

Characterization of Formaldehyde By Gas Chromatography Using Multiple Pulsed-Discharge Photoionization Detectors and a Flame Ionization Detector

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Abstract

Formaldehyde, water, methanol, butanal, and butanone are characterized by gas chromatography using three pulsed-discharge photoionization detectors (PDPIDs) and a flame ionization detector (FID). One of the PDPIDs is operated in helium mode, and the other two are operated in argon and krypton modes. The FID is included for comparison. The PDPIDs are used to efficiently differentiate between and quantitatively identify formaldehyde and the other three compounds in a sample mixture. This is accomplished by using butanone as the internal standard and correlating the relative responses of the four organic compounds in the helium-, argon-, and krypton-mode PDPIDs with their relative retention times.

Introduction

A new method of detecting and characterizing formaldehyde by gas chromatography (GC) has been developed using three pulsed-discharge photoionization detectors (PDPIDs) connected in parallel with a flame ionization detector (FID). Formaldehyde has typically been difficult to characterize by GC because of the lack of sensitivity shown for it by FIDs and thermal conductivity detectors. Photoionization detectors have been used previously to detect formaldehyde by primarily employing lamps of 11.7 eV, but they have the disadvantage of high maintenance because of their lithium fluoride window (1). In 1996, Luong et al. (1) developed a new GC technique using a capillary column. Formaldehyde, acetaldehyde, and other components were separated from a gas-phase matrix, then the aldehydes were converted into methane and ethane, respectively, using a nickel-coated catalyst in a hydrogen atmosphere. The methane and ethane were then detected using an FID.

PDPIDs have recently been used to detect formaldehyde in the atmosphere (2). Because it is the most abundant atmospheric gas-phase carbonyl compound and participates in a number of atmospheric gas-phase and photochemical reactions, there is a significant interest in this compound.

Formaldehyde is produced commercially as a 30% to 50% aqueous solution known as formalin. The practical use of formaldehyde is in the production of phenol-formaldehyde resins, aminoplastics, polyacetal plastics, drugs, cosmetics, food, rubber, and metals as well as in agriculture and other industries (3). Its detection in groundwater is generally very difficult because of its high polarity and low concentration (from nanograms to micrograms per liter) (4).

In this study, we describe the use of three PDPIDs and an FID in order to detect and characterize formaldehyde, methanol, butanal, butanone, and water. The first PDPID was operated in a helium mode (He-PDPID), which brought about the ionization of compounds with ionization potentials less than 17.5 eV. The second detector operated in an argon mode (Ar-PDPID), which ionized compounds with ionization potentials of less than 11.8 eV, and the third detector operated in a krypton mode (Kr-PDPID) ionizing compounds with ionization potentials of less than 10.7 eV. Thus, the He-PDPID and Ar-PDPID can be used to detect and characterize formaldehyde, which has an ionization potential of 10.874 eV.

Experimental

The separations were carried out with a Hewlett-Packard (Wilmington, DE) 5880A GC connected to a 5880 Series A GC terminal. Figure 1 shows a block diagram of the experimental system described in this study. Four GC detectors were used in this experiment. The three PDPIDs were each a Model #D-4 produced by Valco Instruments Co., Inc. (VICI) (Houston, TX).

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These detectors differed from other commercial PDPIDs made by VICI in that the discharge electrodes were at right angles to one another. In general, the most common PDPID design is one in which the discharge electrodes are aligned directly across from one another. The fourth detector (an FID) consisted of a standard 0.18-inch-i.d. jet that was provided with the instrument.

The first PDPID was operated in the He-PDPID. The second PDPID used helium doped with argon at a rate of 0.789 mL/min or 2.65%, and the third PDPID used helium doped with krypton at a rate of 0.600 mL/min or 2.03%. The helium entering the PDPIDs was 99.999% UHP-grade (TriGas, Houston, TX) that was further purified by passing it through two gas purifiers (VICI) connected in series and operated as described previously. The helium flowed through the discharge region of the PDPIDs at approximately 29 mL/min.

The three PDPIDs were mounted in a stainless steel block that was attached to the side of the GC using steel brackets. The block was heated using four 3-W heating bars that were controlled by using a Variac Powerstat (The Superior Electric Company, Bristol, CT). The temperature of the block was constantly monitored by an Omega (Stamford, CT) Digicator and was maintained between 250°C and 290°C. This prevented the condensation of the compounds being eluted from the column inside the detectors. The temperature of the FID was set and maintained at 200°C.

