



Review

Pulsed discharge detector: theory and applications

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I dedicate this article to the memory of Dr. Wayne E. Wentworth, a true pioneer in the field of modern analytical chemistry, who passed away during the preparation of this article. He will be greatly missed by his family, friends and colleagues.

Abstract

The pulsed discharge detector (PDD) is a significant advancement in gas chromatography (GC) detector design which can be operated in three different modes: pulsed discharge helium ionization (He-PDPID), pulsed discharge electron capture (PDECD) and helium ionization emission (PDED). The He-PDPID can detect permanent gases, volatile inorganics and other compounds which give little or no response with the flame ionization detector (FID) and has significantly better limits of detection (minimum detectable quantities (MDQs) in low picogram range) than can be achieved with a thermal conductivity detector (typically not lower than 1 ng). The PDECD has similar or better sensitivity (MDQs of 10^{-15} to 10^{-12} g) than radioactive source ECD but does not require licensing, wipe tests and other administrative or safety requirements which have increased over security concerns. The PDED shows promise as an extremely selective and sensitive elemental detector but a commercial unit is not presently available. In this report, the theory of operation, applications of the PDD and the practical aspects of using this novel detector are presented.

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Keyword: Pulsed discharge detection

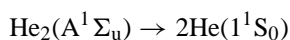
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1. Introduction

The advancement and versatility of gas chromatography as an analytical tool has been largely based on improvements in sample introduction inlets, column technology and detectors. Gas chromatographic (GC) detectors can be grouped into two general types: universal detectors which respond to a very wide range of chemicals and selective detectors which respond to a much smaller group of chemicals. However, some GC detectors such as mass selective or microwave induced plasma (MIP) detectors are capable of both universal and selective modes of operation and have gained wide acceptance by analysts. The lesser known pulsed discharge detector (PDD) is also capable of both universal and selective modes of operation.

First described in 1992 [1,2] the PDD is based on an ionization source resulting from a pulsed high voltage discharge between platinum electrodes. When the discharge occurs in pure helium a photon emission results from the transition of diatomic helium to the dissociative 2He ground state as given below [3–5]:



This transition is known as the Hopfield emission, and occurs at very short wavelengths (60–100 nm) with energies ranging from approx. 13.5 to 17.5 eV. The broad emission provides sufficient energy to ionize all elements and compounds, with the exception of neon. The PDD can be configured as a universal, selective or elemental detector.

For universal detection, the GC column eluents are photoionized directly by the Hopfield emission with the resulting electrons producing a measured current. This configuration is called the helium pulsed discharge photoionization detector (He-PDPID). Selective detection of electron capturing compounds can be achieved by adding a small amount of additional gas (dopant) into the detector, which is ionized to establish a standing current. Electron capturing compounds eluting from the GC column lower the standing current. This configuration is called the pulsed discharge electron capture detector (PDECD). Elemental detection is possible if the PDD is configured with a monochromator and photomultiplier to measure the emission lines resulting from the analytes passing through the helium discharge. This detector configuration is termed the pulsed discharge emission detector (PDED).

2. Helium pulsed discharge photoionization detector (He-PDPID)

2.1. Theory of operation

Compounds eluting from the capillary column are ionized by high-energy photons originating from the helium discharge zone (Fig. 1). The resulting electrons are focused toward the collector electrode by the bias electrodes. Changes

