

White paper on the Dielectric Barrier Discharge Detectors.

Introduction:

This paper is a discussion of the dielectric barrier discharge detector. As such, it is intended to provide insight into the operating principles of the detector, the operating modes of the detector, the detector construction materials, and the potential applications of the detector.

Operating principles:

The detector is based on the use of a dielectric barrier discharge. Developed by Siemens and used for over a hundred years for the production of ozone, the dielectric barrier discharge offers unique features that are highly advantageous for a GC detector. A dielectric barrier discharge is a plasma discharge that is obtained using a high voltage alternating current applied to a dielectric material like glass or pyrex. The application of high voltage to a gas results in a breakdown in the gas and, subsequently, a discharge from one electrode to the other. However, the presence of the dielectric barrier behaves as a capacitor in the localized region of the discharge. This limits the amount of current that can be funneled into any one discharge. This results in each discharge being self-terminating as limited by the capacitance of the dielectric barrier. As a result, each discharge terminates before it can reach a thermal discharge state, that is, prior to becoming an arc. However, it is possible to put a substantial amount of energy into each discrete discharge which allows the discharge to generate highly excited state molecules and atoms such as helium and argon.

Statistically, there are a number of discrete discharges occurring across the surface area of the electrode with each pass above the breakdown voltage. Each of the micro-discharges behaves like a self-limited discharge. If using a 60 cycle source, this process occurs 120 times a second, and each cycle above the breakdown may yield 20 discharges over the surface area of the electrode, yielding thousands of discharges per second. The resulting plasma is essentially continuous and, to the eye, it appears as a continuous glow.

The physical characteristics of the dielectric barrier discharge give it a number of features that make it advantageous as a GC detector. First, since each discharge is self-terminating and non-thermal, electrode wear is significantly reduced. This eliminates the need to operate the system with any sort of cycle time that may be necessary to cool electrodes in more traditional, arc-type, discharge systems. Furthermore, since the system is non-thermal, it is possible to use pure reaction gases, such as argon, instead of blends which may be needed to keep the electrodes cool. It is also not necessary to provide any other cooling to the plasma source other than an air flow across the outer, high voltage electrode. Second, since the system uses the dielectric barrier to limit each discharge, the power supply can be extremely simple and easy to obtain. Rather than designing a pulsing circuit, a simple high voltage alternating current power source is sufficient. These power sources can be readily

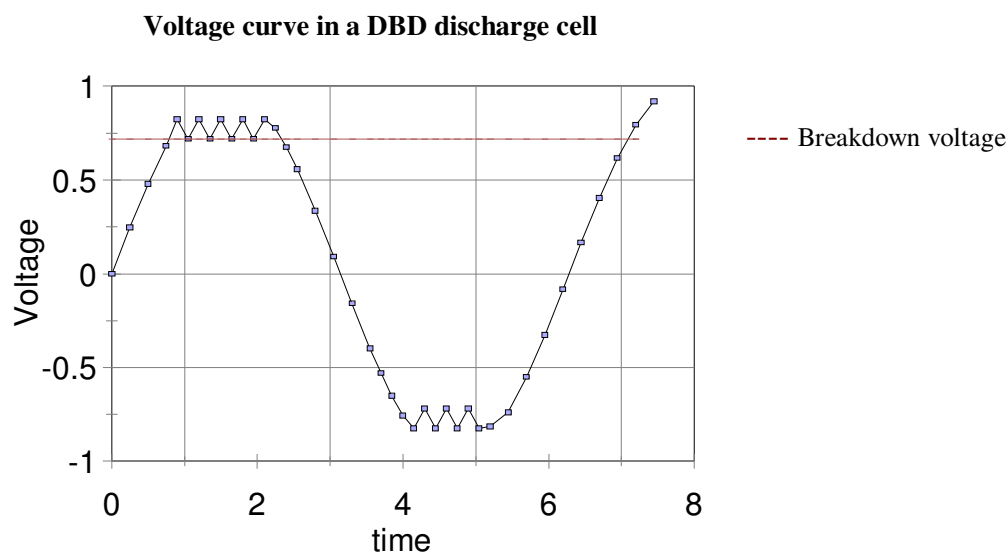


Figure 1: Representative view of the discharge cycle within a DBD detector (arbitrary units)

obtained from the commercial market. Furthermore, they are very reliable and very compact. In addition, since the energy is put into creating excited states and not into heating the gas, it is possible to run these power sources at relatively low power consumption (on the order of 10 - 20 watts.)

