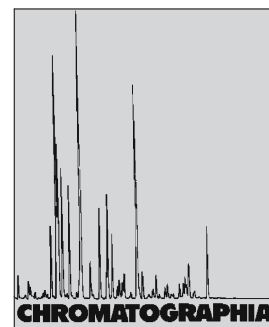


Photoionization Detector for Portable Rapid GC



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Abstract

With the development of portable rapid gas chromatography (GC) for environmental monitoring the photoionization detector (PID) has potential application. The frequent calibration required and the relatively large dead volume have limited the use of the PID, however. An improved PID which resolves these problems is proposed in this paper. Compared with a commercial instrument, signal generation, the main aspect of the improved PID, has also been optimized. In the improved PID the sample is directed to flow across the lamp window, rather than toward the lamp, and a new, simple automatic self-cleaning technique, which effectively eliminates contaminants and substantially reduces drift, has also been adopted. Use of new electrodes has effectively reduced the background noise and dead volume of the PID. As a result of this new design the PID should be more compatible with rapid portable GC in environmental monitoring, because of elimination of most of the tedious cleaning and calibration previously necessary.

Keywords

Gas chromatography
Photoionization detection
Environmental monitoring

Introduction

There has recently been increased interest in the development of field-portable instrumentation. Gas chromatography (GC), one of the most powerful techniques for environmental monitoring [1, 2], has been developed for continuous monitoring, with high sample throughput, much smaller size, and high resolution. Current portable gas chromatographs are still relatively

large, however, because of the compressed gas containers needed for carrier and detector gases [3–7]. Being free from flame and other gases, however, the photoionization detector (PID) enables a new approach to the development of portable GC. The PID is concentration rather than mass-flow-sensitive, so it can be used without loss of sensitivity for portable GC with small samples. It is a compact yet high-performance device with excellent re-

sponse characteristics of the order of seconds and detection sensitivity at the ppb level [8]. It responds to a large variety of organic compounds and some inorganic compounds [9–13]. It is especially suitable for aromatic [14] and unsaturated compounds [15], and without any chemical processing [13, 16]. It has become a powerful tool in use of portable GC for measurement of ambient levels of the vapors of organic compounds in air, especially in high-speed vacuum-outlet GC with air as carrier gas [4, 17] and as a detector used in tandem with other detectors [1, 18].

Continuing progress in continuous environmental monitoring and improvement in the resolution achieved by use of portable GC has shown that PID have several drawbacks resulting from their basic design [19]. Because, in most PID, the sample stream is directed vertically toward the optical window, this window is susceptible to contamination. Polymerization of the sample compounds by UV irradiation also results in window fogging. If the detector is heated to prevent condensation, the polymer seal used in the detector releases compounds which are then deposited on the window [20, 21]. All these problems reduce lamp output [22], which results in signal drift, so frequent calibration is required [20, 23–25]. The detector must be also cleaned frequently [26], after which it must again be recalibrated. The metal electrodes of the detector also suffer from similar contamination and the UV photons cause release of free electrons, resulting in an

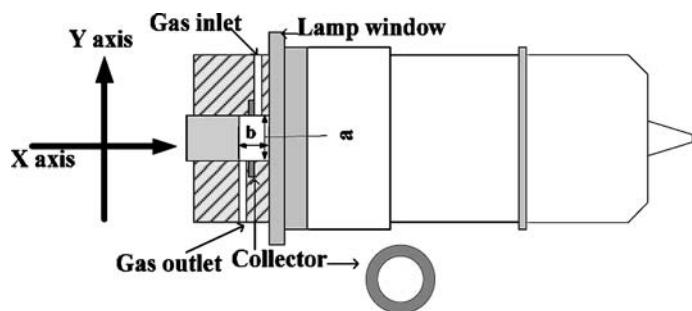


Fig. 1. General schematic diagram of the newly designed PID sensor. Length a was 2 mm and length b was 6 mm

unstable background baseline current and high noise.

Another drawback is the relatively large cell volumes ($\sim 100 \mu\text{L}$) of commercial PID, which have large dead volume [5, 7] leading to distortion of GC elution profiles and reduction of the usefulness of the rapid GC system [2, 5]. Some ions and electrons recombine before being collected, because of the large cell volumes, so the sensitivity and linearity of the detector is reduced and response time and recovery time are longer, because of the large volume of sample to be cleared [27].

