generation of plasma generator. The generator may supply a discharge signal of various frequency up to 1Mhz with various duty cycle and modulator rate. It is a force driven signal that is not affected by the load, i.e. the plasma cell discharge, like in all other commercial system that include our previous technology, copy by some other manufacturers. The current voltage and frequency are monitored and controlled by the generator. All this parameters could be changed during a G.C. run by entering proper values in the event table.

The generator automatically synchronises the stabilisation field with the main driving signal without user intervention required. The generator could also be operated in sweep mode, allowing to change the operating frequency in real-time during a peak following a gaussian or ramp control signal.

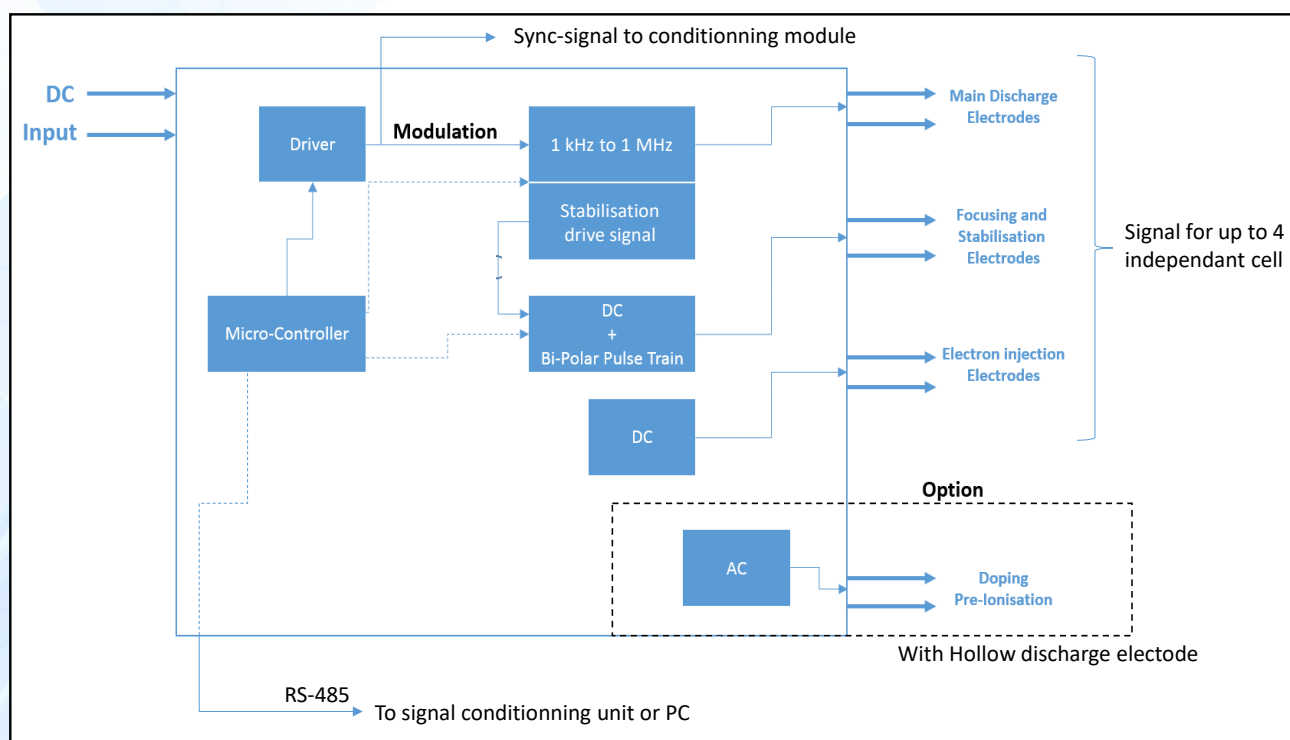


FIGURE 12B: EPD PLASMA CONTROLLER / DRIVER

5.0

SIGNAL MEASUREMENT, CONDITIONING AND
DATA PROCESSING

When the detector cell is operating, a stable and intense plasma discharge takes place between the compound electrodes.

In order to extract spectral information, optical wavelength modules are installed on the cell assembly to measure various emissions from the discharge.

These optical wavelength modules have the physical form of a small cartridge. Figure 13 shows a typical optical module and its function block. These modules have very high-quality optical filter and photodiode set. The photodiode signal is amplified by an adjustable gain pre-amplifier stage. The gain is selectable in real time. There are 4 gains selectable for this pre-amp stage.

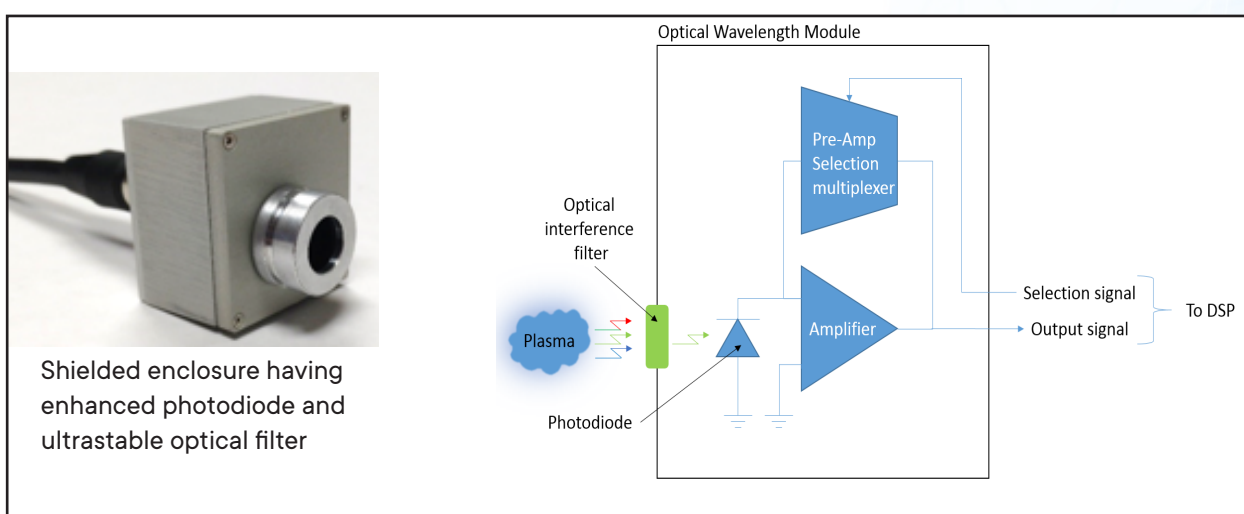


FIGURE 13: OPTICAL WAVELENGTH MODULE

The optical wavelength module is connected to the digital signal processing (DSP) module, through an electrical cable. The DSP has 4 inputs, so up to 4 specific wavelengths or zones can be monitored in real time. This is a major advantage. The DSP processes the analog input by nulling the offset, with the auto-zero feature and provides additional user selectable gain stages. The resulting analog value is connected into digital form with a resolution of 24 bits and simultaneous conversion rate up to 50 kHz.

The DSP module, figure 14, is equipped with a powerful processor that can do high speed digital processing, apply our spectral compensation algorithm (patent pending) and peak modeling algorithm, and many other functions.

The DSP module can do various real time arithmetic functions between input channel, signal addition, subtraction, division, ratio, logarithm relation. The resulting data could be reduced to an analog output and use as final chromatogram.

There are 4 high resolution analog outputs that can be used simultaneously for digital system.

Any signal from any input channel could be redirected to any analog output allowing peak eluting in same time from 2 channels to be retransmitted to one analog output, or one after the other.

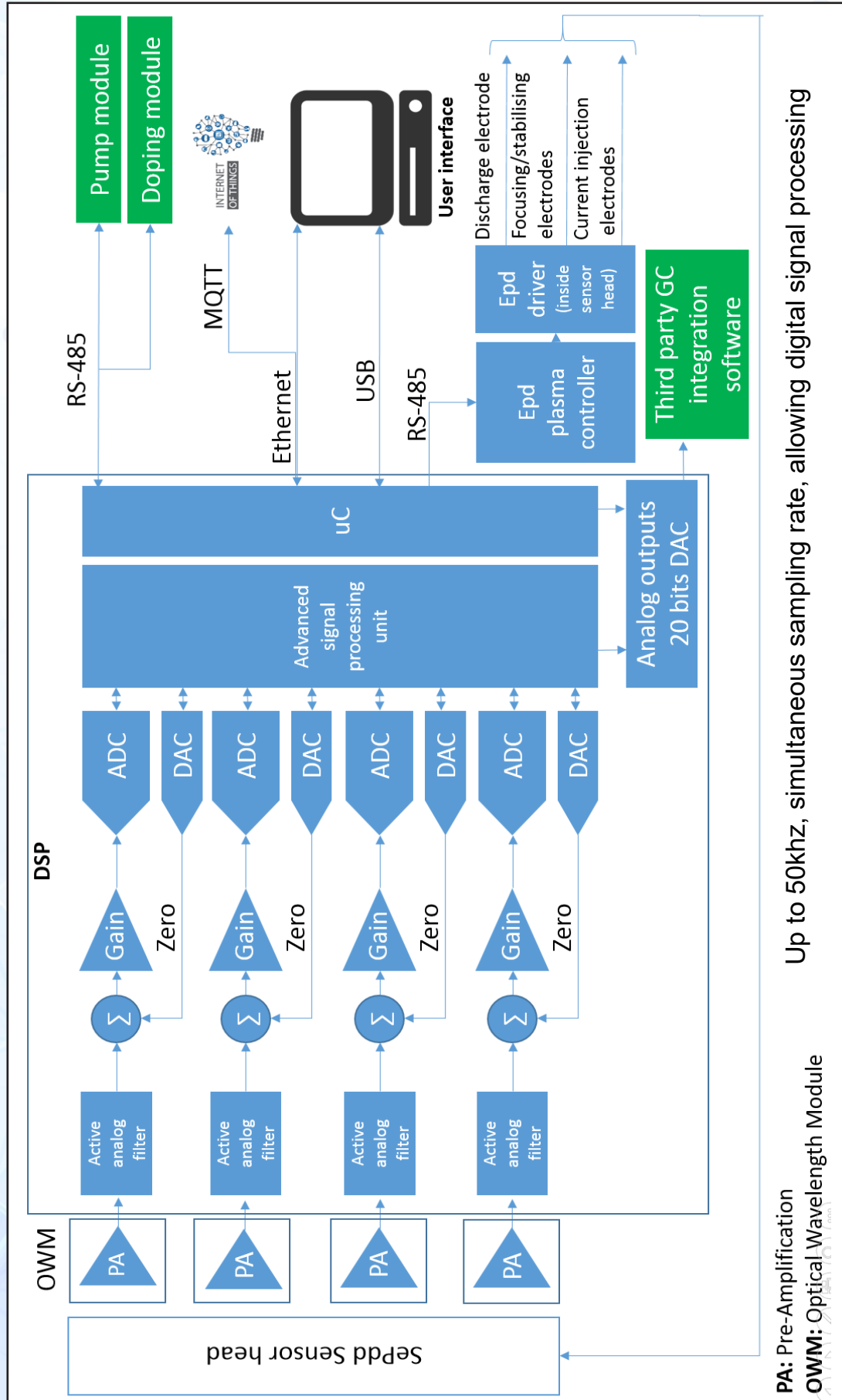


FIGURE 14: SIGNAL CONDITIONING BLOCK DIAGRAM

6.0 USING AND INTEGRATING THE Epd

6.1 USING DOPING GAS

In some applications, plasma doping will enhance system performance and allow more flexibility. When we are referencing to doping it means to add some level of compounds at the detector inlet. It can also be adding percentage of gas having higher or lower ionisation potential than the carrier gas to ease the plasma process by or decrease system sensitivity, this is normally refer as a mix gas discharge.