The basic design of the He-PDPID used a concentric arrangement of alternate insulators and electrodes in the ionization region. In this case, the insulators were made of sapphire, which

allowed the detectors to be operated at temperatures above those normally required for quartz (approximately 200°C). The internal diameter of the PDPIDs used in this study was 3 mm. The high voltage discharge electrode was constructed of Invar and was connected to a 12-V E-30 ignition coil (Borg-Warner, Franklin Park, IL), its ancillary power supply, and the pulse generator. The bias and collector electrodes were separated by sapphire insulators and sealed to these insulators by gold "O" rings. Selectro-type connectors were inserted through holes drilled into the heating block so that they could make contact with the electrodes.

The pulsed discharge was generated using electronic components designed and built by the electronics shop at the University of Houston. The discharge parameters were set at a 220- μ s pulse spacing and a 40- μ s pulse width for which the dc current was applied. The dc potential was variable with a maximum value of 20 V and was adjusted in order to make the discharge the most stable. A 280-V negative bias potential was applied to the coil in order to direct the photoinduced current towards the collector electrode.

The electric current in the cell was measured at the collector electrode with a custom-designed electrometer (VICI), which provided a fixed gain of 2×10^8 . The electrometer collection circuit consisted of a DT-2770 (Data Translation, Marlboro, MA) interfaced to a DT-2802-4 A/D Intel 486 motherboard. The A/D interface board was set to a digital resolution of 19 bits and a sampling frequency of 20 Hz. Data analysis was performed using EZ Chrom version 5.2 (Scientific Software, Pleasanton, CA).

For all of the analyses, the samples were injected via a liquid injection port that was maintained at 200°C. A cup splitter sleeve (4.0-mm i.d., 72- \times 6.3-mm o.d.) suitable for high- or low-molecular-weight samples was used inside the injector. The sample was split using a split injection valve at a ratio of 88:1 prior to passing it through a fused-silica column (Supelco, Bellefonte, PA) that was 60 m in length with a 0.25-mm i.d. and a poly(dimethylsiloxane) bonded phase of 1- μ m thickness. The carrier gas used was 99.999% UHP-grade helium (TriGas) that was further purified by passing it through a gas purifier (VICI) operated in the "bake-out" mode at 400°C. The helium flowed through the column at a rate of 1.12 mL/min.

Upon exiting the column, the sample entered a 1/16-inch stainless steel four-outlet manifold and was split four ways using 0.32-mm fused-silica transfer lines. The ends of three of these transfer lines were positioned close to the bias electrodes in the PDPIDs so that eluents from the column flowing counter to the helium flow from the discharge zones of the detectors were ionized by the high-energy photons from the helium discharge. The bias electrode repelled the resulting electrons towards the collector electrode. The fourth transfer line went into the FID. In this way, the four detectors were connected in parallel with each receiving approximately one-fourth of the