We have attempted to produce an improved PID for rapid portable GC with a more stable response, lower dead volume, improved linear range, and less background noise. To do this we used a new method of sample transmission, with the sample flowing across the lamp lens (in the vertical PID the sample stream flows through the sensor along the direction of the Y axis in Fig. 1 and the light comes from the UV lamp at a 90° angle) instead of toward the lamp lens (in the axial PID the sample stream is directed directly at the lamp along the X axis indicated in Fig. 1 and the light comes from the UV lamp at a 180° angle), and adopted a new simple automatic cleaning technique, which eliminates contaminants effectively and substantially reduces the drift. The positions of the electrodes were also changed, to prevent UV light from striking them directly and thus generating photoelectrons which could cause unwanted background current and noise. The dead volume of PID was also substantially reduced. Because of this new design the PID was more compatible with in-situ rapid portable GC applications and most of the previous

tedious cleaning and calibration problems were avoided.

Experimental

Construction and Design

To evaluate the newly designed PID, the same control and electrometer unit, of a model 8610C gas chromatograph (SRI, USA), was connected to the commercial SRI PID or to our laboratory-made PID in all experiments. For repeated sampling and analysis, the switching valves, sampling pump, mode of heating, and several time sequences and integrators were regulated by PeakSimple-3.39 (SRI). The settings used for operation of the instrument were: carrier gas air; PID gain low; PID temperature 150°C ; lamp current 70 A; lamp potential 1,500 V D.C.

In this study, the laboratory-made PID, shown in Fig. 1, included a UV lamp, an annular ion collector defining an annulus in a plane perpendicular to the direction of energy radiated by the source, an ion accelerator fitted closely around the ion collector, and a variety of seals. The volume of the ionization chamber was approximately $18 \mu\text{L}$. The housing of the laboratory-made detector was manufactured from copper and the electrodes were stainless steel [28]. The electrodes were placed symmetrically, vertical to the center of the lamp.

The output of the PID was amplified by the electrometer, which was connected to a personal computer by means of an RS-232 interface. The electrometer converted the current into a potential, which was fed into the computer. In this paper, all signal data are reported as voltages. The current could be measured during

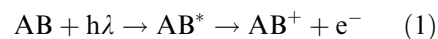
both the “on” and “off” period of the lamp. Because there was no PI process during the “off” period, the signal obtained most probably arose because of system noise or leakage current caused by moisture. By subtracting the “off” period measurement from the “on” period, it was possible to eliminate some of the system errors and improve measurement accuracy.

Equipment and Materials

The UV lamps were low-pressure gas-discharge lamps emitting a line spectrum [20]. In the investigation a 10.2 eV lamp was used with MgF_2 window and krypton gas. All solvents used were of analytical grade quality and were redistilled before use. Standard gases were prepared by injecting known volumes of authentic compound into Teflon bags containing known volumes of air, which was dried and purified by means of a chiller and a series of scrubbers containing desiccant and activated charcoal.

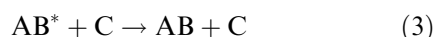
Theory

A photon is absorbed by a molecule, causing ionization of the molecule, a phenomenon known as photoionization (PI) [29, 30]. An ultraviolet (UV) lamp produces energetic photons which are directed into an ionization chamber through an optical window. A pair of electrodes, the bias electrode and the collector electrode (shown in Fig. 1), in the ionization chamber creates an electromagnetic field. The charge carriers generated in the PID—cations and electrons—are accelerated in an electric field toward the ion collector. The current resulting from the following reactions is measured [12]:

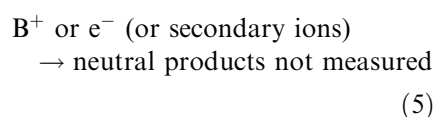
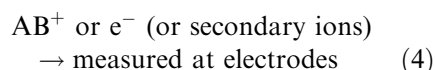


where AB denotes a compound that can be ionized.

In addition to formation of charge carriers, other reactions occur, for example dissociation Eq. (2), energy transfer to a molecule or atom of carrier gas Eq. (3), etc., leading to relaxation of the excited molecules. The concentration of excited molecules is reduced without formation of charged particles, thus reducing the ionization current.



