

Gas Chromatographic Applications with the Dielectric Barrier Discharge Detector*

Ronda Gras¹, Jim Luong^{1,†}, Matthew Monagle², and Bill Winniford³

¹Dow Chemical Canada, P.O. BAG 16, Highway 15, Fort Saskatchewan, Alberta, Canada T8L 2P4; ²Advanced Industrial Chemistry Corporation, 9220 Jill Patricia St. NW, Albuquerque, NM 87114; ³Dow Chemical USA, Texas Operations, 2301 Brazosport Blvd, Freeport, TX, 77541-3257

Abstract

With gas chromatography, there are many more choices for detectors when compared to other separation disciplines in analytical chemistry. The presence of sensitive and selective detectors aids in easing the separation requirements imposed on the capillary column. The current gas phase detectors, however, do not completely fulfill contemporary analytical needs. One example is in the area of ultratrace analysis of permanent gases for semiconductor industry. Another example is in the area of environmental/industrial hygiene monitoring for compounds such as 1,3-butadiene or vinyl chloride. The dielectric barrier discharge detector, a new highly sensitive detector with tuneable selectivity, has recently been innovated and commercialized. In this paper, the principle of operation of the detector, along with critical challenging industrial applications such as the analysis of oxygenated compounds, sulfur-containing compounds, and other compounds of industrial significance is presented.

Introduction

Numerous articles and books have been written detailing the scientific benefits of fused-silica column technology, in which tremendous separation power is available. But this high resolution would be wasted without the ability to detect the separated components.

The current gas phase detectors do not fully address contemporary analytical needs. For example, although the thermal conductivity detector (1) has served practitioners well, the lack of sensitivity and high detection time is a constant limit on its applicability for contemporary applications such as fast gas chromatography (GC). Another example is the monitoring of airborne priority pollutants that often require sample enrichment techniques for adequate detection of compounds of interest. The augmentation of any sensitive and selective detector would, therefore, be very useful in this case.

One of the latest additions to the GC detector family is the dielectric barrier discharge detector (DBD). Invented by Monagle (2), the DBD has recently been commercialized by Advanced Industrial Chemistry Corp. (AIC, Albuquerque, NM) as a sensitive detector available for GC. The detector offers multimode capability. In helium mode, the detector can be used as a universal detector (except neon). In argon mode, detection depends on the ionization potential of the solute of interest and a various degree of selectivity can be attained.

Through a collaboration with AIC Corp., two DBDs were provided to Dow Chemical Canada (Analytical Sciences, Fort Saskatchewan, Canada) for the development of practical industrial applications. This paper summarizes the scientific findings obtained and applications of the detector to an array of analytical challenges.

Experimental

Two Agilent HP-6890 GC were used in the application development. The first GC, an Agilent HP-6890A, was equipped with a split/splitless injector, programmable temperature vaporizer injector, flame ionization detector (FID), and a "3/4 model" DBD. The second GC, an Agilent HP-6890N, was equipped with two split/splitless injectors, an FID, and a "Mini" DBD.

A RVM low thermal mass GC (LTMGC) module model A-68A, Gen-II (RVM Scientific, Santa Barbara, CA), was used for several applications in this project. The LTMGC was moved from one GC to another, depending on the application requirements. LTMGC column modules were obtained from RVM Scientific. Five columns were used for the evaluation: (i) RVM LTMGC coiled with a 2-m × 0.53-mm-i.d. Lowox column; (ii) 50-m × 0.32-mm-i.d., 5- μ m CP-Sil 8CB; (iii) 60-m × 0.32-mm-i.d., 5- μ m CP-Volamine column, (iv) 25-m × 0.32-mm-i.d. CP-PoraBOND Q, and (v) 1-m × 0.32-mm-i.d. CP-MS 5A.

Figures 1 and 2 (see page 3A) show pictures of the detectors installed on respective chromatographs. Figures 3 and 4 (see page 3A) show pictures of the plasma associated with the helium and argon mode, respectively; the pictures demonstrate the colors of

* Part of the content of this paper was presented as a poster at the 28th International Symposium on Capillary Chromatography and Electrophoresis, May 22–25, 2005, Las Vegas, NV

† Author to whom correspondence should be addressed.

the two plasmas when operating.

Standards used for testing were obtained from Aldrich Corporation (St. Louis, MO), Fisher Scientific (Hampton, NH), and BOC Corp. (Alberta, Canada).

Results and Discussion

The design of the DBD detector

The DBD, also known as the silent discharge plasma, utilizes a high voltage alternating current applied to a dielectric material such as glass or Pyrex (3). When the voltage applied exceeds the breakdown voltage of the gas being used, a discharge is initiated from the outer electrode to the inner electrode. This discharge creates meta-stable species and high energy photons. The photons and meta-stables created in this plasma are subsequently used to ionize the analytes of interest. The unique feature of the DBD is that each discharge is self limiting with the number of discharges based on voltage cycling frequency. Because the dielectric barrier acts as a capacitor in the localized region of the discharge, each discharge is self-limiting, which prevents arcing between the electrodes. Thus the design is conducive to longer electrode life, simple to operate because of the elimination of a pulsing circuit, and able to use pure gases instead of blended gases.