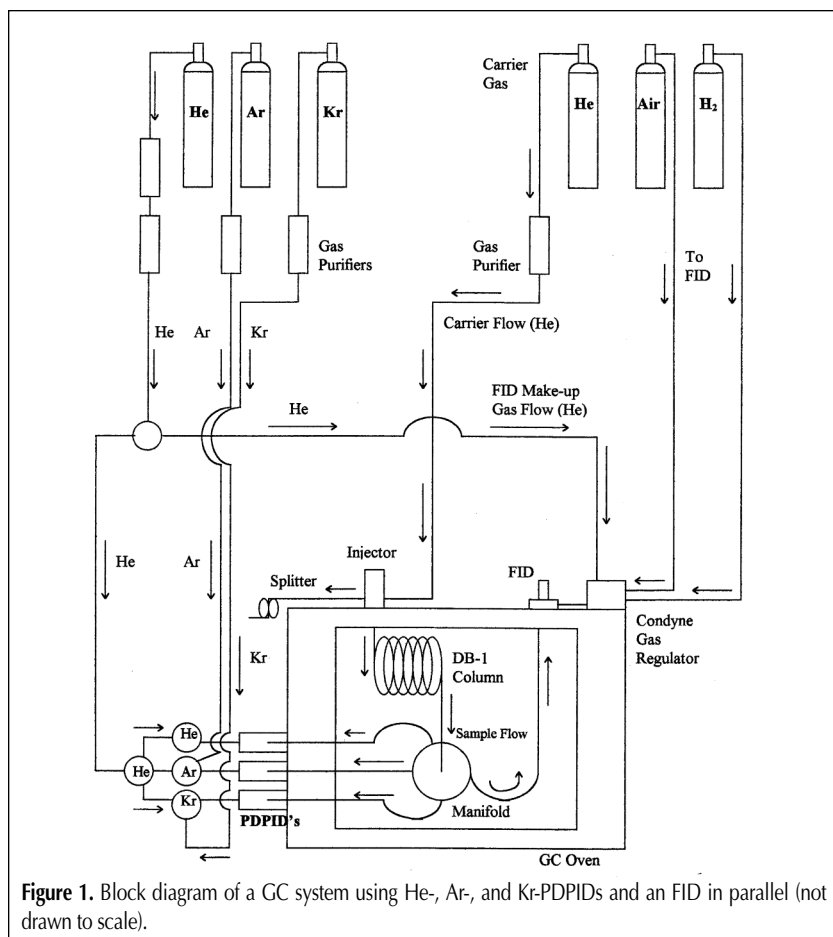


Figure 1. Block diagram of a GC system using He-, Ar-, and Kr-PDPIDs and an FID in parallel (not drawn to scale).

injected sample. The FID was operated at 200°C with a hydrogen flow rate of 37 mL/min. Helium was used as the make-up gas and flowed into the FID at a rate of approximately 33 mL/min, and air was added at a flow rate of approximately 280 mL/min.

The formaldehyde solution (GR-grade) (EM Science, Gibbstown, NJ) consisting of approximately 36.5–38% formaldehyde; 10–15% methanol; 47–53.5% water; and trace amounts of chloride, sulfate, and heavy metals was used as the source of formaldehyde. A sample mixture was made by adding 15 µL of the previously described formaldehyde solution to 2 mL of ethanol into which 15 µL of butanal and 20 µL of butanone had already been added. The butanone served as the internal standard for the analysis, and the butanal provided a basis for comparison. Ethanol acted as the solvent.

The GC oven was temperature-controlled at 35°C isothermal, which allowed for the complete separation of the sample components. Five injections of 0.01 µL each were made using a Precision Sampling Corporation Pressure Lok mini-injector (Baton Rouge, LA). This provided detectable quantities of the components of interest ranging from 1×10^{-10} to 6.6×10^{-11} g.

Results and Discussion

Figure 2 presents an example of the resulting chromatograms from this analysis. The chromatogram shown in 2A was obtained from the sample mixture using the He-PDPID. The chromatograms for the Ar-PDPID, Kr-PDPID, and FID are shown in 2B, 2C, and 2D, respectively. As is predictable from its ionization potential of 10.874 eV, formaldehyde produced chromatographic peaks in helium and argon, but showed no signal in krypton or with the FID. This is unique because all other aldehydes will show a signal with all four detectors. Methanol (which has an ionization potential of 10.85 eV) produced similar results, but gave a slight response to the FID. Air and water were detected only by the He-PDPID. The most obvious advantage of this was seen in the Ar-PDPID chromatogram (Figure 2B) in which a formaldehyde peak was present but the air and water peaks were not. Table I shows the ionization potentials for these compounds as well as ethanal and propanal.

In making a comparison between the four chromatograms shown in Figure 2, it should be noted that the scale of the responses in Figures 2A and 2B were the same (maximum 2.0 V), and those for Figures 2C and 2D were 0.4 and 0.04 V, respectively. Interestingly, the response of the Ar-PDPID was greater than that of the He-PDPID for formaldehyde, showing that the Ar-PDPID

is the best choice for the quantitative analysis of this compound. This is most likely because of a higher photon absorption coefficient at the argon emission wavelength. The added advantage in using an Ar-PDPID for quantitative analysis is the absence of air and water peaks. For formaldehyde, the Ar-PDPID is more sensitive as well as selective.

In past studies that have been conducted in this lab (5,6), most compounds produced a greater response in the He-PDPID. As an example, butanal was included in this experiment as a basis for comparison. With an ionization potential of 9.84 eV, it was expected that it could be detectable with the He-PDPID, Ar-PDPID, and Kr-PDPID as well as with the FID. This was indeed the case. Furthermore, it can be seen from Figures 2A and 2B that butanal gave a greater response with the He-PDPID than with the Ar-PDPID, which is typical of most other compounds. Because propanal and ethanal coelute with ethanol and methanol, they were not included in this study.