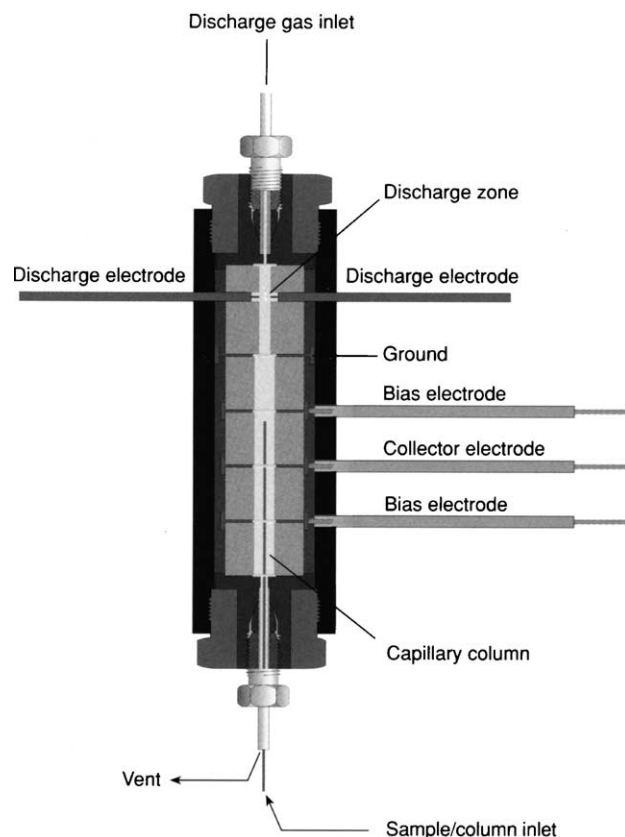


Fig. 1. Cross section of the pulsed discharge helium ionization detector (He-PDPID). The bias and collector electrodes are rings. Reprinted with permission from Valco Instruments Co. Inc.

in the measured current constitute the detector response. The separation of the discharge zone from the ionization zone along with the counter helium gas flow configuration ensures that only pure helium passes through the discharge region, minimizing the possibility of contamination of the discharge electrodes [6].

A comparison between the He-PDPID and FID has shown that the He-PDPID response is linear for most compounds over a range of five orders of magnitude and more accurate than the FID in determining the percentage composition of mixtures containing aromatic hydrocarbons, esters, halogenated compounds, ketones, nitriles and sulfides/mercaptans [7]. The molar response of analytes to the He-PDPID appears to be a function of the number of ionizable electrons present in the analyte whereas a flame ionization detector (FID) response is dependant upon the number of carbon atoms in the molecule [8]. The difference in response mechanism and the high photoionization energy range of the He-PDPID results in the detection of permanent gases, halogenated compounds and other analytes not detected by FID.

It is possible to change the range of photoionization energy in the PDPID by altering the emission spectra with the addition of small amounts (typically 1–3%) of argon or krypton [9] to the helium discharge gas. An advantage to using doped helium rather than pure noble gases is that the ben-

Table 1

Element/compound	Ionization potentials eV
Helium	17.7*
N ₂	15.6
CF ₄	>13.9
O ₂	12.1
H ₂ O	12.6
CH ₃ CN	12.2
Argon	11.8*
CH ₂ Cl ₂	11.3
CH ₃ Cl	11.2
Krypton	10.6*
CH ₃ Br	10.5
N-C ₆ H ₁₄	10.1
CH ₂ =CHCl	10.0
Acetone	9.7
Xenon	9.6*
CH ₃ I	9.5
Toluene	8.8
(C ₂ H ₅) ₃ N	7.5

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efficient characteristics of helium are retained, which include efficient cooling of the discharge electrodes and transparency to the argon or krypton emissions. The argon emission consists of the resonance radiation at 11.8 and 11.6 eV and the diatomic Ar₂ emission ranging from 9.2 to 10.3 eV. The krypton emission has two resonance lines at 10.1 and 10.6 eV and the Kr₂ emission at 8.1–8.8 eV [5,9,10]. Lowering the photon energy of the pulsed discharge by doping the helium discharge gas enables selective ionization of analytes (Table 1). Compounds with ionization potentials greater than the energy range of the doped discharge respond much less than compounds with ionization potentials below the energy range of the doped discharge gas. One example is the loss of detector response to air and water by using argon doped helium [5]. This could be advantageous for environmental air sampling. Another study examining response of chloro alkanes/alkenes also clearly demonstrated selectivity based on the use of argon and krypton doped helium discharges (Fig. 2) [10].

3. Pulsed discharge electron capture detector (PDECD)

3.1. Theory of operation

The PDECD mode is quite similar to the He-PDPID with a pulsed discharge in pure helium providing high-energy photons for ionization. However, a dopant, to produce thermal electrons, is introduced and the bottom two electrodes (bias and collector) are interchanged (Fig. 3). The dopant is introduced closer to the discharge zone than the column. The dopant gas is ionized by the Hopfield emission, resulting in electrons which are focused toward the collector electrode by the bias electrodes. This constitutes the detector standing