After the initial photo-generation process a variety of secondary chemical reactions of the initial ions can occur before they reach the electrodes [31]; these include secondary ion-formation [32] and neutralization, which also reduce the ion current and can be expressed as:



As a result, a current i is produced which is proportional to the gas or vapor concentration [9] and can be expressed as [33, 34]:

$$i = I_0 F \eta \delta N L [AB] \quad (6)$$

where I_0 is the initial photon flux, F the Faraday, η the PI efficiency, δ the absorption cross-section of the substance, N Avogadro's number, and L the pathlength. The product $\eta\delta$ is the PI cross-section, δ_i . For a particular detector and lamp the PID signal is proportional to the ionization yield, absorption cross-section, and molar concentration. It is worth noting that the absorption cross-section depends directly on the photon energy and the ionization potential [34, 35]. In other words, the PID signal will be related to ionization potential through the PI cross-section [35], so any increase in these removal rates or the appearance of new removal mechanisms will lead to increased quenching of the PID response. It is worth noting that the PID is a nondestructive detector and the concentration of the sample in the ionization chamber will not be changed, because:

a negligible fraction is converted into other substances; and

the intensity of the light is too low to keep a significant fraction of the substances in the excited state; because of the speed of light and the rate of photo-physical excitation, deactivation is much more rapid than the rate of generation of photons by the lamp.

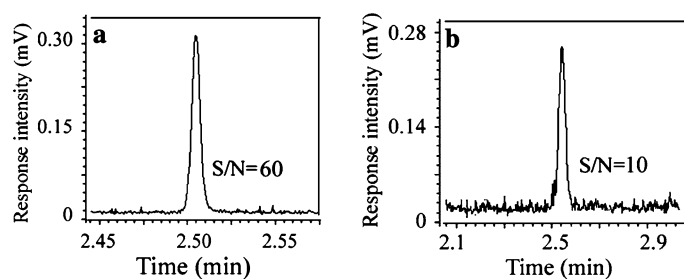


Fig. 2. Comparison of the response to 200 ppb toluene of the laboratory-made PID (a) and the axial PID (SRI) (b). The SRI 8610C GC was used with on-column injection and a $0.5 \text{ m} \times 0.53 \text{ mm i.d.} \times 0.25 \text{ }\mu\text{m}$ film column. The injector temperature was $150 \text{ }^\circ\text{C}$, the sample volume $1 \text{ }\mu\text{L}$, the PID temperature $150 \text{ }^\circ\text{C}$, and the oven temperature $100 \text{ }^\circ\text{C}$

Results and Discussion

Reduction of Background Baseline Current and Noise

The concentrations of volatile organic compounds in ambient air are usually very low and can occasionally be masked by different sources of noise, so detection can be greatly facilitated by noise reduction. For this reason much attention was devoted positioning the electrodes during detector design. Above all, the electrodes should be shaded to minimize illumination by the UV light [33], because this reduces unwanted background baseline current and detector noise. It is apparent from Fig. 2 that the signal to noise ratio (SNR) of the laboratory-made PID was better than that of the commercial detector and the detection limit was reduced by a factor of six. The concentration of toluene that could be detected accurately was reduced to 10 ppb.

Reduction of the Dead Volume

The ionization chamber of the PID has previously been relatively large, to provide sufficient pathlength for absorption of most of the UV light, to achieve the greatest sensitivity. In reality, after leaving the lamp window the photons traveled a very short distance before being absorbed by gas molecules, so the region in which the PI process occurs was just a few millimeters in front of the lamp window. The collector electrode therefore had to be as close as possible to the lamp window and the chamber was the only effective region for PI (Fig. 1). The electrodes were therefore placed directly on top of the lamp to minimize the volume

of the chamber and to substantially reduce the response time of the detector.

In the most of PID lamps used the gas discharge has usually been confined to a central capillary, constraining the flow of ions, to minimize sputtering and to create a point source of vacuum UV radiation originating from the small cross section of the capillary. The intensity of the radiation was high at the center and low at the periphery [36, 37]. The internal diameter of the chamber could therefore be greatly reduced, leading to a much lower dead volume.