Butanone was chosen as the internal standard because it has an ionization potential of 9.51 eV and therefore can be detected by all four detectors. It also elutes cleanly and in a relatively short time period. In previous studies (5,6), we have used both cumene and benzene as internal standards. By relating the relative response of butanone to that of cumene or benzene, a comparison can be made to compounds previously characterized. The

Table I. Summary of Ionization Potentials for Sample Mixture Components and Other Compounds of Interest

Compound	Ionization potential (eV)*
Butanone	9.51 ± 0.04
Butanal	9.84 ± 0.02
Kr second resonance (10.1 eV)	
Propanal	9.953 ± 0.005
Ethanal	10.229 ± 0.0007
Kr first resonance (10.68 eV)	
Methanol	10.85 ± 0.01
Formaldehyde	10.874 ± 0.002
Ar resonance (11.6 and 11.8 eV)	
Oxygen (O ₂)	12.071 ± 0.001
Water	12.612 ± 0.010
Hydrogen (H ₂)	15.42589 ± 0.00005
Nitrogen (N ₂)	15.5808

* Obtained from reference 7.

Table II. Summary of Relative Retention Times and RePIX Values for Compounds in the Sample Mixture

Compound	RT _x /RT _{BUT}	sd	Ar-RePIX	sd	Kr-RePIX	sd	FID-RePIX	sd
Air	0.3470	0.0008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Formaldehyde	0.3712	0.0007	6.2472	0.2063	0.0000	0.0000	0.0000	0.0000
Water	0.3909	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Methanol	0.4273	0.0006	2.3402	0.1226	0.0170	0.0008	0.6729	0.0381
Butanal	0.9761	0.0010	1.4387	0.0972	0.7110	0.0395	1.0588	0.0272
Butanone	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000

choice of an internal standard is somewhat arbitrary with the only requirements being that it should not interfere with the components of interest.

In order to characterize each compound present in the sample mixture, the retention time and peak height were determined for each compound in each chromatogram. Because the fused-silica transfer lines carrying the sample to each of the four detectors were of the same length (30 cm), the retention times of the compounds did not vary significantly for the four different detectors (± 1.2 s).

The relative retention times (RT) and peak height ratios (H) for each compound in the sample mixture were calculated according to equations 1 and 2, respectively:

$$RT_X = \frac{RT_{\text{COMPOUND}}}{RT_{\text{BUTANONE}}} \quad \text{Eq. 1}$$

$$H_X = \frac{H_{\text{COMPOUND}}}{H_{\text{BUTANONE}}} \quad \text{Eq. 2}$$

The results of these calculations are the relative values of the detector responses, which eliminate variations in detector sensitivities and differences in the split ratios of the different detectors. The detector responses for butanone and the components of interest were measured in He, He-Ar, and He-Kr. The differences in the response or peak heights depended on the ionization poten-

tials of the individual compounds, as was discussed previously.

For each compound in the mixture, a relative photoionization index (RePIX) was calculated, which is the ratio of the H_X in equation 2 for a detector in relation to the He-PDPID. The RePIX value is characteristic of a compound and is independent of other factors such as the concentration of the column eluent, carrier-gas flow rates, detector temperature, and variability of the power applied to the PDPIDs. The derivation of the response factor equations has been presented elsewhere and therefore will not be done here (5,6).

The RePIXs for each detector were calculated using equations 3, 4, and 5:

$$\text{RePIX}_{\text{Ar}} = \frac{(H_{\text{COMPOUND,Ar}}/H_{\text{BUTANONE,Ar}})}{(H_{\text{COMPOUND,He}}/H_{\text{BUTANONE,He}})} \quad \text{Eq. 3}$$

$$\text{RePIX}_{\text{Kr}} = \frac{(H_{\text{COMPOUND,Kr}}/H_{\text{BUTANONE,Kr}})}{(H_{\text{COMPOUND,He}}/H_{\text{BUTANONE,He}})} \quad \text{Eq. 4}$$

$$\text{RePIX}_{\text{FID}} = \frac{(H_{\text{COMPOUND,FID}}/H_{\text{BUTANONE,FID}})}{(H_{\text{COMPOUND,He}}/H_{\text{BUTANONE,He}})} \quad \text{Eq. 5}$$

The mean value for the ratios obtained from these equations was determined and a standard deviation (sd) calculated according to equation 6:

$$\text{sd} = \left[\frac{\sum (\text{RePIX}_i - \text{RePIX}_{\text{MEAN}})^2}{(n - 1)} \right]^{1/2} \quad \text{Eq. 6}$$

In this equation, RePIX_i is the individual RePIX value for a compound of a given experiment, $\text{RePIX}_{\text{MEAN}}$ is the mean value of the RePIX values for that compound in all experiments, and n is the number of samples taken. For the purposes of this analysis, five sets of data were obtained and the mean values calculated from which the standard deviation was then determined for each compound.