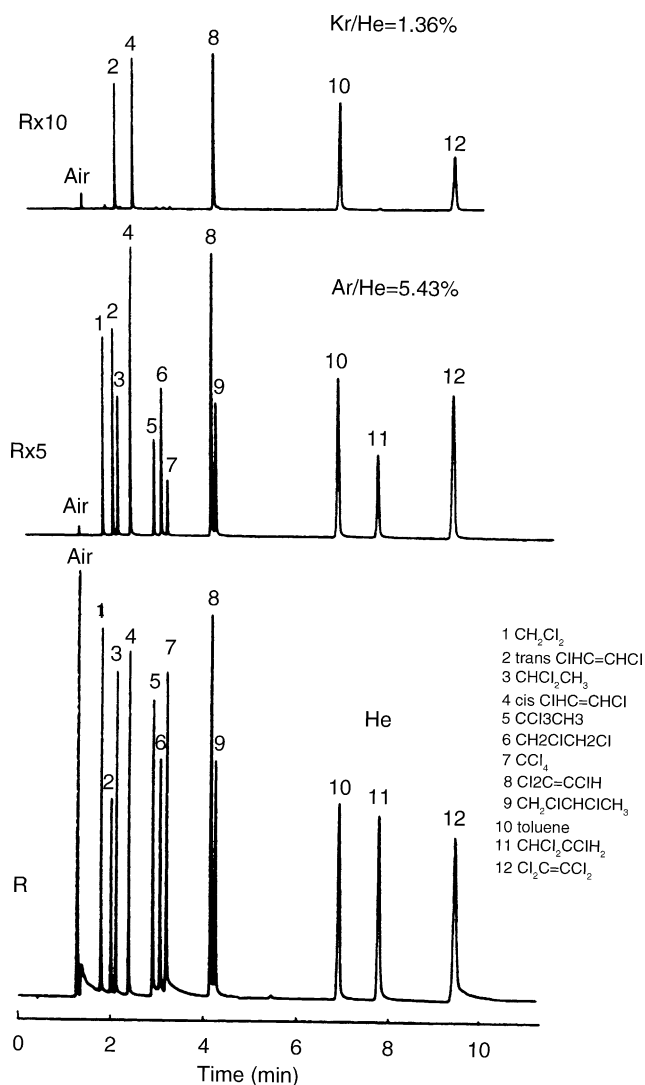


Fig. 2. Chromatograms of HE-PDPID response to a mixture of chloro alkanes/alkenes using helium, argon doped helium or krypton doped helium discharge gas. DB-5MS column, 0.25 mm i.d. × 30 m, 0.25 μm film thickness (J&W Scientific, Folsom, CA). Reprinted with permission from [10].

current. When electron-capturing compounds elute from the column there is a decrease in the standing current, which is measured as the PDECD response [4]. The dopant gas serves two purposes in the PDECD: it supplies the electrons as it is ionized by the high energy radiation from the helium discharge and it also lowers the average electron energy through inelastic collisions. These thermalized electrons can be more readily captured by analytes with high electron capture coefficients [11]. Therefore, the ideal dopant has a low ionization potential and a large cross-sectional area [12]. Hydrogen, carbon dioxide, ammonia, trimethylamine, [6,11] methane, nitrogen [6,11,12] and xenon [12] have been examined as potential dopants. Overall, methane and xenon are considered to provide the best results with preference to xenon since it can be purified to levels similar to helium [12]. Critical impurities in either methane or xenon used as a PDECD dopant gas include water, O₂, CO, and CO₂.