The DBD utilizes a countercurrent flow configuration. Reaction gas comes in from the top of the detector while carrier gas comes in from the bottom of the detector. The combined gases then exhaust out via the side arm of the detector. This configuration prevents the interaction of the solute gas with the plasma during operation, which provides a more stable baseline and limits the possibility of electrode contamination. When the analytes enter the detector chamber, they interact with the reaction gas and become ionized. The charged particles created by ionization in the detector volume are collected by applying a bias potential across two electrodes in the cell. A positively biased direct current electrometer is connected to one of the electrodes while the second electrode is held at ground potential. This induces a current flow caused by the drift of the particles within the electric field generated between the two electrodes.

Two collection electrode configurations are used in the DBD detector. The first is a concentric electrode configuration where the inner electrode is grounded and the outer electrode is connected to the Agilent electrometer. This design was originally developed for use with large diameter columns such as packed and micropacked columns. A second design, the "Mini", was subsequently developed to reduce the internal volume of the detector for use with capillary columns. This design uses an "over-and-under" electrode design where the upper electrode is held at ground and the lower electrode is connected to the Agilent electrometer.

Different background currents and noise levels are observed depending upon the electrode configuration and the operating mode of the detector. These currents can range from 30nA when operating the full size detector in helium mode down to 0.7nA when operating with the "Mini" in argon mode. Background currents are also a function of the bias potential, carrier gas impuri-

ties, atmospheric leakage, column bleed, and other sources of contamination such as moisture or hydrocarbons in the gas lines.

The detector is simple in design and consists of a detector body, power supply, and electrometer. The detector body contains a metal housing, plasma cell, and the necessary gas lines, all of which are replaceable or field-serviceable with common tools.

The detector can operate in two different modes, and conversion from one mode to another can be done simply by changing the reaction gas. No other change of hardware is required.

Helium ionization mode

The DBD is generally considered to operate in the same manner as the pulsed discharge detector (4). Because the analyte does not pass directly through the plasma at any point, as distinguished from Wentworth's earlier work, only one mechanism remains for ionization as given by the following equations:



In helium mode in the DBD, the generation of long lived meta-stables in step 1 (the Penning effect) is believed to be the primary source of excitation (5). These meta-stables result in analyte ionization within the reaction chamber, according to the mechanism of step 2. An extended discussion of the mechanisms of the helium ionization process can also be found in the literature (6-9) and in Hill and McMinn's *Detectors in Chromatography* (10).

Argon ionization mode

In this mode, helium is replaced by argon as the reaction gas. The lowering of the ionization potential from 19.8 eV using helium to argon at 11.8 eV affords greater selectivity and, in some cases, better sensitivity for the detection of certain classes of compounds. The response of the detector in argon mode for solutes that have high ionization potential such as oxygen, nitrogen, carbon monoxide, methane, and water is either totally eliminated or heavily suppressed.

In contrast to helium mode, the mechanism of argon mode is believed to be one of photoionization. The argon meta-stable will be formed in a manner similar to step 1 (discussed previously) for helium with a subsequent photon emission. If the energy of the photon emitted is equal to or greater than the ionization potential of species R and the carrier gas is given by C, then the ionization and the other process shown here will take place (10):



The number of electrons formed in the reaction chamber is considered to be the sum of the direct and indirect ionization steps (steps 3–5), except for those consumed by the quenching steps (steps 6–8). Photochemical rearrangement can lead to the ionization of solutes with slightly higher ionization potential of argon, for example, methane with IP of 12.98 eV. Quenching is an important aspect of the operation of the DBD in both helium ionization and argon ionization mode (11,12).

Applications to compounds of industrial significance

The remarkable strength of modern chromatographic methods ultimately resides in their unique ability to simultaneously separate and determine the individual components of complex mixtures. In some ways, the near simultaneous introduction of capillary column GC and highly sensitive ionization detectors has been historically viewed as a lucky coincidence. James and Martin's publication represents a landmark contribution to the detection era (13). Since then, the scope of chromatographic separations and measurements has significantly expanded with the growing availability of an increasing number of highly sensitive detectors. The column–detector relationship has been emphasized by both the realization that highly efficient chromatographic separations are only feasible primarily when working with minute sample quantities and by the recognition that detection conditions should not compromise optimum performance.

Since its humble beginning, GC has achieved a very important role in analytical chemistry. The knowledge base of chromatography continued to expand, owing to its many applications, the problems of contemporary interest in industry, environmental and life sciences, and even space exploration. Some of the important industrial applications are highlighted here to illustrate the ubiquitous capabilities of the DBD detector and its roles in GC.