Dielectric barrier discharges are able to operate at elevated pressures. Due to the nature of the discharge, the DBD is actually more effective at a slight positive pressure. This positive pressure is currently obtained through the use of a fixed restrictor. This is currently a piece of tubing with a narrow inner diameter. The ability to operate in this manner means that no vacuum pumping systems are required for operation. Furthermore, it means that the detector can easily be used in series with another detector with the effluent from the DBD being fed into a second detector or to an analyte trap.

Finally, due to the large number of discrete discharges present and the high rate that discharges are created, the plasma becomes a very stable and virtually continuous light source. As such, it is an excellent photoionization source for use as a GC detector.

Detector construction:

Advanced Industrial Chemistry Corporation has developed a patented detector based on the use of the dielectric barrier discharge plasma source. The detector consists of a stainless steel body 1 ½ inches in diameter and 4 inches tall. There is a hole in the center of the main body which holds the collector electronics which consists of a bias electrode and its

connection, a collector electrode and its electrical connection/exhaust, and the ceramics which holds these two electrodes in place. In the center of the main body is a ceramic cylinder that holds the bias electrode and collector electrode. Each electrode is connected, via a steel rod or steel tube to an external electrode. Each of these electrodes are retained in the detector through the use of a vespel ferrule sitting within a 1/4 inch Swagelok fitting.

Above the main body is the plasma source. The plasma cell is a 1/4 inch pyrex tube inserted into the upper Swagelok fitting on the main body. This is held in place with a teflon ferrule assembly. The plasma electrode wraps around the outside of the pyrex tube and is connected to the high voltage power supply. At the top of the plasma cell is a Swagelok "T" which holds the ground electrode and the reaction gas supply fittings. This, too, is connected to the pyrex tube via a teflon ferrule. Between the plasma source and the main body electrodes there is a small (1/4 inch o.d.) disk which prevents light from the plasma from impinging directly on the collector and creating photoelectric noise.

The detector is designed with a reverse flow configuration. Reaction gas comes in from the top, the carrier from the bottom and the combined flows exhaust out a side port of the detector body. This design results from a number of considerations. The reverse flow configuration results in generally less quenching for the plasma cell system. It also nearly eliminates the possibility of the analytes of interest making it to the plasma cell itself which yields an added measure of reliability and safety. It also results in less opportunity for the electrodes to become contaminated by the analytes which leads to longer electrode lifetimes.

As a result of this design, it is easily possible to maintain, repair or replace all of the parts within the detector in the field. On the main body there are five components all of which are easily removed and replaced. Access to these components is simply a matter of removing or loosening three Swagelok fittings with a spanner. Once this is complete, a pair of tweezers are all that is needed to remove the entire inner system. Any of the components could then be changed out, the system re-assembled, and, depending on the mode of operation, be ready to run within 30 minutes to 12 hours. The plasma cell can be replaced by removing the teflon ferrules, inserting a new plasma cell, and sliding the high voltage electrode over the plasma cell. All of the Swagelok fittings used within the system can be purchased from any Swagelok distributor.

The materials chosen for the detector were also based on their ability to withstand chemical attack, their electrical resistivity and ease of manufacturing. If alternative materials are necessary, it is possible to build the detector with other materials such as nylon, teflon, or Vespel.