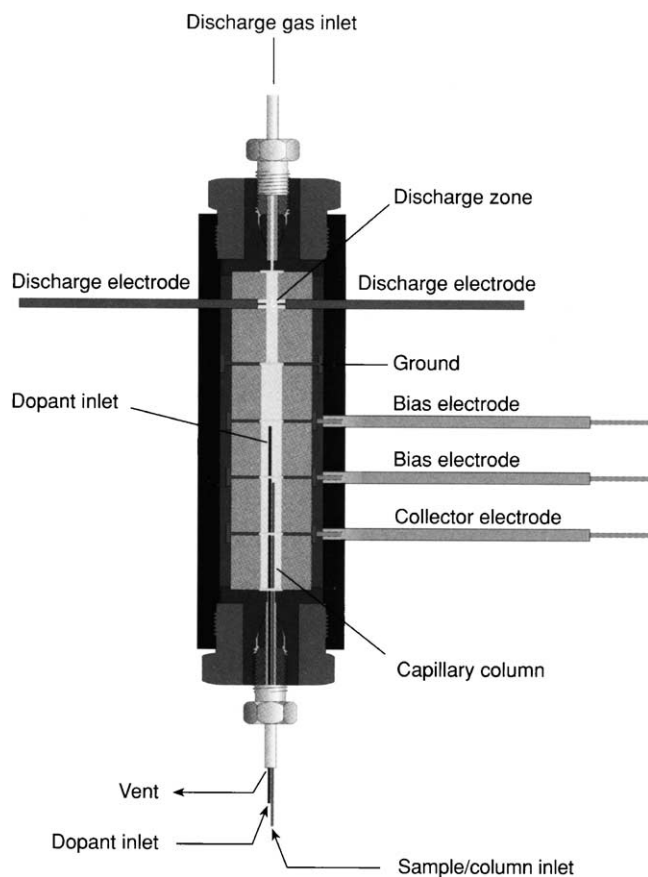


Fig. 3. Cross-section of the pulsed discharge electron capture detector (PDECD). The bias and collector electrodes are rings. Reprinted with permission from Valco Instruments Co. Inc.

A common issue for electron capture detectors has been the lack of linearity of response [13] with various strategies utilized to increase the range of linearity. The raw signal output of the PDECD becomes nonlinear to the analyte concentration when the capture rate exceeds 5% [14]. Therefore, two approaches have been taken to linearize the response. The first commercial PDECD used a low constant potential bias voltage. To get a linear signal the following function was used:

$$R = \frac{I_b - I_e}{I_e} = K[AB]$$

where R is the linearized ECD signal, I_b is the detector standing current, I_e is the measured detector current, K is the electron capture coefficient and $[AB]$ is the concentration of the capturing species [12]. This conversion gave the PDECD a linear dynamic range of 3–4 orders of magnitude [14]. However, more recently, further improvements in sensitivity, response time and operation were made by using a feedback dc bias voltage to establish a constant-current operation mode [14,15] capable of a linear response range of up to 5 orders of magnitude.

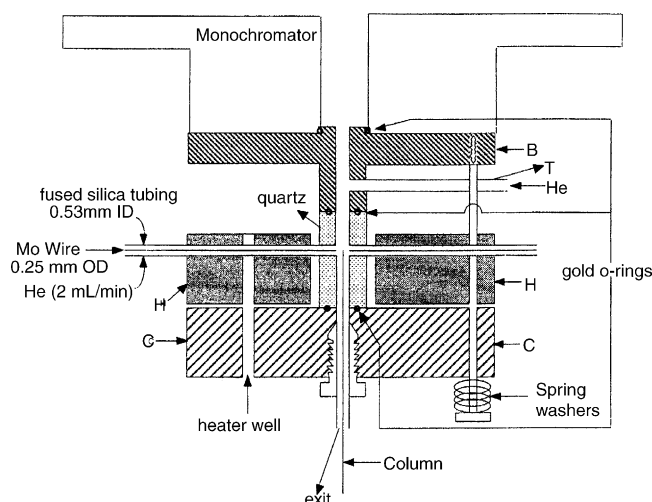


Fig. 4. Schematic diagram of PDED system. C, backplate; H, heater block; B, flange; T, 1/16 in. stainless steel tubing soldered to section B. Reprinted with permission from [16].

4. Pulsed discharge emission detector (PDED)

This detector design uses the pulsed discharge as the source of excitation for emission spectra which are isolated and measured with a monochromator and photomultiplier. Early designs [2,6] used a quartz or MgF_2 window which limited the vacuum UV emissions that could be detected and become discoloured over time by the intense UV radiation. The column effluent also passed through the discharge zone, resulting in carbon deposits on the electrodes. A more recent design [16] addressed these deficiencies by purging the electrodes with helium to prevent the GC effluent from contacting the discharge electrodes. The detector assembly is mounted directly to the entrance of the monochromator (Fig. 4). The replacement of vacuum with helium purging of the monochromator allowed transparency to emissions extending as low as 60 nm and the removal of the window from the detector assembly. Element specific detection was now possible with the measurement of vacuum UV atomic emissions from Cl, Br, I and S [16]. A chlorine-specific detector (Cl-PDED) with a selectivity to carbon of 1000 can be achieved by using krypton doped helium to produce an excited species of $KrCl^*$ which emits at 221–222 nm. The detection limit was estimated to be 50 fg Cl/s ($S/N = 3$) [17]. The response of the Cl-PDED was also compared to the He-PDPID [18,19]. Although the PDED offers some interesting possibilities no commercial version has been released yet and is not discussed further in this review.