Environmental and industrial hygiene applications

Three important environmental and industrial hygiene applications were chosen to illustrate the suitability of the DBD in these fields: the analysis of 1,3-butadiene; volatile organic sulfur compounds; and benzene, toluene, ethyl benzene, and xylenes (BTEX) contamination.

Analysis of 1,3-butadiene. 1,3-Butadiene is a colorless, non-corrosive gas with a mild aromatic or gasoline-like odor. It is used primarily as a chemical intermediate and polymer component in the manufacture of synthetic rubber. Its major uses are as a comonomer for styrene-butadiene rubber to produce tires and tire products and, in monomeric form, to produce impact polystyrenes, industrial hoses, and belts. It is also used as a chemical intermediate for the fungicides Captan (CAS 133-06-02) and Captofol (CAS 2425-6-1), in the manufacturing of latex adhesives, various rubber products, nylon carpet backings, paper coatings, pipes, conduits, appliances, and electrical equipment components.

1,3-Butadiene is classified by the Occupational Safety and Health Administration (OSHA) as a threshold carcinogen (14). It is also defined as a substance that may reasonably be anticipated to be a carcinogen by the U.S. Department of Health and Human Services National Toxicology Program. The presence of two pi-bonds in butadiene makes it ideal for detection by the DBD in argon mode. Figure 5 (see page 3A) shows a comparison of 100

parts per million (ppm) of 1,3-butadiene [ionization potential (IP) = 9.07 eV] (15) to 1-butene (IP = 9.55 eV) and butane (IP = 10.53 eV). When compared to butane and 1-butene on an equal molar basis, 1,3-butadiene is approximately 6.9 and 2.3 times more sensitive, respectively, with the DBD in argon mode. This follows the general trend set out by Langhorst (16). Figure 6 shows the linear dynamic range of butadiene over a range of 10 parts per billion (ppb) (v/v) to 100 ppm with a correlation coefficient of 0.9990, and Figure 7 shows a chromatogram of 1,3-butadiene at 10 ppb (v/v) in air with a split ratio of 10:1. The DBD operating in argon mode is highly suitable for use in the measurement of butadiene.

The analysis of organic sulfur compounds. Although sulfur compounds are very important for many industries, they are considered to have a negative impact on the environment because of odor issues and contributions to acid rain. At low levels, sulfur compounds contribute to odor problems, though sulfur compounds can be very corrosive at high levels. Using a DBD in argon mode, sulfur compounds such as hydrogen sulfide, carbonyl sulfide, and alkyl mercaptans can be measured. Figure 8 (see page 3A) shows an overlay of two chromatograms of 10 ppm (v/v) of hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and ethyl mercaptan. On a per molar basis, the sensitivity is related to the ionization potentials of the solutes of interest. Alkyl mercaptans, such as methyl and ethyl mercaptans, with their lower ionization potentials of around 9.6 eV, are approximately 12.6 times more sensitive than that of carbonyl sulfide, a sulfur compound with

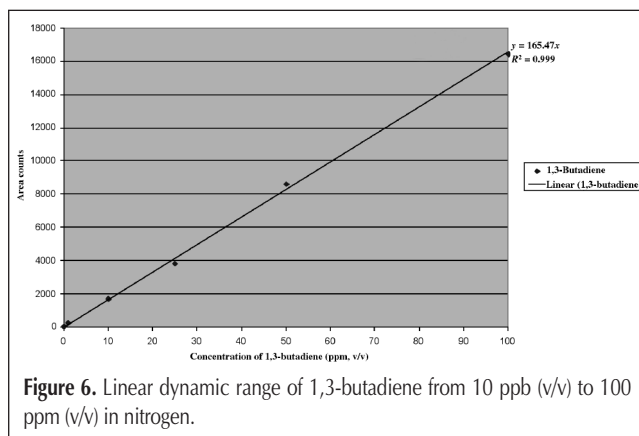


Figure 6. Linear dynamic range of 1,3-butadiene from 10 ppb (v/v) to 100 ppm (v/v) in nitrogen.

