

# Analysis of Low Levels of Oxygen, Carbon Monoxide, and Carbon Dioxide in Polyolefin Feed Streams Using a Pulsed Discharge Detector and Two PLOT Columns

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## Abstract

A gas chromatography (GC) method is developed for rapid analysis of polyolefin feed streams for the catalyst poisons CO, CO<sub>2</sub>, and O<sub>2</sub>. The method uses an HP MoleSieve column in parallel with a CP-PoraPLOT Q column and a pulsed discharge detector (PDD). Detection limits for each of the potential poisons are between 50 and 250 ppb. For a 10-ppm standard, the precision of the method was  $\pm 4.2\%$  for oxygen,  $\pm 7.8\%$  for carbon dioxide, and  $\pm 2.0\%$  for carbon monoxide. In addition to the polyolefin feed stream, nitrogen and hydrogen feed streams are also analyzed. In each case, sampling is observed to be a critical issue, with air contamination of the sample cylinder often the limiting step in determining the true level of oxygen. It is also noted that large amounts of argon are present in the standards when nitrogen is used as a balance gas. Because the trace oxygen peak partly coelutes with the larger argon peak, it is suggested that helium be used as the balance gas for all standards. This general experimental arrangement should be effective when applied to feed streams for other polymers as well.

## Introduction

At the heart of all polyolefin polymerizations is catalyst chemistry. The type of catalyst dictates polymer properties such as molecular weight, polydispersity, stereospecificity, and even microstructure. The efficiency of the polymerization is also largely governed by catalyst activity. For these reasons, it is critical to ensure that losses in catalyst activity are kept to a minimum. However, polymer catalysts are extremely sensitive to contaminants in the reaction system such as moisture, air, and trace levels of other contaminants such as mercaptans. It suffices to say that almost any compound with  $\pi$  or nonbonding electrons is a potential catalyst poison. Because less than 1 ppm of catalyst poison in a reaction system may be enough to cause a significant decrease in catalyst activity, there is a need for accu-

rately detecting various poisons at this low level.

In this paper, a method for detecting sub-ppm levels of the common catalyst poisons CO, CO<sub>2</sub>, and O<sub>2</sub> in polypropylene feed streams is presented. The method uses gas chromatography (GC) with pulsed discharge detection (PDD) and is capable of detecting each of these components in the sub-ppm range. This method is general in nature and should be readily applicable to many types of polyolefin work.

In modern "high yield" polypropylene polymerization systems, extremely high purity propylene is necessary for efficient polymerization. Compounds that bind to the active centers of the catalyst such as carbon monoxide, mercaptans, and arsine can only be tolerated in ppb levels (1). Other poisons such as carbon dioxide, oxygen, and water can be tolerated at the slightly higher levels of 2–5 ppm. Molecular sieves are effective at removing water and carbon dioxide from systems, and catalytic processes are available to remove other poisons. However, these precautions do not guarantee that all catalyst poisons will be removed from a system. Purification beds can fail because of being overloaded or not properly regenerated. There are many opportunities for feed stream integrity to be compromised. When catalyst poisoning occurs, the negative financial impact is tremendous. For these reasons, a fast and reliable method for determining the presence of catalyst poisons in the low- to sub-ppm range is critical.

Traditional GC detection methods are limited in their abilities to detect catalyst poisons in this range. The thermal conductivity detector (TCD), though universal, suffers from relatively poor sensitivity. The flame ionization detector (FID) is more sensitive, but responds primarily to compounds with a hydrocarbon backbone. The helium ionization detector (HID) is an extremely sensitive detector and responds to the permanent gases, but the detector has several disadvantages: (a) the response is highly dependent on the applied voltage, (b) the source can become easily contaminated, and (c) the radioactive source material must be licensed and closely monitored. The PDD offers the sensitivity and universal response of the traditional HID with none

of the drawbacks (2). For these reasons the PDD is the detector of choice for many applications in which traditional HIDs were previously used. There are several types of the PPD including pulsed discharge photoionization detector (PDPID), pulsed discharge electron capture detector (PDECD), and pulsed discharge emission detector (PDED). The abbreviation "PDD" often refers to the pulsed discharge detector operated in photoionization mode. Cai et al. have shown that the PDECD compares favorably with traditional radioactive electron capture detectors (ECD) for pesticide analysis (3,4). The PDECD has also been shown to be effective for environmental applications such as the analysis of polychlorinated biphenyl (PCBs) and chlorofluorocarbons (CFCs) (5,6). Wentworth et al. have shown that qualitative identification of organohalogen- and sulfur-containing compounds can be achieved by coupling a PDED with a PDPID using pure helium as the discharge gas (7). Sun et al. also have developed a chlorine-selective PDED that is promising for a broad range of environmental analysis applications (8–10). Judging from the versatility of the PDD, the application of the detector to petrochemical analysis should be something that is straightforward in principle. A PDD operated in photoionization mode was used in this study. PDD refers to pulsed discharge photoionization detector in this paper.