Modes of operation:

There are a number of modes of operation for this detector depending on the analytes which need to be detected. At the present time, there are two modes of operation for this detector; AID mode, and HID mode. Each of these modes relies on variations in the reaction gas to vary the selectivity of the detector.

Argon mode operation:

In argon mode operation, the detector acts as a cross between an FID and a PID. While the detector is not sensitive to fixed gases and methane it is sensitive to a wide range of hydrocarbons. In argon mode, the detector is capable of ionizing any hydrocarbon with an ionization potential less than about 11.5 eV. Between 11.5 and about 10.5 the detector is about as sensitive as an FID. Below about 10.5 the detector is more sensitive than an FID, often by a factor of 20 or more. For this reason it is an excellent detector for compounds such as BTEX constituents. The detector is not sensitive to methane. As a result it would be also be able to do non-methane hydrocarbons.

The detector also has the advantage of not needing to support a flame to operate. While it does need argon for the reaction gas, it can use hydrogen, helium, or nitrogen as the carrier gas in argon mode. A flame-less detector may prove beneficial for certain customers who are worried about the presence of a flame in their facilities. Operation with only two gases, argon and carrier, both of which can be inert, may yield access to markets which are concerned about flame based detector systems. Unlike FID's where everything is burned, often creating caustic by products, the DBD does not create these by-products and should not pit metallic components within the detector.

The detector is windowless. This is advantageous from a number of perspectives. First, the lack of a window means that all of the energy of the plasma is directed directly at the analytes of interest. This enhances the sensitivity of the overall system. Second, the absence of a window means that cleaning operations (like those done on PID lamps) is not necessary. This should result in significantly longer operations between routine maintenance. Quenching is still possible with this system, as it is with PID's, although it does not result in extinguishing the plasma under typical operating conditions.

In argon mode, the detector is capable of using existing commercial electrometers without modifications. In argon mode background currents are on the order of 0.1 to 0.2 nanoamps which is close to that of an FID. For this reason it is not essential to modify an FID electrometer in any way.

Helium mode operation:

In this mode of operation, the detector uses a flow of pure helium as the reactor gas. As such, the detector is sensitive to all organic and inorganic volatile components except neon. In this mode, the background current is directly related to the quality of the carrier and reaction gas with typical baseline currents on the order of 2-10 nanoamps. A leak free system is also important in this mode of operation. More importantly, the noise in this mode is in the picoamp range which means that sensitive detection is still possible.

It is possible to use currently available flame ionization electrometers in helium mode. Flame ionization electrometers are designed for background currents that are on the order of a few picoamps of current. Since the helium mode results in nanoamps of background current, it is suggested that the auto-zero circuit be modified to buck out the higher background current.

The detector can also use standard plumbing configurations. AIC Corp. routinely operates their detectors in HID mode using standard GC flow controllers, Grade 5 helium without further purification, and 1/8 inch copper tubing to supply their instruments. Operating in this mode, it is still possible to see sub-p.p.m.. levels of the fixed gases.

Finally, in helium mode the detector is sensitive to changes to base temperature fluctuations which is probably a function of capture coefficients. For this reason, it is essential to utilize a stable base temperature that is above the upper temperature of a programmed oven. However, the detector has been run with temperature programmed analysis without significant signal changes except those due to column bleed.

Possible applications:

In HID mode, possible applications of the detector include:

- the measurement of gas impurities in other high purity gases,
- measurement of freons,
- measurement of transformer gases
- measurement of impurities in ethylene
- measurement of CO and CO2 without the use of a methanizer.

In AID mode, possible applications of the detector include:

- the measurement of BTEX compounds at very low levels,
- measurement of phosphine or arsine,
- measurement of ethylene oxide,
- measurement of formaldehyde in formalin, and
- measurement of ammonia.

Other modes of operation:

AIC Corp. is currently investigating the use of the dielectric barrier discharge detector as an electron capture detector. It is expected that this mode of operation will be ready for release in early 2003.

Further information:

For further information about this detector, please contact:

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