Adding some doping gas to the plasma allows the following to be done;

- When using a dry packed column, it will eliminate peak tailing aspect for more reactive compounds. This is done by adding a little bit of moisture to the discharge zone. This can be easily done with a plasma doping module based on a permeation tube maintained in a temperature controlled environment. Varying the temperature change the moisture level added to the system. Only a few ppm is require when operating with lower excitation potential carrier gas, like argon. Much lower level is required when using helium. This is all under the control of the signal conditioning board that have a precise temperature PID loop.
- Using a doping gas as a tracer gas. For example O_2 could be used as a tracer for hydrocarbons measurement. The other emission base detector are using CN or CH emission wavelength that are closer to UV. By using O_2 as tracer, monitoring the oxygen deficiency at 777 nm emission wavelength, where the optical response of the system is almost at peak performance. Furthermore, the CO and CO_2 could be measured without the need of a methaniser.
- Using a doping agent to generate a by-products into the plasma and measuring the related emission or absorption spectrum. This could also be used with the constant emission mode.

Referring to figure 16, some amount of the selected doping agent will be added to a cylinder having the same background gas type used as carrier gas. A capillary flow orifice is used to control the amount of doping mixture added to the carrier gas.

The pressure at the orifice inlet is set at a relatively high value, for example 100 to 150 psig, in order to be in the sonic range. This way flow velocity through the orifice is constant, only the gas density changes. This results in a very stable system whatever the hydrocarbon compound, or VOC type passing through the detector. It will react with the O_2 and O_2 intensity emission will decrease.

In other words, impurities are measured using the oxygen deficiency caused by the interaction of any impurities with the oxygen doping. Some chromatographers said this method reminds them the basic concept of ECD systems. Within an ECD system, electron deficiency is measured.

Adding O_2 is not only a method to measure organic and other type of compounds but also improve sensitivity and peak shapes. When measuring organic compounds, there will be some carbon release into the plasma cell and a part of it will get deposited on the inner walls, creating active sites. These active sites will delay the passage of impurities making their peaks larger and tailing. Furthermore the free carbon will react with the incoming impurities and reduce the peak height. Some of the O_2 doping will act in this case as a scavenger avoiding carbon deposition and transforming the free carbon in CO and CO_2 , before it coats the cell walls. In fact it keep carbon volatile.

Even if there is some change in the flow of the doping mixture at the inlet of the detector cell, the measurement accuracy will still be good. This is due to the baseline signal being zeroed before each peak or between GC run. There is also more doping agent than the maximum level of impurity to be measured.

Doping can also be used in other situations. An example is when a short chromatogram cycle is desired, and a relatively high value of impurity of a few ppm and higher, has to be measured in a sample background different from the carrier gas. As a doping agent, a compound of the same type of sample background can be used. This will reduce a lot baseline upset caused by the presence of some amount of sample background, mainly if combine with the differential measurement capability of the system.

A practical example can be found in the air separation industry. It is required to measure N₂ level in crude argon. Crude argon is a mixture of Argon and oxygen, oxygen value could be fairly high based on air separation plant design, it may range from single digit percentage to 80% of oxygen. The N₂ concentration value is used to control the reflux of the low pressure distillation column. So response time and precision are of prime importance. See reference [31] and [32]. Adding some level of oxygen, or Air as doping agent will decrease the sensitivity of the baseline to the sample background. This way a simpler GC configuration could be used.

Indeed an extra column and switching valve could be eliminated. This would be normally done with the standard heartcut or backflush method to eliminate sample background. Furthermore, with this particular application, argon carrier gas is used eliminating the heartcutting problem when using helium as carrier. Accordingly a much faster time could be achieved. In such applications, a GC is used as a process transmitter that inputs a process value to a real-time PID control loop.

Another source of problem is that in many cases a sample may have some level of moisture. This is not uncommon when monitoring various process stream, ambient air, catalysts base reactor or purity control of tanker, and where in such case the use of quick connector coupling is common. Over the time moisture accumulates into the column. Based on operating conditions i.e. change in moisture sample level, carrier quality or impurity level, the level of moisture will change into the detector. This will react with the impurities and generate peak tailing. This is a common problem when working with packed columns and some type of PLOT and capillary.

In this case, the doping module could be added at the inlet of the detector to add some level of moisture. This extra level of moisture will eliminate peak tailing. The ASD doping module has a specific permeation tube releasing a stable amount of moisture into the carrier gas. An internal heater keeps the temperature constant. The temperature set point can be set by the user to control the level of moisture released into the carrier gas. The ASD doping module could be also use with other chemical reagents.

Doping can also be used to reduce the sensitivity of the system. For example, adding Nitrogen or Argon to the carrier will reduce the sensitivity to an air sample, while still measuring other impurities.

Both methods of doping can be use at the same time if necessary.

There are several possibilities when using doped mode of operation.

- As such, another interesting alternative method for adding doping reagent consists to release it directly into the discharge zone. This allows to control the time when to release or interrupting it by reversing the flow into the tubing that bring the reagent.
- Furthermore such arrangement allows vaporization or atomization of a doping agent originally in liquid phase. See [27]. This is a common way in semiconductor manufacturing plasma process. This requires a different cell design having two (2) inlets ports connect to independent tubing. One inlet allow column effluent to flow through the detector while the other one bring the doping reagent. Proper valves routing allows flow reversal into the doping line. In such case the inlet doping line is then switch to the pressure controller inlet or to a source of carrier gas or the flow can be simply stop.

These are driven by the application. There are numerous chemical compounds that can be measured by the detector. The Epd system offers an easy way to find out optimal operating conditions for very specific application.



Figure 15, permeation module, thermally controlled

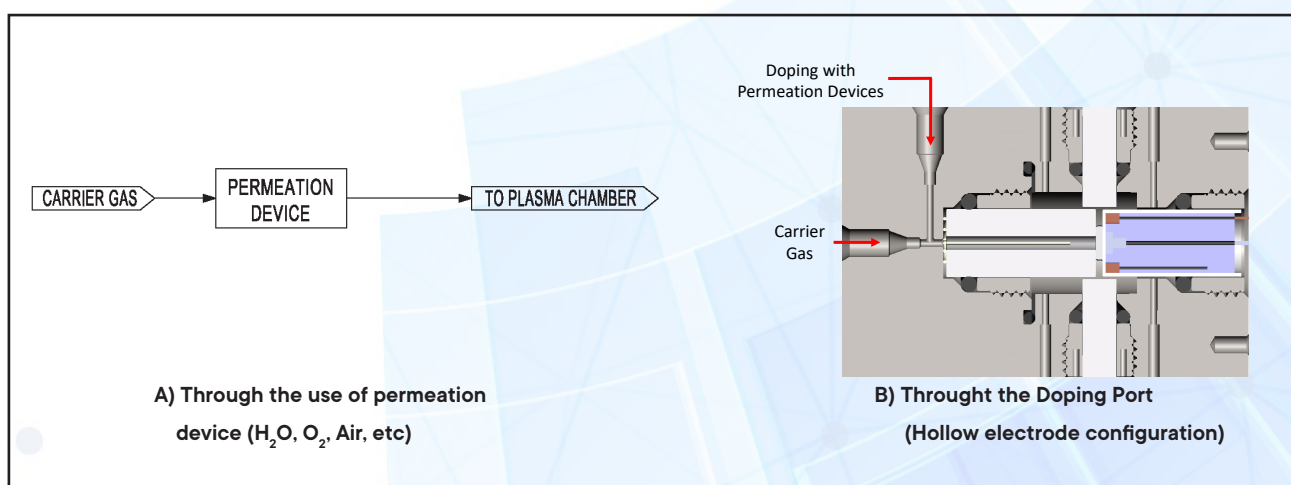


Figure 16, various doping configuration

6.2 PLASMA OPERATING PRESSURE

Ideally, the system would be used with the pressure control module that allows to set and control the gas discharge pressure at any sub atmospheric value. This change a lot of things. Doing this, the excitation process is improved by increasing mean free path of the injected electrons. Their kinetic energy is increased and more energy is available for the excitation/ionization of neutral atoms and molecules. An important benefit of operating under these conditions is the reduction in quenching of a target impurity, which has a higher excitation/ionization potential than the gas background or carrier gas. Quenching occur when an excited molecule or atom is de-excited without any photon emission. This is generally done during collision and energy transfer to a colliding particle.

Reducing plasma pressure allows the low population of the target analyte to be de-excited by the emission mechanism before colliding with other particles or the wall of the cell. When the later happens, the de-excitation mechanism is not radiative, so not very useful in our case. The electrons surplus generated by the injection electrodes further increases the excitation/ionization probability of such analytes, when operating at sub atmospheric pressure.

A practical application is the measurement of Neon in Argon. Some interesting sensitivity has also been obtained for Neon in N₂.

Reducing the detector operating pressure has the following impact on the Epd:

- Reduces the emission spectrum baseline while increasing impurities emission, so increasing the sensitivity.
- Eliminates the need for make-up gas to improve peak shape. This allows us to eliminate peak dilution, broadening or tailing by virtually controlling the internal volume of the detector. The introduction of an additional gas flow normally higher than the GC flow, decrease the residence time of the analyte through the discharge and it leads to worse detection limits and expensive gas consumption. See [14].
- Lowering the boiling point of chemical impurities, reducing the need to heat the detector. Water will boil at 66°C when operating at 10kpa absolute, a substantial gain.
- It allows the measurement of impurities having higher excitation potential than the carrier gas used.
- Provide a fast recovery after an overload, by reducing or avoiding wall and tubing impurity absorption.
- Allow the detector to be switched between two (2) different GC streams operating under different carrier gas. For why example it is possible to switch between a helium and an argon carrier GC stream.
- Eliminating any baseline drift generated by atmospheric pressure variation from one day to another. A gas discharge is very sensitive to the operating gas pressure or more precisely its density.
- When using mix carrier, reducing pressure allow to reduce the discharge potential, so the field across the gap, favoring Penning Ionisation. Very useful to more difficult to ionise species.
- A small plug and play pump module is available to sub-atmospheric operation mode.

7.0

CONFIGURATION AND USER INTERFACE SOFTWARE

A fill in the blank type software included with the system allows an easy system start up and use. Even non-technical peoples could easily use it. We have designed it for practionners and all levels of technical chromatographers since the on board firmware automatically controls plasma parameters. The user only needs to select the proper operating parameters and save them to the onboard processor.

The software allows complete configuration of the system, monitoring and trending any parameter such as pressure, temperature, flow, raw count data converter value, chromatogram signal, saving chromatograms, and reload them for further processing, configuring calculation between channels, data logging.