Even though the PDD can detect the permanent gases and carbon dioxide in low levels, chromatographic separation that allows for quantitation of CO, CO<sub>2</sub>, and O<sub>2</sub> is not a trivial matter. Molecular sieve or zeolite columns separate molecules based (predominantly) on size. These columns are popular because of their ability to separate the permanent gases. However, water, carbon dioxide, and other polar compounds adsorb on these columns (11–13). Samples containing water and other polar compounds can often be analyzed using porous-layer open tubular (PLOT) columns coated with porous synthetic polymers of styrene and divinylbenzene. In order to analyze for all of the compounds of interest here, an HP MoleSieve column and a PoraPLOT Q (PPQ) were used in parallel as shown in Figure 1. This experimental arrangement worked nicely for the permanent gases including H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, as well as CO<sub>2</sub>.

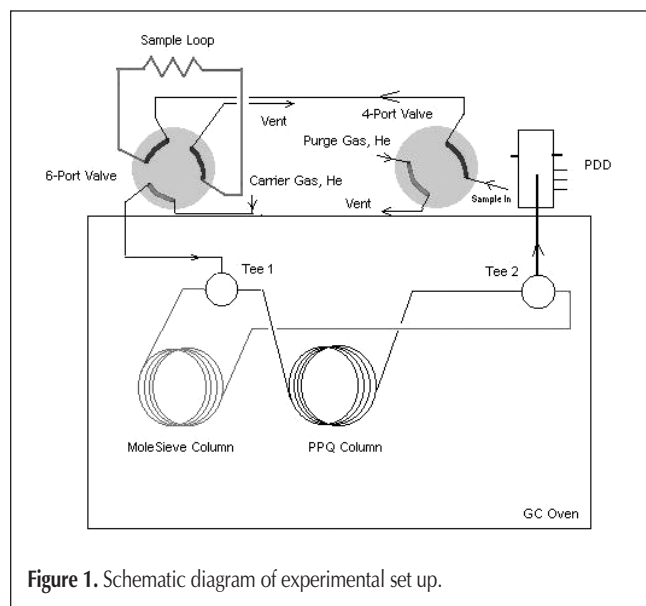


Figure 1. Schematic diagram of experimental set up.

## Experimental

The experimental configuration is shown in Figure 1. An HP 5890 A gas chromatograph (Agilent Technologies, Wilmington, DE) was used to carry out the separations. An HP MolSieve column (Agilent Technologies, 15-m × 0.53-mm i.d., 50- $\mu$ m coating) and Varian/Chrompack PPQ (30-m × 0.53-mm i.d., 20- $\mu$ m coating) (Varian, Middelburg, the Netherlands) were used in parallel as shown in Figure 1. The temperature was held at 30°C for 1.5 min, then ramped at 20°C/min for 1 min, and held at 50°C for 7.5 min. The carrier gas flow rate was 12 mL/min, and the sample loop was 100  $\mu$ L. The Model D-1 PDD (Valco Instruments, Houston, TX) was used. The PDD temperature was 140°C, and a high PDD discharge gas flow rate of 45 mL/min was used for the megabore capillary columns. Columns were baked overnight at high oven temperature to ensure that the PDD background was low. All standards were custom mixed by Scott Specialty gases (Plumsteadville, PA). Typically, a large amount of sample was used to purge the fittings of all residual air that entered the system when switching sample containers until the constant O<sub>2</sub> and N<sub>2</sub> concentrations were obtained. Polyolefin feed samples were collected in a piston cylinder under high enough pressure to maintain the samples in a liquid state. Simply bleeding a small amount of sample into the sample loop was an effective means of delivering the sample.