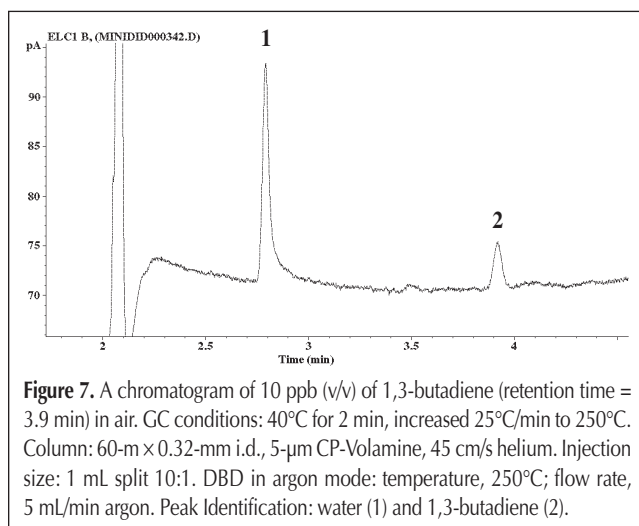


Figure 7. A chromatogram of 10 ppb (v/v) of 1,3-butadiene (retention time = 3.9 min) in air. GC conditions: 40°C for 2 min, increased 25°C/min to 250°C. Column: 60-m × 0.32-mm i.d., 5-μm CP-Volamine, 45 cm/s helium. Injection size: 1 mL split 10:1. DBD in argon mode: temperature, 250°C; flow rate, 5 mL/min argon. Peak Identification: water (1) and 1,3-butadiene (2).

high ionization potential (11.4 eV). Note the absence of significant tailing even for the highly reactive hydrogen sulfide and carbonyl sulfide.

Although there are many selective detectors available for sulfur analysis such as sulfur chemiluminescence, flame photometric, pulsed flame photometric, electrolytic, pulsed discharge detector, and atomic emission detector, the DBD offers an economical and simple solution for the measurement of sulfur compounds, particularly in air where a minimum amount of matrix interference is encountered.

The analysis of BTEX. The analysis of BTEX is another very common application in the environmental industry. The identification of BTEX components indicates the presence of a leaking underground gasoline storage tank. Figure 9 is a chromatogram of 10 ppm (w/v) benzene, toluene, and xylenes in methanol. The highly sensitive nature of the DBD detector for said compounds in argon mode can help eliminate the concentration/enrichment step (purge and trap, headspace, and extraction) and allows sub-ppm detection of the compounds by direct injection technique. This makes the detector ideal for rapid analysis and field portable analysis.

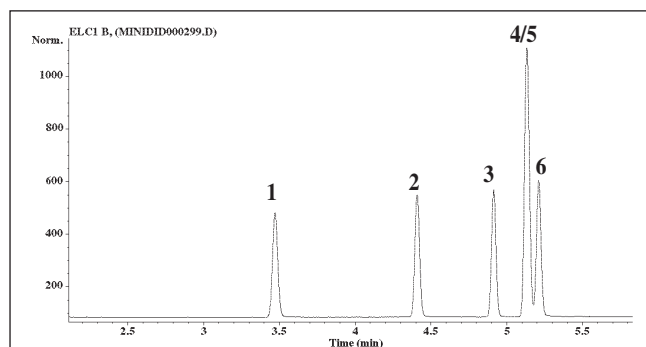


Figure 9. A chromatogram of 10 ppm (v/v) of BTEX. GC conditions: 60°C for 2 min, increased 30°C/min to 280°C. Column: LTMGC 60 cm, 0.1-mm restrictor coupled with 2-m × 0.53-mm i.d. CP-Lowox. DBD in argon mode: temperature, 250°C; and flow rate, 5 mL/min argon. Peak identification: benzene (1), toluene (2), ethyl benzene (3), *M,P*-xylenes (4 and 5), and *O*-xylene (6).

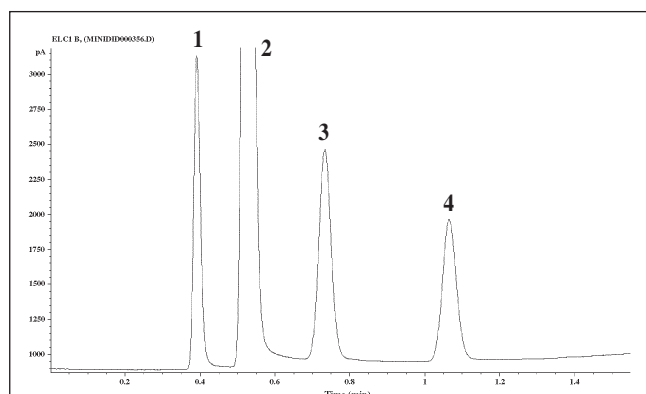


Figure 10. A chromatogram of 70 ppm (v/v) of oxygen, 500 ppm (v/v) nitrogen, 40 ppm (v/v) of methane, and 70 ppm (v/v) carbon monoxide. GC conditions: 50°C for 0.5 min, increased 50°C/min to 100°C. Column: 1-m × 0.32-mm i.d., CP-MS 5A. Injection size: 100-μL split 10:1. DBD in helium mode: temperature, 250°C, flow rate: 20 mL/min helium. Peak identification: oxygen (1), nitrogen (2), methane (3), and carbon monoxide (4).

Common industrial applications

A number of common industrial applications were selected for the evaluation of the DBD, both in argon and helium mode.