Special data filtering and signal processing can be selected to discriminate noise and allowing a clean signal recovery in order to extract chromatographic peaks of extremely low value. Indeed the built-in in DSP can manage high speed fourier transform. The chromatogram data point are input to a fourier transform alorgytm. This way the equivalent DC component (i.e. slow baseline drifting) and spurious noise harmonic removed remaned from the chromatogram signal, and the final chromatogram is the inversed fourier transform. Other chromatogram data processing sub routine could be selected.

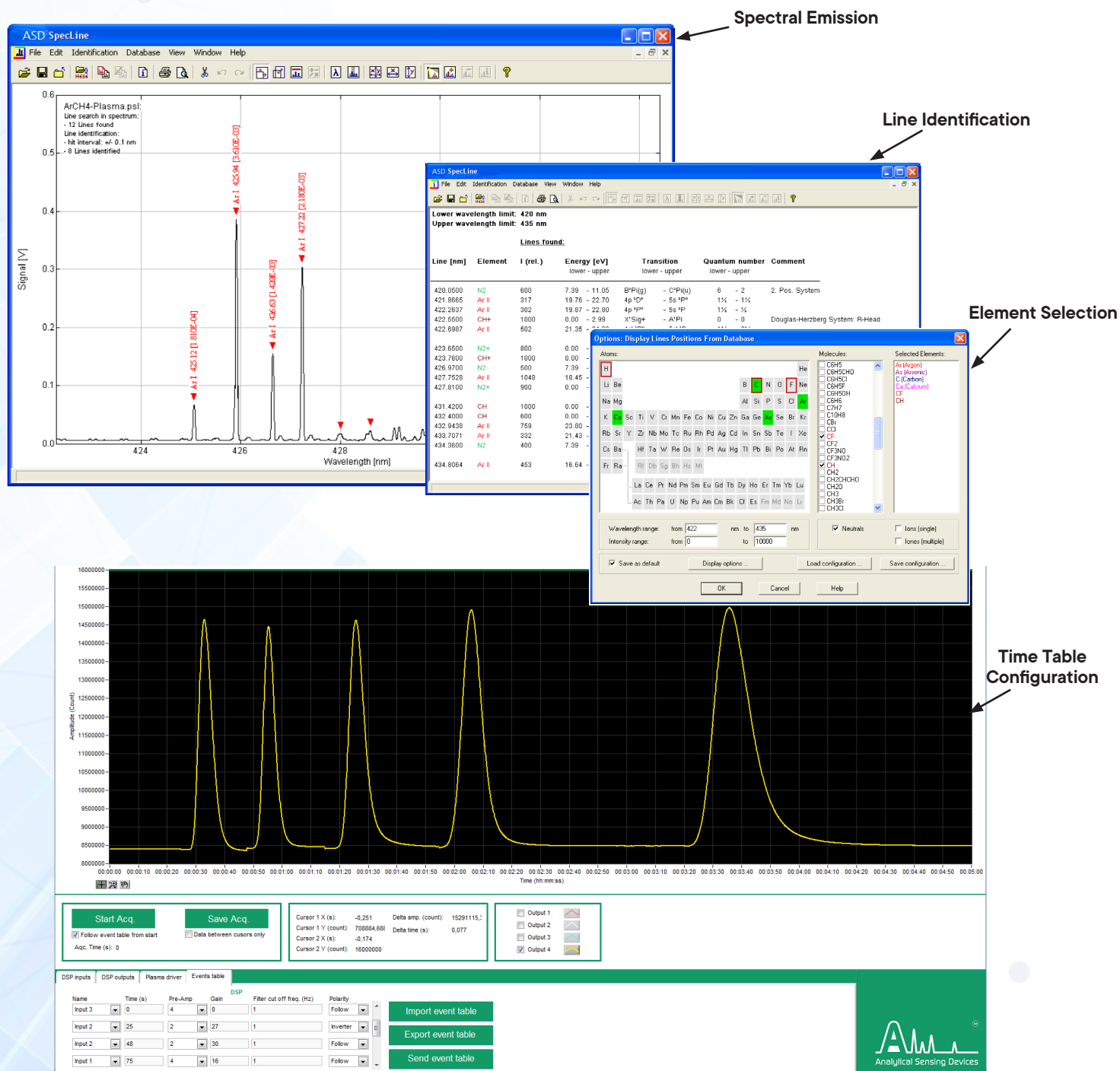
All these various functions are user selectable, for each individual peak in a chromatogram.

A user can also configure a time table event or sequencer. When a sequence or a run is started by a digital input, or through software, the system will change operating parameter in real-time according to the selection made in the time table. Time table allow the selection of optical channel number, zeroing time, setting electronic gain, expected peak starting and ending time, plasma power, system operating pressure, peak signal processing, control of digital I/O, and user define custom parameters and some other optional parameters.

Software features

- Fill in the blank type user interface
 - Plug and play philosophy
- Allows easy configuration of all system parameters for all operation modes.
- Real time monitoring and trending of all parameters. User configurable.
- Time or sequencer table editing.
- Single point or multi-point calibration for peak value calculation
- Monitoring and saving several chromatogram and real time
- Filtering and signal processing for noise discrimination and low peak intensity recovery
- Editing arithmetic calculations between channels
 - Baseline compensation in real time
 - Signal addition or ratio
- Automatic mode
 - Cycle re-start at the end of the time table
- Manual mode : Cycle started with a digital input trigger signal, through a software command or by click of a mouse
- Diagnostic mode

- Labview driver available.
- Zooming, scaling trend or chromatogram
- Data logging function
 - All parameter could be logged in real time and later on reload and compare with chromatograms signal. Excellent tools for configuration optimization.
- Digital I/O can be controlled with an external optional digital I/O module.
- Peak calibration and selecting engineering units is also provided. Calibration can be linear, or multi-point, for any peak. This allow peaks integration to be reported in proper engineering unit if a third party integration software is not use.
- Custom driver and development.



8.0

SYSTEM PHILOSOPHY AND THIRD PARTY TOOLS

8.1 SYSTEM PHILOSOPHY, OPEN ARCHITECTURE

The detector module could be delivered as a stand-alone unit, without signal conditioning or other optional module. In its basic form it include only the plasma generator and the discharge cell. This opens the door for custom OEM development. Any OEM can design and use its own electronic to work with the cell with or without optical fiber. Only one optical window or channel could be use as minimum configuration and still, quite impressive what can be done with this minimal configuration. Using a large bandpass filter, all permanent gases and light hydrocarbons and many other impurities could be done at ppm level, and helium or argon could be use as carrier gas. Detector module could be custom fit to any OEM requirement to ease integration, like in portable system.

Being an open architecture design means that the technology could be packaged in a custom way for any qualified OEM. ASD made available the electronic design circuit schematic, bill of material, firmware code, driver as an open source for its customers. This dramatically reduces development cost. CAD file could also be supplied. In order to ease the development process, ASD have made a development kit. This kit include an isothermal valves/columns oven, the iMOv, loaded with our intelligent valve driver i.e. IVD, and a Epd mounted on the top of it. The iMOv could be populate with up to 6 ulnProve ISV valves of any of our models. Column could be mounted directly into the oven. No mechanical work required. Pre-cut tubing, Liplok fittings, valve footprint indicated on the mounting plate, thread insert, tools kit and enough space for third party hardware and plug and play software that allow easy control of all parameters, speed up configuration work and dramatically reduce cost. A mini Mov™ will be available for smaller and compact system.

8.2 THIRD PARTY TOOLS

The Epd is also designed to be easy to use with off the shelf third party hardware like spectrometer, light source (laser lamp), photodiode module. There is plenty of these devices readily available on the market with excellent and useful supporting hardware. As for example Ocean optics and Avantes companies, to name only these ones, manufacture optical spectrometer that can be directly connected to the Epd. These can be used for emission or absorption measurement. They are also very useful for troubleshooting by allowing on the fly impurities identification, easily identifying inboard leaks or other contamination. A spectral line identification software database that can be use with most of miniature spectrometer, is available from ASD. This allow quick and easy identification of emission lines and related transition. No need to search in numerous database, a tedious job. A spectrometer is a useful tool to optimize system configuration, allowing easy spectral line identification that in turn could be used for the selection of optical filter for a specific application

For example, figure 18 shows two research setup with Epd technology. The first setup, which is based on a 5890, uses a combination of our own optical wavelength module with a third party spectrometer for spectral line identification. The other setup, is based on a Agilent 7890 which has been configured for ultra trace measurement of permanent gases.

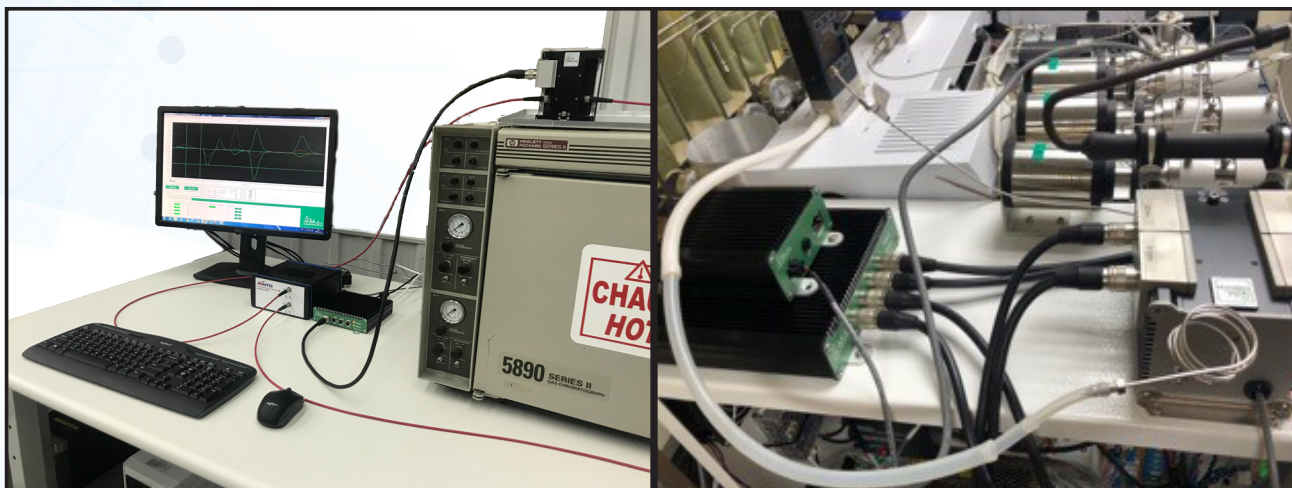


FIGURE 18: EPD INTEGRATION EXAMPLES

Figure 19 shows an argon emission plasma with few PPM of air in it. Clearly showing the N₂ emission at 337nm, O₂ at 777. Moisture is shown by the OH emission from 305 to about 308nm.

This is very useful to visually identify air contamination in a system. It is like a snapshot of the system integrity. As soon the source of leak is corrected the air emission disappear.