The effect of different chamber volumes on signal intensity was tested at a given potential for ionization chambers of different internal diameter and, therefore, light pathlengths. The results are shown in Figs. 3 and 4. It is apparent the PI current grew slightly with the increasing ion-chamber volume [28], whether by increasing the chamber internal diameter or by increasing the length of the light path. Because the internal diameter of the chamber was reduced, although the peak-to-peak background noise was increased, resolution increased substantially. This it is possible to substantially improve the resolution at the cost of a little sensitivity. With the longer light path the signal increased slightly but the linear range and resolution decreased critically (Figs. 4 and 5). Under these conditions the detector suffered more from competitive light absorption by matrix gases and neutralization of ions, which resulted in narrower linear range. Taking into consideration the SNR, which determines the detection limit, and acceptable resolution and linear range, a 2-mm internal diameter and 6-mm sample pathlength were found to be optimum; this resulted in a sensor volume of approximately $18 \text{ }\mu\text{L}$.

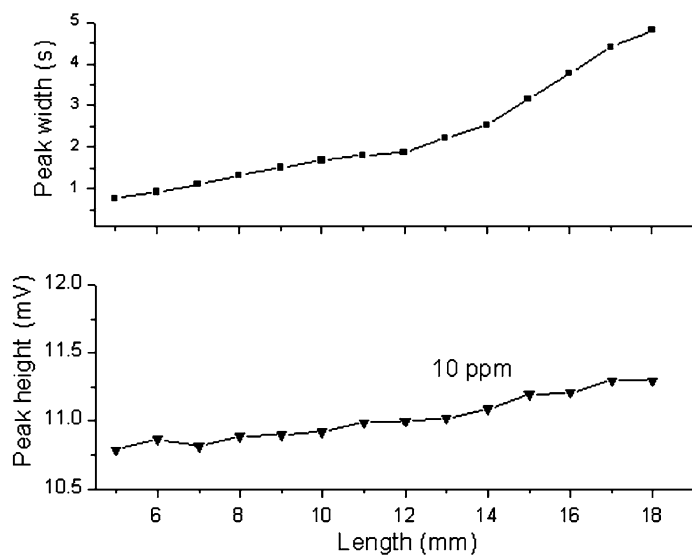


Fig. 3. Effect of different light pathlengths on peak height and peak width (baseline) of toluene (length b in Fig. 1 was varied). Detection was with the newly designed PID. Other conditions were as for Fig. 2

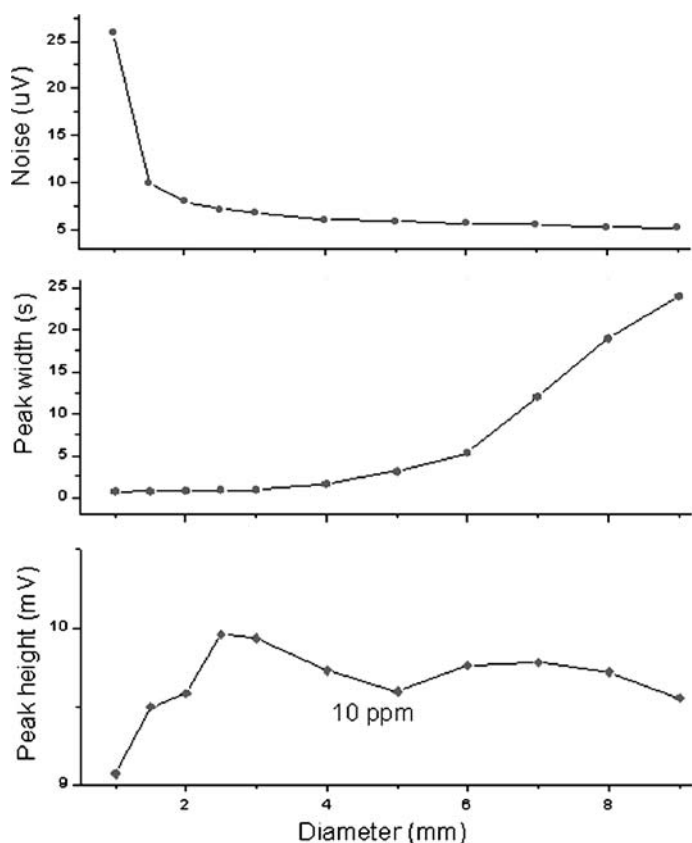


Fig. 4. Effect of different electrode internal diameters on the response to toluene and on the background (baseline) noise (length a in Fig. 1 was varied). Other conditions were as for Fig. 2

The dead volume of the ionization chamber could also certainly be compensated by use of make-up gas [20]; this would, however, dilute the sample and make the instrument more complex with a relatively small effect on band width [21].