## Results and Discussion

As alluded to previously, it was necessary to use two columns in parallel to adequately resolve and quantitate the components of interest. In order to demonstrate the feasibility of this approach and to determine retention times and elution order of the analytes, standards were run on each of the columns separately. Figure 2 shows a chromatogram for a 1000-ppm mixture containing all of the analytes for the PPQ column. As expected, there was no resolution of the fixed gases, but the carbon dioxide peak clearly eluted at approximately 2.2 min. The same separa-

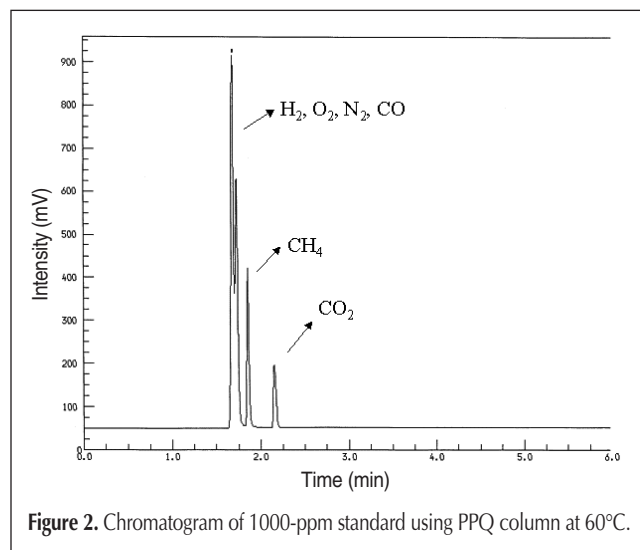
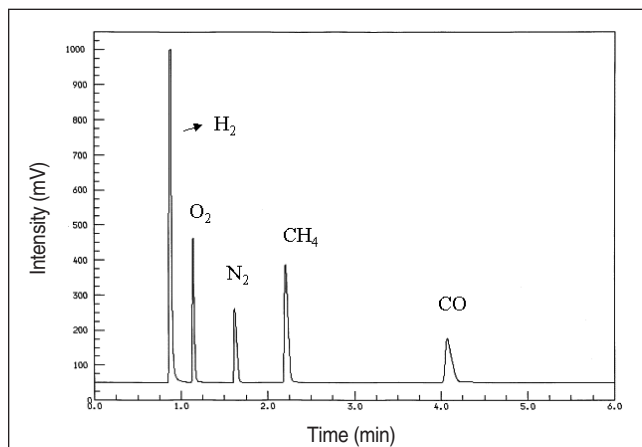
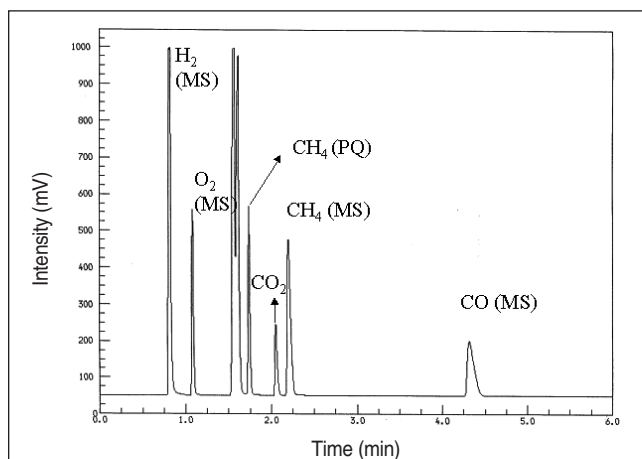


Figure 2. Chromatogram of 1000-ppm standard using PPQ column at 60°C.

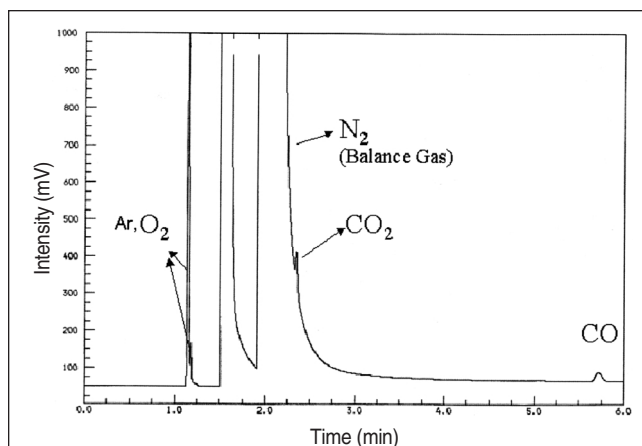
tion using the MoleSieve column is shown in Figure 3. Here, the fixed gases were readily resolved. Because polar compounds and carbon dioxide adsorb to molecular sieve columns, no peak was evident for carbon dioxide. By connecting the columns in parallel as shown in Figure 1, one should expect to see discreet peaks for all of the permanent gases because of the MoleSieve