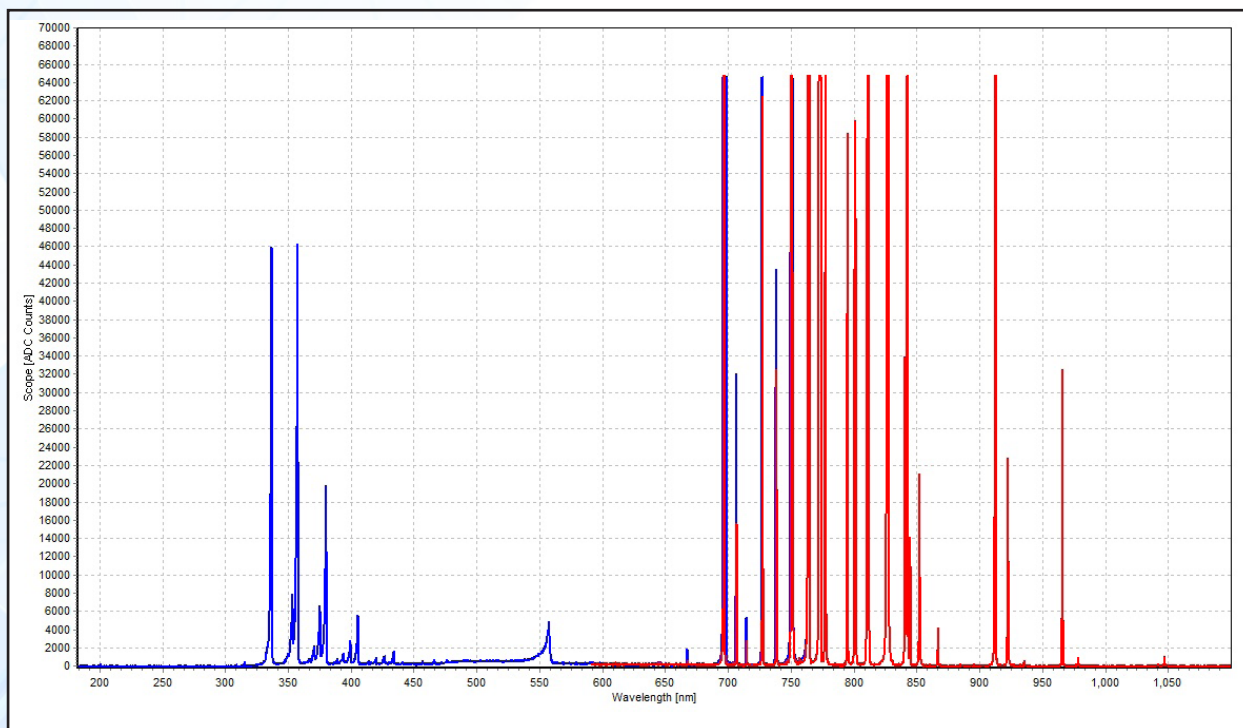


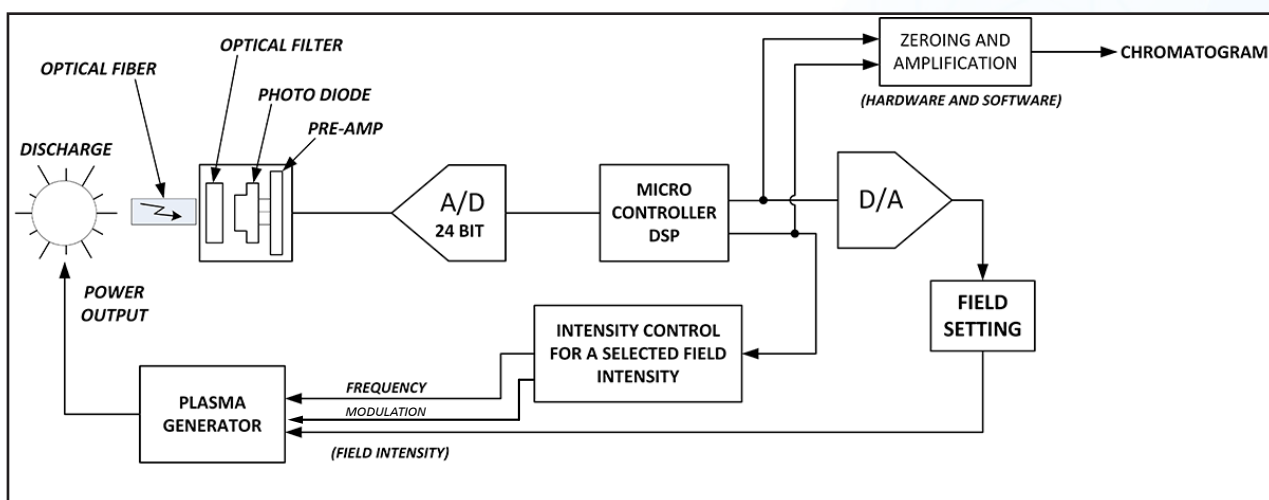
FIGURE 19: ARGON PLASMA WITH AIR

9.0

CONSTANT EMISSION OR POWER BALANCE MODE

This mode of use is a basic mode and uses only one optical channel. It could be made selective or with universal response, based on the optical filter selected. The idea behind this concept is to maintain constant the emission intensity when an impurity peak is going through the cell. This is shown in figure 20. First, a discharge field intensity is selected by setting the digital to analog (D/A) converter value. This set the voltage output of the plasma generator. At different discharge field intensity, there is a different energy level transfer to free electrons. In turn this affect the system sensitivity. So setting a discharge field intensity set also impurities sensitivities, based on various plasma operating parameters, like doping, pressure and the measured wavelength or spectrum. The frequency of the applied voltage on the cell is varied in order to maintain the emission intensity constant when an impurity is going through the discharge. The frequency is converted to a voltage. This voltage is zeroed before a chromatographic peak and this signal is amplified and represent the chromatogram.

It can be seen like a typical feedback control loop. Feedback gain is set automatically by the system to achieve stability and avoid oscillation. It all transparent for the user.



■ FIGURE 20: CONSTANT EMISSION

A particular wavelength band or total emission spectrum could be use as measurement input to the signal conditioning module.

This is an interesting mode, even if an impurity that go through the detector doesn't generate an emission line, the power distribution into the plasma is change by quenching, affecting the overall emission.

It is still possible to dope the plasma or change the operating pressure. This mode of operation allows multiple impurity detection with only one optical measuring channel.

10.0

DYNAMIC LINEAR RANGE, LIMIT OF DETECTION AND REPEATABILITY

10.1 DYNAMIC LINEAR RANGE AND LOD

For most of detector use in gas chromatography, the dynamic linear range and limit of detection or sensitivity, are the most important specifications for figure of merit. Detectors like TCD, FID, ECD, FPD, DID, PDID and mass spec, have been in use for many years and users know their performance figures and these are generally fixed ones. (See Table 1)

In this regard, the Epd system is really different. The plasma detector is not only a detector discrete part, but a complete system.

The Epd is a fully user configurable system, where measurement performance and characteristic could also be tuned by the user. Any zone of the response curve versus signal level could be linearized through a simple look up table, i.e. multipoint calibration or with the use of linear fit mathematical function. This can be done for each individual peak in a chromatogram and save into Epd. These are plasma physic related behavior and it will not change over the time. This is like the gravity!!

The Epd is an intelligent system. Limits of detection and linear operating range are not a constant figure of merit. As for example of this fact is the measurement of N_2 in emission mode when using argon as carrier gas. The response is linear from sub PPB to a few thousand of PPM, when monitoring the emission wavelength of 337.1nm, the strongest N_2 emission under an atmospheric argon plasma. If we increase the N_2 concentration, the response flattens and the emission line disappears. During this process another emission line at 380nm appears. This emission line exists only at high N_2 concentration values, and the intensity is linear with N_2 concentration up to several percent concentration. There is a transition zone where both wavelength exist at the same time.

The system can select optical channel and maintain full linearity while having low range ppb sensitivity, and for the high range (i.e. several thousand ppm or percent measurement), ppm resolution. A 1000ppm N_2 measurement range will still have less than single digit resolution.

Taking into consideration all parameters; type of carrier gas, operating plasma pressure, selection of wavelength, band head, or overall emission, working mode selected (i.e. constant emission mode, emission or absorption and all this with or without doping), open the door for a large number of possibilities and broad range of system performance. It will require a few hundreds of page to describe the various possibilities.

It is possible to have a large dynamic linear range by doing proper configuration, the same is true for the limit of detection.

The limit of detection for the system is not the same for all impurities. However with proper detector configuration, GC configuration, enabling the data processing algorithm and peak processing for low level measurement, sensitivity down to 100PPT could be achieved.

10.2 REPEATABILITY

In this regard too, the Epd is really different. Since all parameters controlling the discharge are built around feedback loop, the discharge energy level and ionization degree are constant figure. As long as the same number of molecules of analyte is injected, the response will still the same, practically 100 % repeatability over 24 hours.

The gas chromatograph where the Epd is in use is in fact the limiting factor for the repeatability. Indeed, column degradation or pollution, stability of various flow, pressure and temperature, leak integrity, hardware like carrier pressure regulator, quality of electronic pressure controller (presence of O-rings), stability of sample injection (GC sample valve), tubing, fittings and the GC configuration or design are as much factors that can affect not only repeatability but obviously the LOD too. Several times we have disconnect the Epd from the GC front end and inject directly the analyte directly in the Epd through a capillary tubing to act as a column (providing some amount of back pressure), to find out a very nice peak that wasn't there at all with the GC front end. Such experimentations lead the author to file a patent for a method to resolve some of the issues that affect peak sensitivity, and stability. See Ref [46].

To really see and characterize the repeatability of the Epd a very specific configuration must be use having only ulnProve valve, diaphragm proportional valves, Liplok fittings and ASD tubing. This will make sure to eliminate other variables that affect the repeatability. Only these hardware and a specific procedure can be used to get a real figure about Epd repeatability. Repeatability is characterize in emission mode.

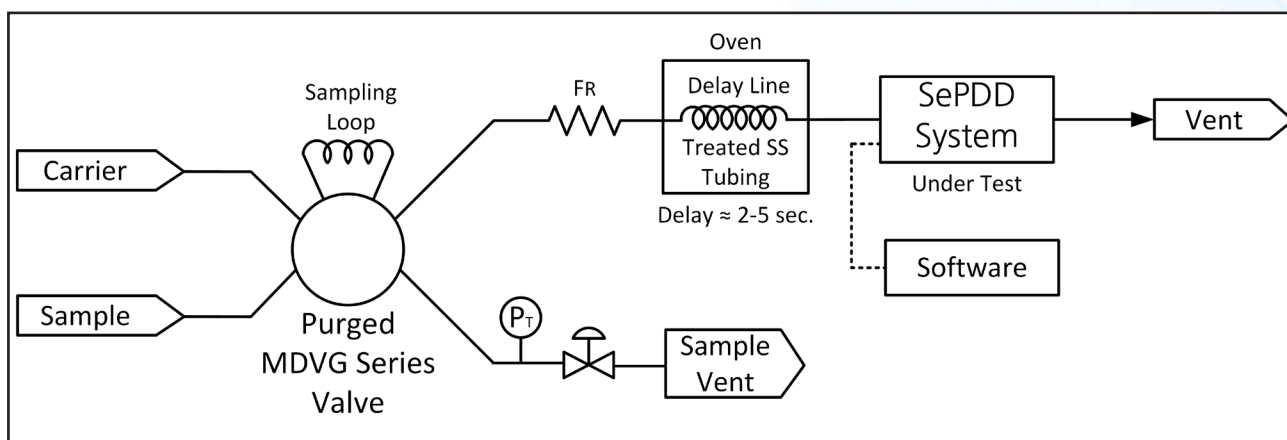


FIGURE 21: EPD, PERFORMANCE TEST TYPICAL BENCH

11.0

APPLICATION EXAMPLES

Finally, the most interesting part i.e. applications. A cookbook on how to apply our technologies is under preparation. Here there is just few examples to show what the system is capable of.