The analysis of fixed gases (helium ionization mode). The analysis of fixed gases such as oxygen and nitrogen is one of the most common applications performed. Typically, this analysis is conducted via the use of a molecular sieve column in conjunction with a thermal conductivity detector or micromachined thermal conductivity detector. The columns used can be a packed, micropacked, or porous layer open tubular column. A typical detection limit for this application is approximately 2 to 5 ppm (v/v), depending upon the volume of sample injected. Major limitations of this analysis are imposed by the lack of sensitivity delivered by the thermal conductivity detector, especially for the semiconductor industry. In addition, in the case of micromachined thermal conductivity, specialized equipment is required.

Figure 10 shows a chromatogram of 70 ppm (v/v) oxygen, 500 ppm (v/v) nitrogen, 40 ppm (v/v) of methane, and 70 ppm (v/v) of carbon monoxide in helium using a DBD operating in helium

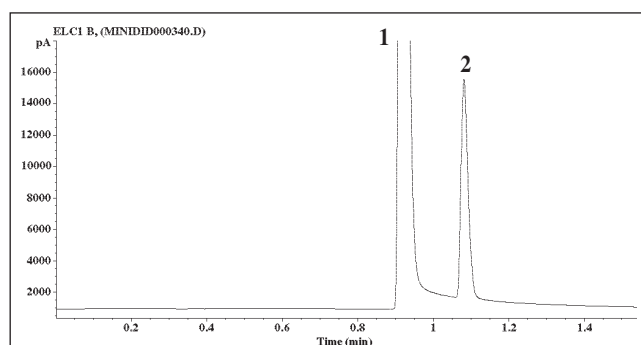


Figure 13. Feasibility for carbon dioxide analysis. GC conditions: 45°C for 2 min, increased 15°C/min to 150°C. Injection size: 100 μL split 10:1. DBD in helium mode: temperature, 250°C; flow rate, 20 mL/min helium. Concentration: 500 ppm (v/v) carbon dioxide in nitrogen. Peak identification: air (1) and carbon dioxide (2).

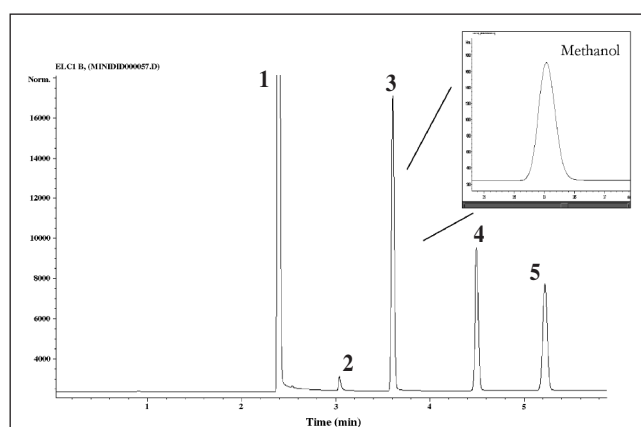


Figure 14. A qualitative chromatogram of methanol, ethanol, and propanol in air with DBD–helium mode. Note the excellent peak symmetry of methanol. Column: 60-m × 0.32-mm i.d., Varian CP-Volamine, 45 cm/s helium. Solute identification (left to right): air, carbon dioxide, methanol, ethanol, and propanol. Note the excellent peak symmetry of methanol (inset). Oven profile: 50°C for 1 min, increased 15°C/min to 100°C for 5 min. DBD in helium mode: temperature, 250°C; flow rate, 20 mL/min helium. Peak identification: air (1), water (2), methanol (3), ethanol (4), and propanol (5).

ionization mode. The chromatogram illustrates the high sensitivity of the detector towards the compounds cited. The chromatogram also demonstrates that, in helium ionization mode, solutes with high ionization potentials such as oxygen (12.08 eV), nitrogen (15.58 eV), methane (12.61 eV), and carbon monoxide (14.01 eV) can be successfully ionized by dielectric barrier discharge technique.

The analysis of hydrocarbons (in helium ionization or argon ionization mode). The measurement of hydrocarbons is commonly carried out in gas chromatographic laboratories using the ubiquitous FID. Although the DBD offers similar sensitivity to that of the FID, the key benefit of using the DBD for the measurement of hydrocarbons is that it requires no fuel gas (hydrogen) and does not have an open flame, which allows the DBD to be operated in certain safety restrictive areas. Figure 11 (see page 4A) shows the separation of 10 ppm (v/v) alkanes and alkenes from C₁ to C₃ in helium mode. The chromatogram in blue is a component mixture in air and the red chromatogram is a different hydrocarbon mixture in a nitrogen balance gas. Note that water can also be detected in the helium ionization mode. It is believed that the water is the source of the asymmetric peak shape in the air injection.