5. Applications

The design of the He-PDPID and PDECD confers some distinct advantages over other detector designs. The separation of the discharge and ionization zones enables the discharge electrodes to remain clean, providing a stable flow

of photons for ionization of analytes (HE-PDPID) or dopant (PDECD). Other detectors, notably FID and ^{63}Ni ECD detectors have the column effluent pass directly through the source of ionization and can become contaminated. Generally, only thermal cleaning is recommended for radioactive source detectors and it has been the author's experience that when used with high molecular weight compounds, such as PCBs and dioxins, certain ^{63}Ni ECD detector designs must have their source replaced periodically (1–2 years) to maintain sensitivity.

The He-PDPID also has a truly universal response, except for neon, which means it can be used for the detection of permanent gases (such as H_2 , Ar, O_2 , N_2 , CO, CO_2), volatile inorganics as well as all classes of organic compounds. Applications that would have required a TCD and FID can now be done with a single detector with similar or better sensitivity.

Since the He-PDPID can detect hydrogen, the use of hydrogen rather than helium as a carrier gas would result in a high background signal unless operated with krypton doped helium discharge gas. This would, however, result in lower sensitivity. Hydrogen carrier gas (at typical capillary column flow rates) can be used with the PDECD with no effect on sensitivity.

The PDECD requires no site licensing for a radioactive source, eliminating the increasing amount of paperwork and site inspections commonly required for radioactive source detectors. Recent heightened security concerns have made these administrative requirements increasingly difficult.

However, the helium used as the discharge gas must be extremely pure (99.999% or better) to prevent contamination of the discharge electrodes and minimize the background signal. Our experience with He-PDPID/PDECD installations has shown that the manufacturer's recommendations for installation should be closely followed. Use 5 nines (or better) helium, stainless steel chromatographic grade tubing and fittings, and a heated zirconium alloy getter (model HP2, Valco Instruments Co. Inc., Houston TX) to remove impurities such as water and oxygen. Other types of oxygen, hydrocarbon or moisture filters are not recommended. Factory supplied restrictors should be used rather than flow controllers to minimize potential sources of leakage and regulators must have stainless steel diaphragms. However, the side benefits of ensuring an extremely pure helium supply include improved GC column life and lower chromatography background contamination.

5.1. Drugs

A FID and He-PDPID were compared for the determination of some commonly abused drugs, amphetamine, methamphetamine, 3,4-methylenedioxy-amphetamine (MDA), 3,4-methylenedioxy-methamphetamine (MDMA), 3,4-methylenedioxy-*N*-ethylamphetamine (MDEA) and phencyclidine (PCP), in urine. The He-PDPID was found to give greater peak area and peak height response than the FID [20].

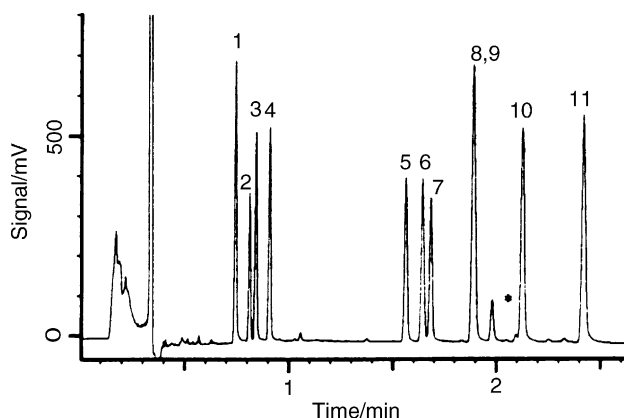


Fig. 5. A chromatogram obtained from a $1\ \mu\text{l}$ injection of a standard pesticide calibration mix at the $100\ \text{ng}\ \text{ml}^{-1}$ level. Split level was 10:1. Peaks: (1) TCMS, (2) α -BHC, (3) β -BHC, (4) δ -BHC, (5) *cis*-chlordane, (6) *trans*-chlordane, (7) *p,p'*-DDE, (8) *p,p'*-DDD, (9) endrin, (10) endosulfan sulfate, (11) endrine ketone, (*) endrin aldehyde. Bonded methyl 5% phenyl silicone column, 0.1 mm i.d. \times 5 m, $1\ \mu\text{m}$ film thickness (Quadrex Corp., Woodbridge, CT). Reprinted by permission of the Royal Society of Chemistry.