The Epd could be used for a very wide range of applications with or without GC front end. Here we are showing only few examples, but enough to show the versatility of the system. Generally the emission and the constant emission mode of operation are all that you will need for gas chromatographic application, i.e. with a GC front end. On line applications i.e. without GC front end for continuous analyze are possible in some specific case. Absorption mode is available for spectroscopy. Many applications can be done in absorption mode combine or not with GC front end. Before to show some examples of application, we would like to point out some rules of thumb that we are following at ASD. It is possible to resolve the same analytical application in several different way. There is some method we are suggesting that have been label as non- chromatographic by traditional chromatographers.

Hardware Use:

- ulnProve series, 6 and 10 ports. Mandatory to avoid inboard contamination and to maintain a thermodynamic equilibrium in term of diffusion and permeation. See ref [28].
- Liplok fitting family; these have the sealing integrity of a VCR fitting, but without the associated dead volume and the flexibility of a compression fitting, eliminating completely the need of any welding, orbital or brazing. These are also the perfect packed column end fitting. This fitting concept have two point sealing, see ref [30].
- ASDevices Tubes; these are passivated tubing, pre-cut in various length and have a coating on each end for about 1 cm, allowing extremely good sealing. See ref [47].

The Following Rules Apply:

- We never cut any tubing mechanically, this eliminate a lot of problems in regard to valve damaging, leaks and tubing deformation. It also eliminate the creation of active sites that interfere with low level measurement and reactive compounds.
- Cleanliness, don't touch any part that will be in the path leading to column and detector with your bare hands. We have seen system drifting for weeks for this reason. Use proper powder free gloves.
- On all critical parts of a system i.e., sample manipulation and all tubing routing up to the detector, we are using Liplok fitting and ASD tubing.
- In house made packed column must be done with passivated tubing, without silanized quartz wool to retain packing, but use ASD's column end fitting specifically design for this purpose. Molecular sieve based column must have a minimum of particles size variation. For example

instead to use 60–80 mesh, sieve it for 60–65 mesh range. Proper washing and cleaning procedures must be follow before packing and conditioning. These procedure are done after the grinding process and sieving. In some specific cases ASD use a specific treatment to encapsulated or embedded specific compound into the zeolite cage. This require high temperature and pressure treatment process. Further to this, specific ion exchange could be done to enhance resolution of co-eluting peaks.

- Porous polymer base columns must be dust free and have as much as possible constant sieving.

The above rules are the only way that ASD is recommending to use the Epd. Using the Epd with other commercial parts will have a negative impact on the detector performances and **are not supported by ASD and may void system warranty.**

This being said, add to these rules above there are features offer by the Epd that will make integrators life easier. For example the Epd can be turn OFF or ON at any time, during a chromatographic run, avoiding reaction of reactive balance of sample background, like silane and the like. The flow can also be reversed with proper valves routing. This allow doping interruption and can also be used to resolve specific problem. The Epd can be switched from different GC stream operating under different carrier gas. For example a GC stream under argon carrier and another one under helium could use the same Epd in real time. Up to four detector i.e. cell module could be use with the same signal conditioning.

First set of example show the Epd use for permanent and bulk gases analysis. Generally speaking such applications is dealing with He, Ne, H₂, Ar, O₂, N₂, CO, CO₂ and due to the column use for these applications, we are including CH₄ and THC. Any of these compound may be analyzed in any other ones as when these are the sample background. It all depend on the GC configuration. The separation columns use could be capillary, PLOT, micro-packed or packed columns.

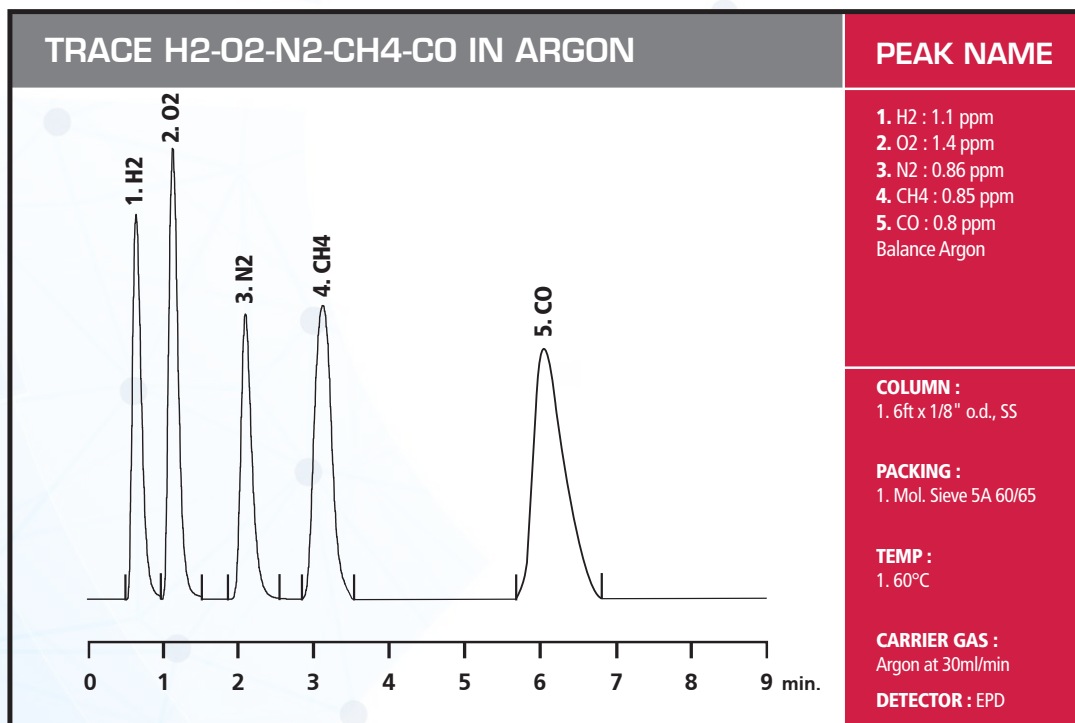
Generally, the choice of column technology depend on the level to be measured, at low level i.e. less than few ppm, ppb or lower, packed column are preferred due to larger sample capacity, leading to higher sensitivity at a much lower cost than capillary. I can already hear the GC gurus complaining about the separation efficiency of a packed column, for them the holy land is the capillary columns.

However base on a market study, referred by Grob, see ref [17], market value for separation column was estimated at over 1 billion dollar and from this 20 to 25 % was still the traditional packed column. When column efficiency or the HETP is not a critical requirement and an instrument have to be operated as a standalone unit all year long, like in process GC, packed column is a good and robust choice, see [55]. In brief, here, low level bulk gases measurement are made with packed column, higher level of impurities with PLOT or capillary.

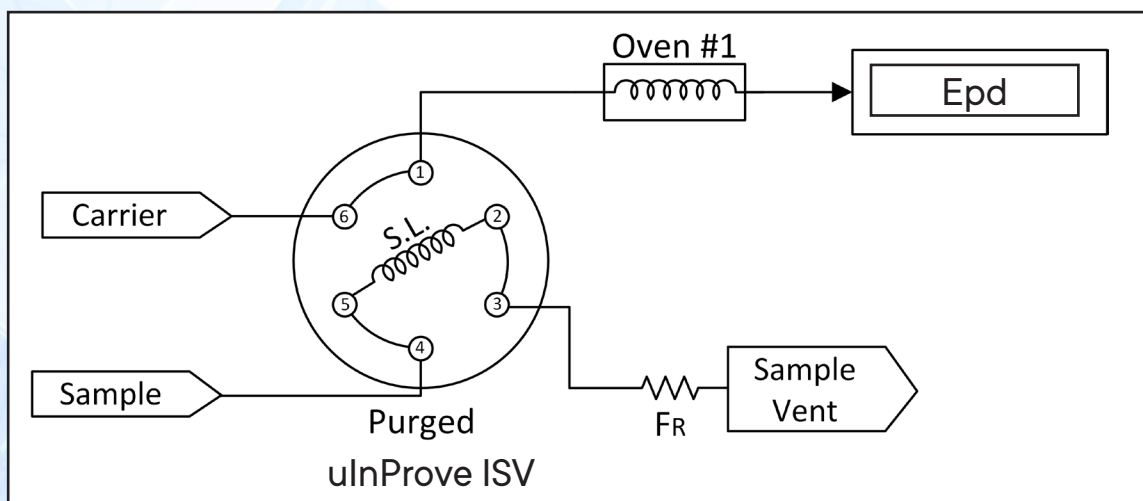
Example 1

Trace of H_2 , O_2 , N_2 , CH_4 and CO , all at 1 ppm or less. This is a very basic and straight forward application. Column 1/8" passivated and coated SS, 2 meter long, MS-5A, 60/65 mesh, with Liplok column end fitting, no quartz wool.

Injection valve : ulnProve, 1/16" port connections



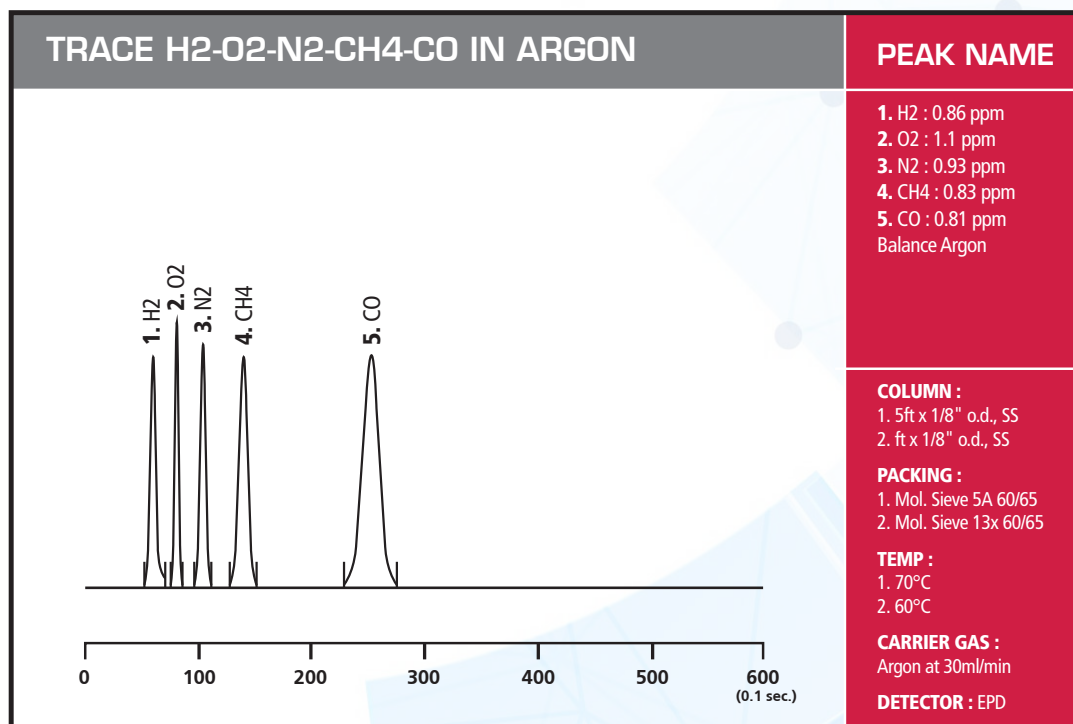
* Chromatograms show with argon as carrier gas. Helium could be also use.*