With the reduction of ionization potential from 19.8 eV (helium) to 11.8 eV (argon), enhancement of selectivity can once

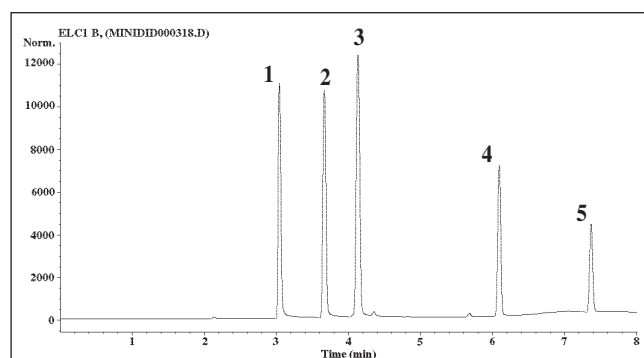


Figure 15. A chromatogram of 10 ppm (v/v) of methanol, ethanol, propanol, butanol, and pentanol in helium with DBD-argon mode. GC conditions: 40°C for 2 min, increased 25°C/min to 250°C. Column: 60-m × 0.32-mm i.d., 5- μ m CP-Volamine, 45 cm/s helium. Injection size: 1-mL split 10:1. DBD in argon mode: temperature, 250°C; flow rate, 5 mL/min argon. Peak identification: methanol (1), ethanol (2), propanol (3), butanol (4), and pentanol (5).

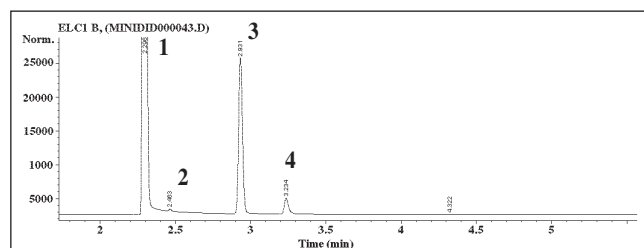


Figure 16. A qualitative chromatogram of formaldehyde (2.9 min) and water (3.2 min) in air with DBD in helium mode. GC conditions: 40°C for 2 min, increased 25°C/min to 250°C. Column: 60-m × 0.32-mm i.d., 5- μ m CP-Volamine, 45 cm/s helium. Injection size: 1-mL split 10:1. DBD in helium mode: temperature, 250°C; flow rate, 20 mL/min helium. Peak identification: air (1), carbon dioxide (2), formaldehyde (3), and water (4).

again be observed. Figure 12 (see page 4A) shows an overlay of chromatograms of alkanes and alkenes from C₁ to C₆. Note the suppression of response for ethane and the enhancement of alkenes over alkanes. The sensitivity improvement for ethylene and propylene over ethane and propane are almost double.

Analysis of carbon dioxide (helium ionization mode). Carbon dioxide is used in the carbonation of commercial beverages. It has also been indicted as a greenhouse gas and is an impurity that can decrease catalyst efficiencies. The measurement of carbon dioxide and carbon monoxide typically is conducted with the use of a thermal conductivity detector at ppm level or a nickel catalyst, known as a methanizer, operating in a reductive mode to hydrogenated either carbon dioxide or carbon monoxide to methane at a temperature around 375°C. The employment of a methanizer can incur more cost and maintenance to the analytical system. Figure 13 shows a chromatogram of 500 ppm (v/v) of carbon dioxide in nitrogen.

Analysis of oxygenated compounds (in helium or argon mode). Depending on the analytical requirements, alcohols can be analyzed by both helium ionization and argon ionization mode. If the measurement of a low level of methanol is required, then helium ionization mode is needed. Figures 14 and 15 show chromatograms of alcohols analyzed in helium and argon ionization modes, respectively. Oxygenated compounds such as formaldehyde can also be analyzed with the DBD in helium mode, as illustrated in Figure 16. Again, note the excellent peak shape for the highly reactive formaldehyde.

The analysis of arsine (in helium ionization mode). Arsine, the most toxic form of arsenic, has some properties that may make it useful as a chemical warfare agent; it is a colorless, odorless, non-irritating gas that is 2.5 times denser than air. At concentrations above 0.5 ppm, a garlic-like odor may be noted, but arsine is toxic at much lower concentrations. Although it has been investigated as a chemical warfare agent, arsine has no recorded battlefield use. During and prior to World War II, the British studied this agent and rejected its use in the field. They concluded it was more than 10 times less toxic than phosgene (17). In addition, it is difficult to manufacture and is highly flammable. Industrial applications of arsine include the semiconductor industry during microchip production and other industries in which workers are involved in galvanizing, soldering, etching, and lead plating. Figure 17 shows a chromatogram of 1 ppm (v/v) of arsine (retention time = 1.55 min) in nitrogen, demonstrating the capability of