5.2. Pesticides

The PDECD has been applied to pesticide analysis during development of the detector [4,11,12,14] with a minimum detectable quantity (MDQ, $S/N = 2$) as low as 16 fg for lindane. Other studies have examined the use of the PDECD with micro bore ($100\ \mu\text{m}$ i.d.) capillary columns for rapid determination [20,21]. The achieved analyte peak shape (Fig. 5) clearly demonstrates that the PDECD does not degrade even rapid chromatography performance. Again, reported limits of detection (LODs) for various organochlorine pesticides ranged from 10 to 50 fg [22].

5.3. Volatiles

The He-PDPID has been applied in studies of atmospheric contaminants, particularly for analytes that give little or no response to FID. Hunter et al. [23] compared the He-PDPID and FID response to volatile oxygenated compounds, hydrocarbons, chlorinated and sulfur containing volatiles. The He-PDPID/FID response ratio ranged from 2.6 for benzene to >300 for formaldehyde, demonstrating that the He-PDPID sensitivity was significantly better than the FID for this type of study. The response for formaldehyde was found to be greater using argon doped helium discharge gas than with pure helium while the response to air and water is absent, improving both the sensitivity and selectivity of the He-PDPID for this analyte [24]. Two studies on the measurement of ambient atmospheric formaldehyde using the He-PDPID (with 1% argon in helium) reported detection limits of 32 pptv [25] and 42 pptv [26]. The measurement of peroxyacetyl nitrate (PAN), a photochemical atmospheric contaminant using a PDECD has also been reported [27].

Other studies using the He-PDPID/PDECD to measure volatiles have been quite varied, including: dissolved gases

and moisture in mineral insulating oil [28], trihalomethanes in water [29], composition measurements of natural gas [30] hydrogen and methane in human breath [31] and oxygen, carbon monoxide and carbon dioxide in polyolefin feed streams [32].

5.4. Organometallics

Our laboratory has tested the response of organotin, organomercury and organolead compounds by He-PDPID and PDECD [33]. The reported limits of detection ($S/N = 3$) ranged from 0.4 to 1.2 pg in the He-PDPID mode. Tetraethyllead was the only analyte which responded in PDECD mode with a LOD of 0.1 pg ($S/N = 3$). We have continued the use of the PDECD in a recent study of methylmercury (determined as methylmercury bromide) in predatory fish species [34]. The sensitivity of the PDECD was similar to those reported previously in the literature for radioactive source ECD.

5.5. Inorganics

Impurities in tungsten hexafluoride (H_2 , O_2 , N_2 , CO , CO_2 and SF_6) have been measured by He-PDPID [35]. A backflush-to-vent valve switching technique separated the impurities from the matrix which was too corrosive to allow contact with the analytical column and detector. The limits of detection ($S/N = 3$) ranged from <10 ng/l to <500 ng/l.

6. Future directions

Although there is not yet been a large number of published studies using the He-PDPID/PDECD it is not unusual for new technology to be slowly accepted, particularly when it is an alternative for matured, widely used technology such as the FID and radioactive source ECD. However, the advantages of the He-PDPID and PDECD are clearly demonstrated in the literature and, as placement of radioactive sources becomes more difficult, more researchers will turn to the PDED. Valco Instruments Co. Inc. has also produced a miniature version of the PDD detector but it has not been released yet. This model has been developed for compact, field portable analytical systems.

7. Conclusions

The wide range of analytes reported in this review demonstrate that the PDD has great versatility, particularly for applications which require the sensitivity of FID with the universal response of a TCD. The PDECD offers similar or superior performance to the radioactive source ECD but without any requirements for security or safety protocols for radio-nuclides which are becoming increasingly stringent in laboratories. It is anticipated that over time, the PDD will be increasingly selected as an alternative to FID and radioactive source ECD.

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