Example 2

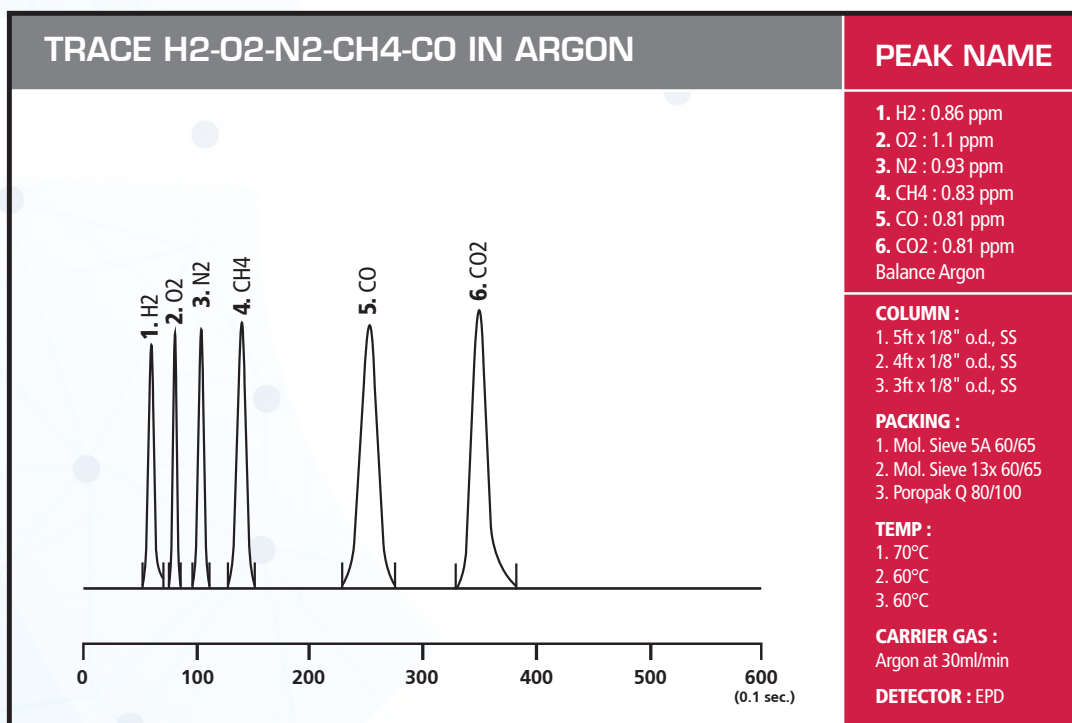
In the typical application of example 1, the trouble maker is the CO peak. With molecular sieve 5A this peak come far after the CH₄ and depend of it concentration, it will exhibit some tailing and large base. With the molecular sieve 13X , CO peak elute faster and have a better shape but chance are that H₂ and O₂ separation will be poor, mainly with a 1/8" O.D. column. The relative importance of the appearance of these phenomenon are directly dependent of operating conditions and level of impurity to be measured. At high level peak shape are good, and it is easier to get the job done.

Now here we are showing an alternative to resolve this issue, which work whatever is the impurity level. The idea is to use a separate short column only for the CO peak. This column is packed with molecular sieve 13X with mesh size of 60/65. Upon injection H₂, O₂, N₂ and CH₄ will elute as one large peak follow by a nice CO peak. The other column in the system is made long enough to resolve H₂ and O₂, based on the sample level and sample loop volume.



Example 3

Here we adding the CO₂ on the impurities list to be measured. This is done by the addition of a porous polymer packed column. Also show use of capillary columns.



12.0 CONCLUSION AND OUTCOMING

We have briefly described the concept of DBD gas discharge and show how we exploit some of its behavior to identify and measure impurities in GC mode or continuous mode for some specific case. The right combination between mode used and operating parameters could be found and run in real time for each individual peak in a chromatogram, optimizing individual impurity compounds measurement. New GC methods could be easily developed by any practitioner, opening the door to a new way to do gas chromatography. By using high performance valves and accessories offered by ASDevices, one could quickly setup a system in a short period of time compared to the traditional way. The Epd is so flexible that it is possible to do several different configurations for the same application, this is driven by the user's imagination and creativity. When system parameters and conditions of use have been defined, OEMs can specify and use only what they need for their target system, offering many possibilities for cost reduction and system footprint. Marketing philosophy allows licensing and technology transfer and support, securing the investment and the future of the use and availability of the technology.

We have explained the use of the Epd in emission, absorption and constant emission mode. Other modes of use are still open for investigation by the experimenters and developers. In the future we wish to establish an open user community through an online forum providing tips and hints.

Other system configurations are under development to extend the application range. This includes also a high temperature version.

Never before a GC detector has been available with a so high level of possibility and ease of integration.

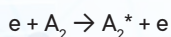
See the application bulletin for examples of applications and system configuration recipes.

ANNEX A - THE CHEMISTRY OF SILENT DIELECTRIC BARRIER DISCHARGE (DBD)

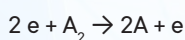
The main plasma reactions are electron/molecular reactions, atomic/molecular reactions, decomposition, and synthesis. In the ensuing reactions A, B represent atoms, A₂, B₂ represent molecules and e is used for electrons, M stands for temporary collision partner, ions have a + or - superscript, and the excited species are superscripted with an asterisk. All the equations listed below are from the works of Eliasson and Kogelschatz, 1991b and they have been represented below without any modifications.

Electron/molecule reactions

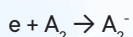
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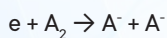
Dissociation:



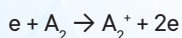
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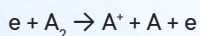
Dissociative Attachment:



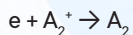
Ionization:



Dissociative Ionization:

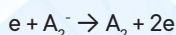


Recombination:



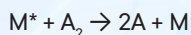
* Silent discharge term come from the fact that a DBD don't generate noise like an arc discharge do.

Detachment:

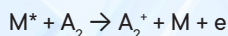


Atomic /molecular reactions

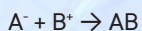
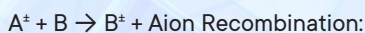
Penning Dissociation:



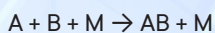
Penning Ionization:



Charge Transfer:

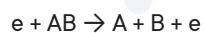


Neutral Recombination:

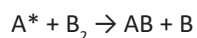


Decomposition

Electronic:

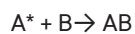
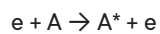


Atomic:

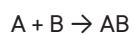


Synthesis

Electronic:

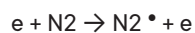
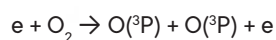


Atomic:

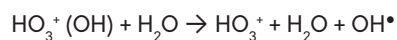
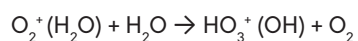
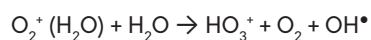
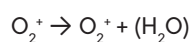
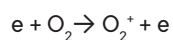


The generalized equations given above can be exemplified with oxygen and nitrogen as follows, $O(^1D)$, $O(^3P)$, $OH^\bullet$ are the radicals.

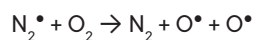
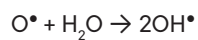
Electron impact



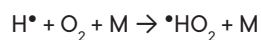
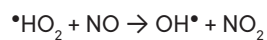
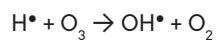
Ionization clusters



Quenching

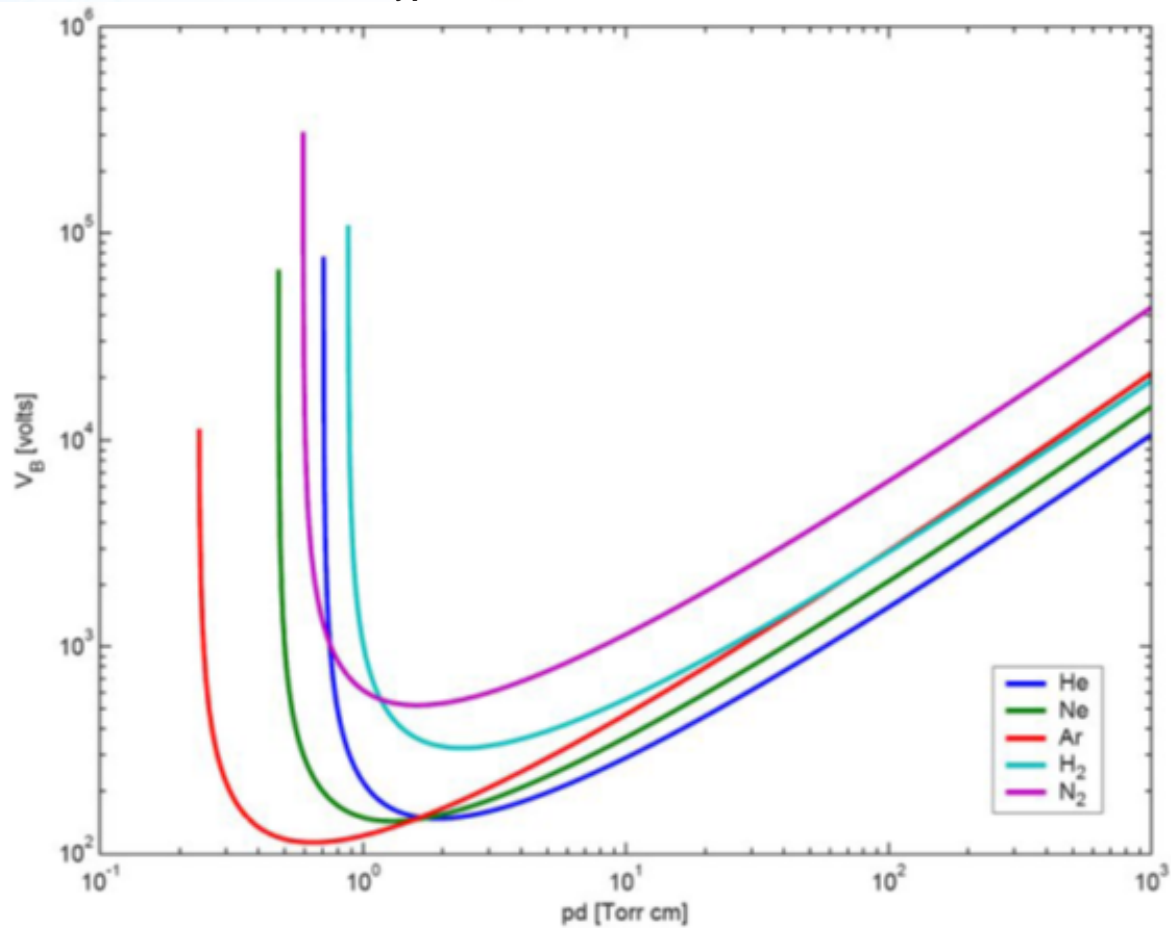


Other



ANNEX C - RELATED TO INTER-ELECTRODE DISTANCE

Typical Paschen curves



The graphic show above are call Paschen curves. They show the relationship between the breakdown voltage of a pure gas and the pd value. The pd value is the discharge operating absolute pressure p , time the distance between the discharge electrodes, d .