Linearity and Flow Rate

The cathode and anode were set coaxially along the energy axis of the source, and the collector electrode was closely adjacent the radiation source; this enabled use of a smoother sample flow path and a

lower dead volume. Figure 5 shows the linear range was increased substantially by reduction of the dead volume. Because the direction of the gas flow in our laboratory-made PID was perpendicular to the electrical field and the direction of the UV light propagation, formation and collection of ions were also more efficient, so concentrations of gases up to approximately thousands of parts per million could be measured accurately. Figure 5 shows the response of the laboratory-made PID to toluene, which mimicked the light-absorption equations at low and high concentrations. It is apparent that for PID of different volumes linear raw response in the ppb and ppm range began to deviate slightly at higher concentrations. In the optimized detector deviation began slightly above $\sim 1,000$ ppm (not shown in the figure). The upper limit of the response was approximately 5,000 ppm; higher concentrations resulted in double peaks, which has been attributed to recombination of ions [20] and could be explained as response saturation of the PID [32] and must be because of a decrease in the efficiency of collection of the ions. With increasing concentration neutralization reactions became the main trend. Such a drop in response at high concentrations is inherent, and has also observed for other photochemical systems [38] in which the products could recombine to form undetected compounds.

PID measurement, as reported by Freedman [12] and others, was observed to be independent of flow rate. This result was in accord with the Lambert–Beer law of light absorption, for which there is a necessary condition that the sample concentration in the flow was constant. In this work, when the PID was used with a short GC column, although the resolution was increased and detector dead time was reduced, sample concentration decreased with increasing flow rate [5]. So flow rate should be optimized as compromise between detector dead time and sensitivity.

Reducing Contamination

Contamination of the PID can be reduced by using window sweep gas [39], which needs additional tubing and an electronic pressure controller to feed a purge gas to the space adjacent to the lamp window. In this way, sample com-

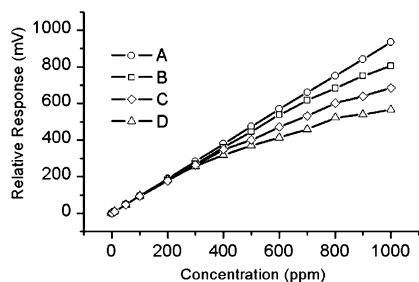


Fig. 5. Effect of ionization chamber volume on the response of the laboratory-made PID to toluene: *A* 18, *B* 50, *C* 100, *D* 150 μL . Other conditions were as for Fig. 2

pounds can be swept away. Irrespective of this, material released from the lamp gasket can still easily become deposited on the lamp window and reduce the sample concentration, resulting in an increased detection limit. Such a system is, in addition, not compatible with a portable instrument.

In the new generation PID sensors the sample was directed so it flowed across the lamp window, rather than toward and in contact with the lamp window, as in most current PID, which results in a fogged window. This greatly reduced accumulation of contaminants on the lamp window because, in theory, the sample should flow past the face of the lamp. Our experimental results were in good agreement with the literature. Compared with axial PID the new PID clearly reduced the loss of sensitivity from 25.8 to 15.9% (Figs. 6a, b).

We also propose a new method for elimination of contamination—automatic self-cleaning. After detection of one sample was complete and the temperature of the column had decreased to below 100°C we turned off the carrier gas and kept the lamp on for a while to clean the sensor and lamp surface. The effect of this automatic cleaning was very obvious when sample concentrations were in the low ppm range or below, as is shown in Fig. 6b. The reason might be that the ultraviolet (UV) light in the PID generated a very low level of ozone, which was relatively minor compared with the total concentration of the sample. When the carrier gas was flowing the amount of ozone was inconsequential and did not interfere with the measurement. When carrier gas flow into the detector was stopped, however, the amount of ozone remaining in the ionization chamber could increase to ppm levels. This reactive compound is very efficient at