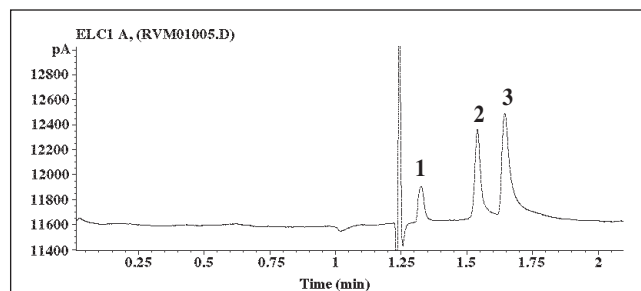


Figure 17. A chromatogram of 960 ppb (v/v) of arsine in air by DBD-helium mode. GC conditions: 40°C for 2 min, increased 25°C/min to 250°C. Column: 50-m × 0.32-mm i.d., 5- μ m CP-Sil 8CB, 45 cm/s helium. Injection size: 250 μ L. DBD in helium mode: temperature, 250°C; flow rate, 20 mL/min helium. Peak identification: interference (1), arsine (2), and water (3).

the detector for use in the measurement of low levels of arsine.

Overall detector performance

As a general observation, the DBD in helium ionization mode operates more or less as a universal detector. In argon mode, however, the detector sensitivity appears to depend on factors such as carbon number, functional group (R-OH, R-O-R, R-X), and bond type (double bonds and aromatics). From the data gathered, sensitivity of the detector increases as carbon number increases. At low carbon numbers, the functional group is the primary factor affecting sensitivity. This effect is negated when the carbon number increases. Branched compounds are generally more sensitive than nonbranched compounds. For substituted benzenes, electron-releasing groups (i.e., ring activators) increase sensitivity and, conversely, electron withdrawing groups (i.e., ring deactivators) decrease sensitivity.

After approximately 2 years of operation, the detector was found to be reliable with a low cost of ownership because of its low gas consumption. It was also found to be stable for day-to-day operation. The ignition of plasma has been very consistent and reliable over the course of use and the electrodes remain virtually intact, a testimonial to the reliable design of the detector and technology. A procedure for changing out gas cylinders in helium mode has been developed to minimize the disruption of service. Using this procedure, the detector can be placed back into service within 2 h of cylinder replacement. In argon mode, plasma ignition is easier when the detector reaches its operating temperature.

When compared to a contemporary ionization detector such as the helium ionization detector (HID) and pulsed discharge detector (PDD), the DBD does possess attractive features such as the being totally field serviceable with a respectable maximum operating temperature range of up to 250°C. The detector plasma is easy to ignite with no damage to electrodes, should there be a disruption to the reaction gas supply.

The detector was found to be compatible with wall-coated open tubular (CP-Sil 8CB and CP-Volamine) and porous layer open tubular columns (CP-Lowox, CP-PoraBOND, and CP-MS 5A) in various dimensions.

Constraints and rectifiable limitations

Hurst and Klots have stated that the origins of the Penning phenomenon are "complex, subtle, and subject to reinterpretation" (18). Indeed, the mechanism of the helium ionization is still not fully understood. The response for most species, nevertheless, can be adequately explained. It does account for the high sensitivity of the detector and provides a plausible explanation for the increase in ionization observed when most compounds are introduced into the detector. It was also observed that, for certain classes of compounds such as water, the linear dynamic range is only around 2 order of magnitudes and has, so far, been attainable. The reasons for this limited linear dynamic have not yet been identified but is the subject of on-going development work.

Like any highly sensitive detector, utmost care must be taken to ensure overall chromatographic component cleanliness is preserved. Wherever possible, deactivated liners, low bleed septum, and ultra low bleed columns are recommended. Cleanliness of gas is highly important, especially in applications where a low detec-

tion limit is required. It is also important to have a leak-free chromatographic system. The presence of leak can drastically reduce the sensitivity of the detector, especially in helium mode.

Other rectifiable issues were identified in our evaluation of the detector. These include the need for a more rugged signal cable, ground wires, and a better insulation scheme for the detectors to ensure good thermal stability.

Future work

Future works include detector performance comparison between the two operating modes: helium ionization and argon ionization, and also industrial application developments, especially where there are unarticulated needs such as the measurement of water, ammonia, and higher molecular weight mercaptans. This work reported has been focused mainly on gas matrices. Work with liquid matrix is in progress.

Conclusion

A new GC detector has been invented and commercialized. The detector offers multimode capability. In helium mode, the detector can be used as a universal detector (except neon), and in argon mode, which depends upon the ionization potential of the solute of interest, various degrees of selectivity can be attained.

The DBD was found to be simple, reliable, and easy to operate. It has a low cost of ownership because of its low gas consumption nature. When compared to contemporary ionization detectors such as the HID and PDD, the DBD does possess attractive features, such as the detector being totally field serviceable, respectable maximum operating temperature range of up to 250°C, easy and reliable plasma ignition with no damage of electrodes should there be a disruption to reaction gas supply, and cost effectiveness. The detector was successfully demonstrated in a number of industrial, environmental, and industrial hygiene applications.