A minimum breakdown voltage point is reached if an optimum balance between the pressure and gap distance is achieved. If pressure is too low, collision are unlikely and ionization will not take place. If the pressure is too high for an applied electrical potential or electrical field, there will be too much collision between electrons and neutral particles before electrons gain enough kinetic energy to ionize the neutral molecules.

If the distance d is too short an avalanche cannot take place because too few collision can happen during electron drift. If distance is too large, recombination take place and higher voltage is then require to eliminate or reduce its effect.

Paschen curves hold true for the first micro discharge in a DBD system, after that, memory voltage on the dielectric are added to the driving potential, reducing the voltage necessary to maintain the discharge. The Paschen curves provided information for discharge cell size and also it operating voltage. Furthermore it explain why decreasing the operating pressure ease the ignition and stabilization when under N_2 , H_2 . Paschen curves doesn't hold true for mix gases discharge. For example using a mixture of N_2 and argon will decrease the ignition voltage while using a mixture of helium and argon will increase it. Penning ionization play an important role in a mix gas discharge.

ANNEX D - FEW EMISSION WAVELENGTH EXAMPLES

O₂: 777 nm, 845 nm

H: 486 nm

D: 656 nm

H₂: 656 nm

HE: 706 nm

CH₄: 385 nm

CO: 385 nm , 219 nm

CO₂: 385 nm , 288 nm

C: Atomic Carbon Emission, 174 nm, 193 nm

F: 739.9 nm

Cl: 479 nm, 837.6 nm

Br: 478nm, 827.2 nm

P: 177nm, 213.6 nm

S: 182 nm

Hg: 253.6 nm

Ag: 189 nm

N₂: 337.1 nm, 357.6 nm, High Concentration 406 nm, 391.4 nm (He)

Ar: 696 nm, High concentration 347 nm

He: 502 nm

Xe: 473 nm

H₂O: 309 nm

NO: 240–250 nm

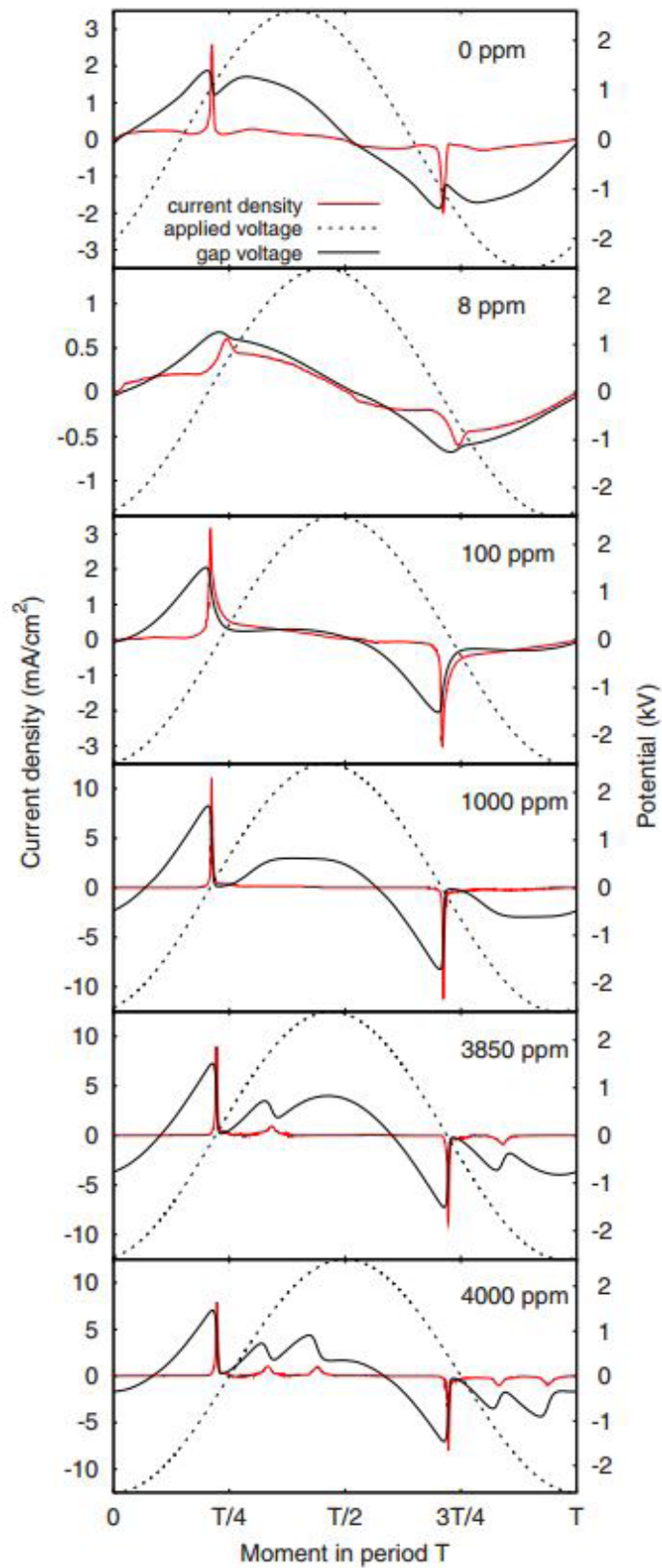
F: 685 nm

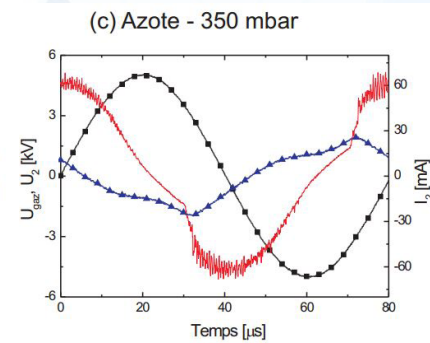
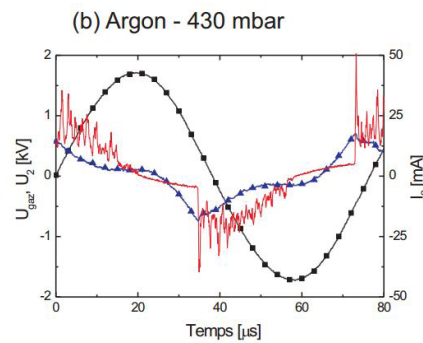
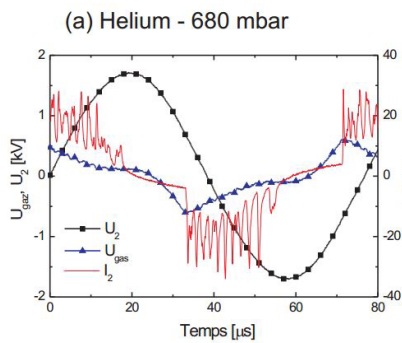
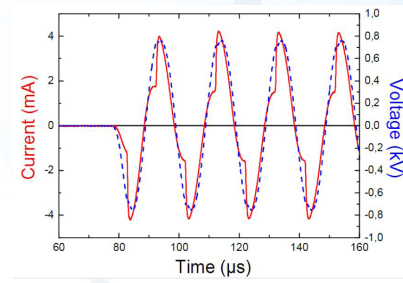
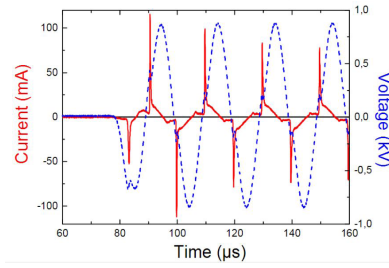
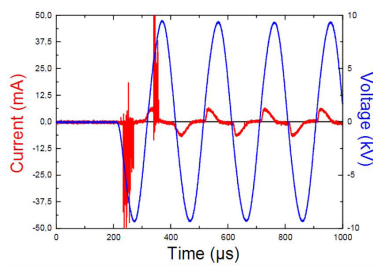
Hg: 253 nm

Halogenerated compound: CCL₂F₂, CHCLF₂, CCL₂F₂, CCLF₃, LOD → ppt

ANNEX E - IMPEDANCE CHANGE WITH IMPURITIES LEVEL HARMONIC CONTENT AND DISTRIBUTION CHANGE WITH THE IMPURITIES LEVEL AND PRESSURE

ELECTRIC CHARACTERISTIC





LIST OF REFERENCE

- [1] Contrôle Analytique K4000 and K2001 product Brochure, and "An Improved system and method on-line N2 measurement in noble gases ", Yves Gamache 2005, AN-05, Contrôle Analytique. See also publication #US8239171 B2 System and method of eliminating interference for impurities measurement in noble gases, by Yves Gamache et Al.
- [2] Servomex products brochure available from Servomex website
<http://ww3.servomex.com/gas-analyzers/product-ranges/servopro/nanochrome>
<http://ww3.servomex.com/gas-analyzers/product-ranges/servopro/servopro-chroma>
- [3] Plasma Chemistry by Alexander Fridman, Cambridge University Press, ISBN-13 978-0-521-84735-3, 2008
- [4] Micro capillary dielectric barrier plasma jet discharge, characterisation by optical spectroscopy. Dissertation, by Stefan Bogdanolenici-Craciunescu, technische Univertäi Dortmund, July, 2011.
- [5] Kogelschatz, U. Dielectric barrier discharge: Their History, discharge physics and industrial application. Plasma chem. Plasma process, 2003 23 (1) : Page 1-46
- [6] Massines F. et al. Experimental and theoretical study of a glow discharge at atmospheric pressure controlled by dielectric barrier discharge. Journal of applied physics, 1998. 83(6): Page 2950-2957
- [7] T.C. Manley, Trans. Electrochem, SOC 84, 83 1943
- [8] Capacitance between an atmospheric discharge plasma and the dielectric in the parallel cell reactor. Gon-Ho Kim et Al. Plasma application laboratory, department of nuclear engineering Seoul National University, 2005
- [9] Spectroscopic Analysis of gas mixtures. O.P. Bochkova and Ya. Shreyder, Lenigrad State University, Academic Press, 1965
- [10] Low temperature plasma technology, by Paul K. Chu and XinPei Lu, CRC Press, 2014, ISBN-13 978-1-4665-0990-0
- [11] Low power miniature plasma emission cell, by Yves Gamache, Contrôle Analytique, 1998, AN-02
- [12] Pulsed Discharge Emission Detector-Application to Analytical Spectroscopy of Permanent Gases. W.E. Wentworth et Al., Chromatographia, Vol. 34 No. 5-8, September/October 1992
- [13] Pulsed Discharge Helium ionization/electron capture/emission detector of chlorinated compounds W.E. Wenworth et Al. Elsener Science B.V., 1993, Process and control and Quality, 5(1993) 193-194
- [14] Microplasma-based atomic emission detectors for gas chromatography. M. Miclea et al. Anal Bioanal Chem (2007) 388:1565-1572. Springer Publishing
- [15] Introduction to gas discharges. N. St J Braithwaite, Plasma source Sci. Technol. 9 (2000) 517-527, UK
- [16] A Sensitive Detector for Gas Chromatography, J.E. Lovelock, Journal of Chromatography, Vol. 1, 1958
- [17] Modern Practice of gas chromatography, fourth edition, edited by Robert L. Grob and Eugene F. Barry, Wiley Interscience, 2004, ISBN-0-471-22983-0
- [18] Introduction to Analytical Gas Chromatography, Raymond P.W. Scott, Chromatographic Science series Volume 76, Marcel Pekker inc., ISBN-0-8247-0016-3
- [19] US Patent Publication, 2004/0189314 A1, Le Full et Al.
- [20] Gas chromatography, Colin Poole, ISBN 978-0-12-385540-4, P.15, sec 1.7.5
- [21] PPT level analysis of UHP hydrogen with APIMS. Article publish by Air Liquid, Jean-Marc Girard and Yves Marot, 1999.
- [22] New APIMS application analysis of UHP hydrogen. Microcontamination conference Proceeding, K. Sieferting, W. Witlockand
- [23] Fourier spectrometry and its applications, by R. Jozwicki and M. Rataj, opto-electronics review 6(4), 233-244 (1998)