Table II shows the results of the previously described calculations for this data set. The magnitude of the standard deviations for the retention indices was of the order of 10^{-4} and those for the RePIX values were 10^{-1} to 10^{-2} , thus showing good reproducibility. The values of the RePIXs were found to be reproducible and quite accurate over long periods of time (5,6).

As stated previously, the quantity (RePIX) eliminates the concentration dependence and accounts for the variation in the chromatographic properties (i.e., the split ratio and instrumental properties such as a change in the sensitivity of the detectors because of a variation in the applied power to the discharge) (5,6). In this experiment, butanone was used as the internal standard, and all of the relative responses were referenced to it. Butanone was selected as the internal standard because it has a relatively low ionization potential (9.51 eV) and is easily detected by all three of the detectors. Other compounds could be used as the internal standard provided that they elute cleanly and have low enough ionization potentials so that they can be detected with all three PDPIDs.

The retention times were determined relative to butanone in order to account for minor changes in the carrier-gas flow rate. However, this does not precisely account for changes in the

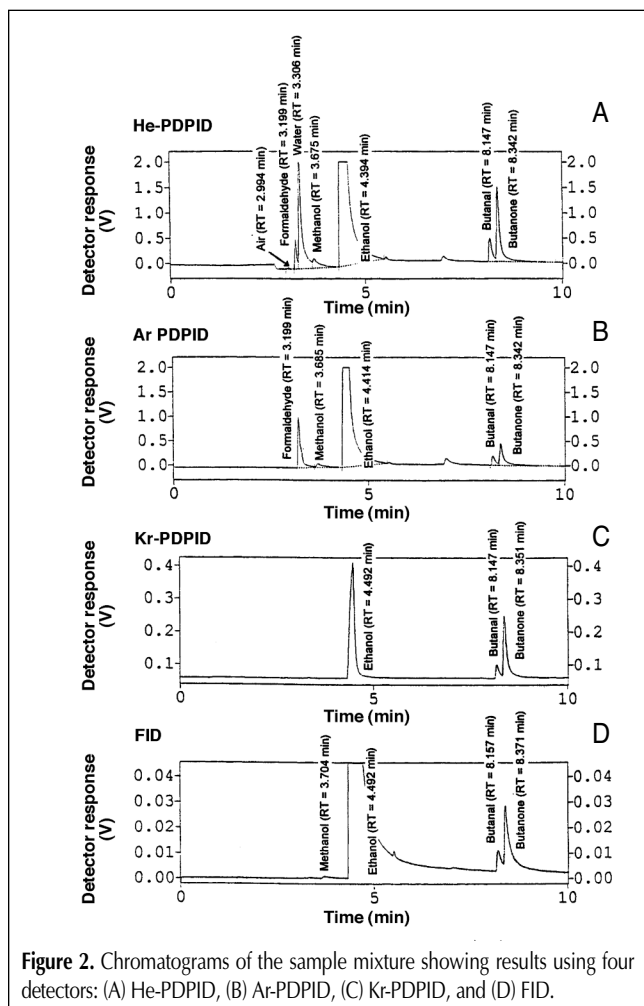


Figure 2. Chromatograms of the sample mixture showing results using four detectors: (A) He-PDPID, (B) Ar-PDPID, (C) Kr-PDPID, and (D) FID.

column temperature. In this case, the experiments were run isothermally at 35°C, which provided a good separation of the components as well as small deviations in the relative retention times.

The sample mixture was analyzed on a different chromatographic system that was equipped with an He-PDPID and an electron capture detector. Although the He-PDPID gave comparable results with those obtained using the He-PDPID on the system described, the electron capture detector showed no significant capture for formaldehyde. Thus, this data was not included in this study.

Conclusion

By using three PDPIDs and an FID in parallel, we have characterized formaldehyde, water, methanol, butanal, and butanone using unique RePIX values. Because the Kr-PDPID and FID showed no responses to formaldehyde, this compound was unique among the aldehydes. Because of the high sensitivity of the Ar-PDPID for formaldehyde and the lack of response by this detector for air and water, the Ar-PDPID is an excellent choice for quantitative analysis.

Applications of this technique include the detection of formaldehyde and acetaldehyde in food-grade CO₂⁸ and trace gas analyzers (VICI), which are used by the bulk gas industry to determine parts-per-billion to parts-per-million levels of H₂, O₂, Ar, N₂, CH₄, CO, CO₂, N₂O, Kr, and Xe as well as other gases in process streams.

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