Acknowledgments

The late Professor Dr. Wayne Wentworth of the University of Houston, TX, is gratefully acknowledged for the many personal communications, fruitful discussions, and teachings he offered on the topic of mechanisms of ionization of helium and argon. Special thanks to Dr. Mary Fairhurst, Vicki Carter, and the Separations Leadership Team of the Dow Chemical Company, Analytical Sciences, for their support of this project. This project is partially funded by the Dow Chemical Internal Development Funds (IDF).

References

1. R.P.W. Scott. *Chromatographic Detectors, Design, Function, and Operation*. Marcel Dekker, Inc., New York, NY, 1996.
2. M. Monagle. *Trace Constituent Detection in Inert Gases*. U.S. Patent 5,892,364, April 6, 1999.

3. B. Eliasson and U. Kogelschatz. Modeling and applications of silent discharge plasmas. *IEEE Trans. Plasma Sci.* **19(2)**: 309–23 (1991).
4. W.E. Wentworth, S.V. Vasinin, S.D. Stearns, and C.J. Meyer. Pulsed discharge helium ionization detector. *Chromatographia* **34**: 219–25 (1992).
5. F. Andrawes and R. Ramsey. The helium ionization detector. *J. Chromatogr. Sci.* **24**: 513–18 (1986).
6. E. Bros and J. Lasa. Concentration characteristics of the helium detector for gas chromatography. *Chromatographia* **13**: 567–76 (1980).
7. F. Andrawes, T. Byers, and K. Gibson. Standardization of helium carrier gas for helium detector applications. *Anal. Chem.* **53**: 1544–45 (1981).
8. F. Andrawes. Determination of trace levels of water in gaseous samples by gas chromatography with helium ionization detection. *Anal. Chem.* **55**: 1869–72 (1983).
9. F. Andrawes and S. Greenhouse. Applications of the helium ionization detector in trace analysis. *J. Chromatogr. Sci.* **26**: 153–59 (1988).
10. H.H. Hill and D.G. McMinin, Eds. *Detectors for Capillary Chromatography*. John Wiley & Sons, New York, NY, 1992.
11. J. Driscoll. Evaluation of a new photoionization detector for organic compounds. *J. Chromatogr.* **134**: 49–55 (1977).
12. J. Driscoll. Applications of a photoionization detector in gas chromatography. *Am. Lab.* **9**: 71–74 (1976).
13. A.T. James, A.J.P. Martin. Gas liquid partition chromatography. *Biochem. J.* **50**: 679–90 (1952).
14. Benchmark Concentrations and Associated de Minimis Values. http://www.apcd.org/star/bac_and_de_minimis.html.
15. *National Institute of Standards Chemistry Webbook*. NIST, Washington, D.C., 2005, <http://webbook.nist.gov/chemistry>.
16. M.L. Langhorst. Photoionization detector sensitivity of organic compounds. *J. Chromatogr. Sci.* **19**: 98–103 (1981).
17. *Chemical Warfare Agents*. U.S. National Library of Medicine, Bethesda, MD, 2005, <http://www.sis.nim.nih.gov/Tox/ChemWar.html>.
18. G. Hurst and C. Klots. *Advances in Radiation Chemistry*. M. Burton and Meagee, Eds. Wiley (Intersciences), New York, NY, 1976, p. 1.
19. J. David. *Gas Chromatographic Detectors*. Wiley (InterSciences), New York, NY, 1965.
20. A. Nicholson. "Detectors and Chromatography". Australian Scientific Industry Association, Proceedings of an International Conference, University of Melbourne, Australia, May 30–June 3, 1983.
21. P. Marriott. "Flame photometric detection—the problems of a compound dependent—non-linear detection mode in chromatography". Department of Chemistry, National University of Singapore, Lecture given at University of Melbourne, June 1983.
22. M. Lee, F. Yang, and K. Bartle. *Open Tubular Column Gas Chromatography*. ISBN 0-471-88034-8, John Wiley and Sons, Inc., New York, NY, 1984.
23. G. Schomburg. *Gas Chromatography*. ISBN 3-527-27879-6, VCH, Weinheim, Germany, 1990.
24. H. McNair and J. Miller. *Basic Gas Chromatography*. John Wiley and Sons, Inc., New York, NY, 1997.
25. W. Jennings, E. Mittlefehldt, P. Stremple. *Analytical Gas Chromatography*, 2nd ed. Academic Press, San Diego, CA, 1997.
26. W. Jennings, W. Wyllie, and S. Alves. Photoionization detection in a high resolution gas capillary system. *Chromatographia* **10**: 426–29 (1977).

Manuscript received July 26, 2005;
revision received November 10, 2005.