- [24] Data analysis and signal processing in chromatography, 1st edition, by A. Flinger, 1998, ISBN 9780444820662
- [25] Hinkley, Appl. Phys. Lett. 16(1970) 351
- [26] Thin film deposition Book, Principles and practice, Donald L. Smith, McGrawhill, ISBN 0-07-113913-3
- [27] Development of a new Ionization Detector for Gas Chromatography by Dielectric Barrier Discharge by Kei SHINADA et Al. Shimadzu Review, 2012
- [28] High Performance GC Diaphragm Valve and AN-04 Getting Full Benefit From The Purging Feature Of The ELDV/MDVG GC Diaphragm Valve Rev. 1.2 by Yves Gamache et Al., 2016
- [29] Analytical Instrumentation Tight Shut-off Diaphragm Valves Rev.1.2, by Yves Gamache et Al., 2016
- [30] High Performance Analytical Fittings, by Yves Gamache et Al., 2015
- [31] Process for Argon Recovery, by Wilhelm J. Rhode, CryoGas International, January 1994
- [32] Improving Argon Recovery in air separation plants with the use of proper process analytical tools, Contrôle Analytique, by Yves Gamache et Al., 2007
- [33] The electron capture detector and the study of reactions with thermal electrons, by E.C.M. Chen and E.S. Chen, Published by John Wiley & Sons Inc. ISBN 0-471-32622-4
- [34] US Pat. # 5,541,519, Photoionization detector incorporating a dopant and carrier gas flow, by Wayne Wentworth, 1996
- [35] US Pat. # 5,317,271 High voltage spark excitation and ionization detector system with adjustable sample input for sensitivity control, by Wayne Wentworth et al., 1994
- [36] Detectors in gas chromatography, by Jiri Sevcik, Journal of Chromatography Library-volume 4, Elsevier, 1976
- [37] Modeling of and driver design for a dielectric barrier discharge lamp, by Amgad Amin El-Deib, 2010
- [38] Sample analysis with miniaturized plasmas, Joackim Franke and Manuela Miclea, applied spectroscopy, volume 60, number 3, 2006
- [39] US Pat# 6,133,740, Chlorine specific gas chromatographic detection, Wayne Wentworth et Al., 2000
- [40] Pulse Discharge emission detector - Application to analytical spectroscopy of permanent gases. Wenworth et Al., Chromatographia Vol.34, September/Octobre 1992
- [41] Capacitively coupled microplasma for on-column detection of chromatographically separated inorganic gases by optical emission, Renato Guchardi and Peter C. Hauser, Journal of chromatography A, 2004
- [42] Microplasma for analytical application of lab-on-a-chip, Daibing Luo and Yixiang Duan, Trends in Analytical Chemistry, Vol.39, 2012
- [43] Characteristic response of an atmospheric pressure DC micro-plasma detector for gas chromatography to organic functional groups, Yu-Mao F, Shih-Chi Chu, Chia-Jung Lu, Microchemical at ScienceDirect, 2007
- [44] Microplasma-based atomic emission detectors for gas chromatography, M. Miclea et Al., Anal. Bional Chem(2007), 388:1565-1572
- [45] An atmospheric pressure dc glow on a microchip and its application as a molecular emission detector, Jan C. T. Eijkel et Al., JAAS communication, 2000
- [46] Chromatographic system and methods for eliminating interference from interfering agent, by Yves Gamache et Al. US# 60,727,850 October 2005
- [47] Coated Tip Tubing, Short Form Catalogue, Analytical Flow Products, by Yves Gamache et Al., 2015
- [48] Introduction to plasma physics and controlled fusion, Page 4-5, Volume 1: Plasma Physics, Francis F. Chen, ISBN 0-306-41332-9
- [49] Atomic spectrometric detectors for gas chromatography, Chenghui Li et Al., Trend in analytical chemistry 77 (2016), 139-155

- [50] Recent advances in the understanding of homogeneous dielectric barrier discharges, by Massines F., Gherardi N., Naudé N., Ségur P., Hakone XI Oleron Island, September 7-12, 2008
- [51] Jing Hu, Wei Li, Chengbin Zheng & Xiandeng Hou (2011), Dielectric Barrier Discharge in Analytical Spectrometry, Applied Spectroscopy Reviews, 46:5, 368-387, DOI: 10.1080/05704928.2011.561511, P.373
- [52] Spatial and temporal instability of DBD, see document: Gas Detector, file# 1602.06242, PDF
- [53] Multiple working gas PID system RAE Patent# US6,333,632B1
- [54] Patent# US6,795,178B1, Method and apparatus for analysis of gas composition, Räsänen et al., instability
- [55] Practical gas chromatography, A comprehensive reference, Katja Dettmer-Wilde, Werner Engewald, Springer, ISBN 987-3-642-54639-6
- [56] Influence of electron injection into 27 cm audio plasma cell on the plasma diagnostic. Review of scientific instrument 84, 083301 (2013)
- [57] A survey of non-thermal plasma and their generation methods. International journal of renewable energy and environmental engineering. ISSN 2348-0157, vol. 04., No.01, January 2016
- [58] An experimental study on the influence of trace impurities on ionisation of atmospheric noble gas dielectric barrier discharge. Analyst, 2016, 141, 5842, royal society of chemistry.
- [59] Breakdown of gaseous insulation, high voltage engineering, JR Lucas, 2001
- [60] Introduction to gas discharges, plasma sources Sci. Technol. 9(2000) 517-527.
- [61] Measurement of electrical characteristics of atmospheric pressure non-thermal He plasma. Measurement Sci. Technology 18 (2007), 2642-2648
- [62] Penning transfer in argon-based gas mixtures. Jinst, 2010 IOP publishing Ltd and SISSA.

INTELLECTUAL PROPERTY

At ASDevices, we pride ourselves at our level of innovation which we are introducing to the market and bringing to our customers. All of our innovations are consequently proprietary and fully patented by a substantial patent portfolio.

The Epd technology is covered by a total of 6 patents.

MULTI-MODE PLASMA-BASED OPTICAL EMISSION GAS DETECTOR

A plasma-based detector using optical spectroscopic techniques for analysing the constituents of gas samples are provided. The detector includes a plasma-generating mechanism and a plasma-localizing mechanism. Electron-injecting electrodes may be provided in the plasma chamber of the detector. A Pressure control mechanism as well as a doping module may optionally be included. In accordance with some implementations, the collection, detection and analysis of light extracted from the plasma may enable one or more of various operation modes, such as an emission mode, an absorption mode, and indirect detection mode or a constant emission mode.

DISCHARGE-BASED PHOTO IONISATION DETECTOR FOR USE WITH A GAS CHROMATOGRAPHY SYSTEM

A discharge-based photo ionisation detector (PID) for use with gas chromatography systems is provided. The PID includes a discharge zone in which a plasma can be generated, resulting in the emission of energetic photons. The PID further includes an ionisation zone in which the gas sample to be analysed is bombarded by the photons created in the discharge zone, photo ionising the impurities in the gas sample. The generated current is measured in order to measure the concentration of impurities in the gas sample. Plasma localizing of the plasma in the discharge zone and optical monitoring of the emission from the plasma in the discharge zone may be provided. Methods using such a PID with a split input from a chromatography column or with inputs from two different chromatography columns are provided.

EMISSION-BASED DETECTOR FOR CAPILLARY GAS CHROMATOGRAPHY

An emission-based detector for use in conjunction with capillary chromatography or other applications involving a gas sample having a small volume is provided. The detector is based on optical emission from a plasma medium. An optical cartridge or other detection and/or processing means may be provided to receive and analyse the emitted radiation and thereby obtain information on the gas to be analysed. The emission-based detector includes a gas inlet, a gas outlet and a capillary channel which is in fluid communication with the gas inlet and gas outlet. The capillary channel acts as the plasma chamber. Preferably, the capillary channel has transversal dimensions of the same order as the cross-section of typical chromatography capillary columns and defines a winding path within the detection area. A multi-cell emission-based detector and a method of analysing a gas sample using multiple detection cells are also provided.

ELECTRIC DISCHARGE-BASED DETECTOR AND METHODS USING THE SAME FOR MEASURING AND MONITORING PROPERTIES OF A GAS

Plasma discharged, purifier end-of-life detector based on compound electrode.

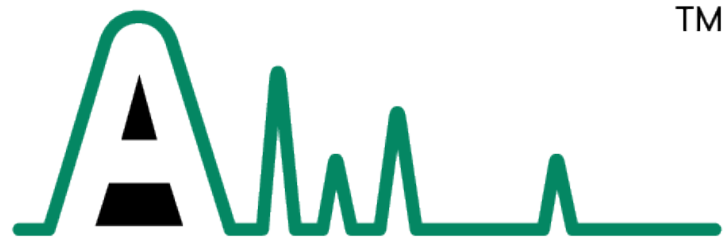
COMPOUND ELECTRODE

Discharge stabilisation and electron injection electrode embedded into a quartz shell. This compound electrodes can be mounted in various plasma discharge chamber to create analytical detectors or chemical reactors.

METHOD AND APPARATUS FOR ANALYSING A GAS CHROMATOGRAPHY ELUTION PEAK

Methods and systems for measuring, in a gas stream, an analyte concentration level from a gas chromatography elution peak outputted by a gas chromatography system are provided. The method includes receiving an analyte signal representative of the gas chromatography elution peak in the time domain, converting the analyte signal from the time-domain to the frequency domain, in the frequency domain, preprocessing the analyte signal to distinguish frequencies of the analyte signal, integrating the analyte signal after preprocessing to obtain a redressed analyte signal in the time domain, the redressed analyte signal having a substantially Gaussian shape, and processing the redressed analyte signal to obtain the analyte concentration level. The system includes a detector operable for generating the analyte signal and one or more processors configured for preprocessing and integrating the analyte signal to obtain the redressed analyte signal and processing the redressed analyte signal to obtain the analyte concentration level.





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