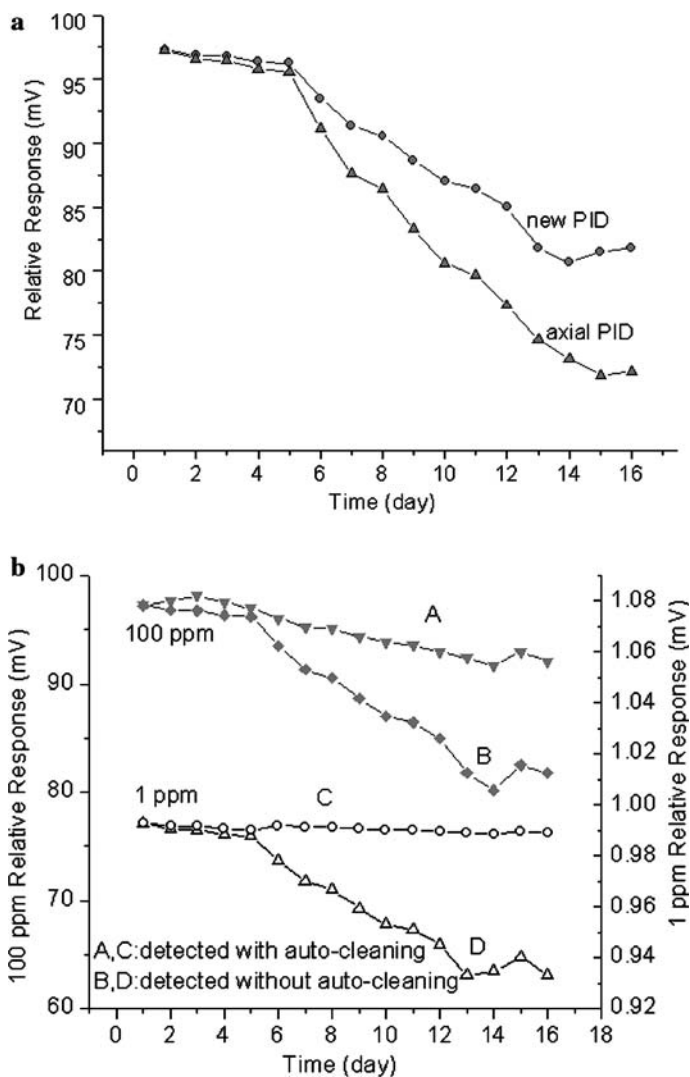


Fig. 6. Performance of the new method for eliminating contaminants: **a** Comparison of response (peak height) to 100 ppm BTEX mixture (benzene, toluene, ethyl benzene, and xylene) of the axial PID (SRI) and the laboratory-made PID. **b** Comparison of the response (peak height) to 100 and 1 ppm BTEX of the laboratory-made PID with and without auto-cleaning. The response of the axial PID in **a** was normalized to that of the 'new PID' by multiplying by 1.2 (the ratio of response of the two detectors on the first day). The SRI 8610C GC was used with purge-and-trap sample introduction and a 10 m \times 0.32 mm i.d. \times 0.25 μm film column. The adsorption material was Tenax-GR, the adsorption and desorption temperatures 40 and 200 $^{\circ}\text{C}$, the bake-out temperature 250 $^{\circ}\text{C}$, the PID temperature 150 $^{\circ}\text{C}$, and the oven temperature 100 $^{\circ}\text{C}$. The experiment was running 16 h a day 7 days a week. The relative response is the sum of the responses to the BTEX components

“scrubbing” compounds from the detector. With this cleaning treatment loss of sensitivity could be substantially reduced. The activity of the gas-phase ozone was low and the ozone decomposed catalytically, so the cleaning time was relatively long. We could perform the cleaning process for a short time after detection of every sample was complete, however. In this way we could clean the detector without stopping experimental work. Although the amount of ozone was small, it was very useful when detecting environmental volatile organic compounds, most

of which are in the low ppm range or below. As shown in Fig. 6b, the sensitivity to 1 ppm toluene was almost unchanged after continuous detection for 16 days if automatic self-cleaning was used.

Conclusions

The objective of this study was improvement of PID used for rapid portable GC. The features of the improved PID can be summarized as two points:

the sample is directed to flow across, rather than toward, the lamp lens; and a new simple automatic cleaning technique has been adopted.

Both of these improvements effectively reduce contamination and, therefore, greatly reduce signal drift and the background noise. As a result of these improvements the new redesigned PID was more compatible with in-situ rapid portable GC applications and simplified the previous time-consuming operating procedure. The new arrangement of the electrodes also reduced background (baseline) noise and also enabled effective reduction of the dead volume of the PID. The resolution, linear range, and response time of the detector were all improved.

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