**Figure 3.** Chromatogram of 1000-ppm standard using MoleSieve column at 60°C.

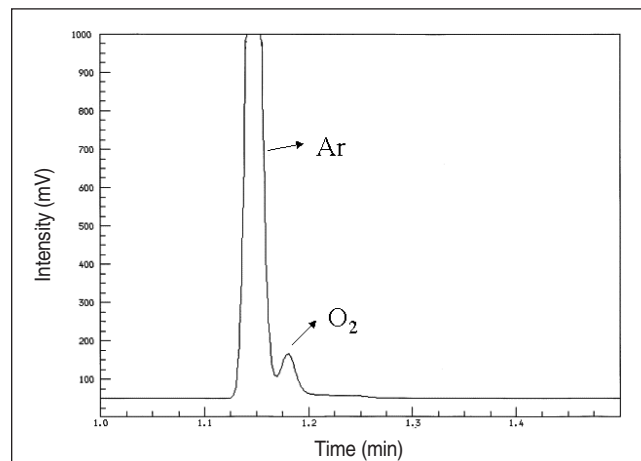


**Figure 4.** Chromatogram of 1000-ppm standards using the PPQ and MoleSieve columns in parallel.

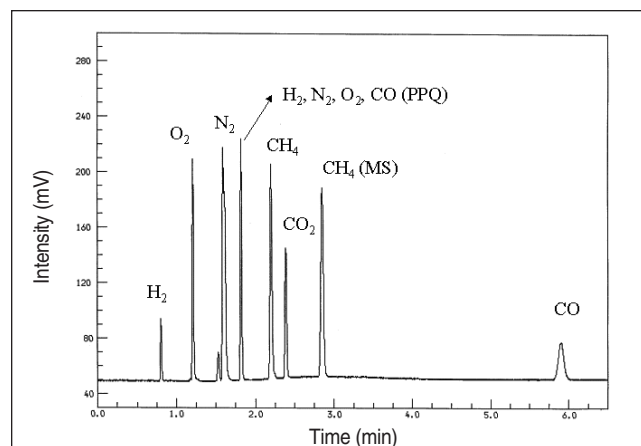


**Figure 5.** Chromatogram of 10-ppm standards with nitrogen as the balance gas.

column. There should be two peaks for methane, as this component elutes from both columns, and several coeluting peaks caused by poor resolution of the permanent gases on the PPQ column. This is what was seen, as demonstrated in Figure 4. A custom standard containing 10 ppm by mole CO, CO<sub>2</sub>, and O<sub>2</sub> with N<sub>2</sub> as the balance gas was then analyzed, resulting in an unsatisfactory chromatogram, as shown in Figure 5. As seen in this figure, the carbon dioxide coeluted with the major nitrogen peak. Also, the oxygen peak appeared to be much larger than one would expect for a 10-ppm standard. Closer inspection revealed that there were actually two peaks, as shown in Figure 6. From prior experience with the elution order on a MoleSieve column, it was reasoned that the larger of the two peaks was possibly argon. A call to the vendor of the mixed-gas blend confirmed this hypothesis. According to the vendor, high-purity nitrogen typically contains up to 500 ppm argon. For better results, a 10-ppm custom standard with helium as the balance gas was obtained. A chromatogram for this standard is shown in Figure 7. The expected results were seen with excellent resolution of the permanent gases, and carbon dioxide clearly resolved. Detection limits for each of the components at 3 times signal to noise was 50–250 ppb, depending on how noisy the baseline was. The relative standard deviation was typically 2–8%.



**Figure 6.** Chromatogram showing the large amount of argon typically found in samples that have nitrogen as the balance gas.



**Figure 7.** Chromatogram for 10-ppm standards with helium as the balance gas.

A typical chromatogram for propylene feed is shown in Figure 8. There was at least 30 ppm oxygen in each of the initial samples that were analyzed, as well as a large amount of moisture. Because this amount of oxygen and moisture would result in an almost immediate loss of catalyst activity, it was suspected that contamination occurred during the sampling process. The nitrogen peaks were also sufficiently large as to be

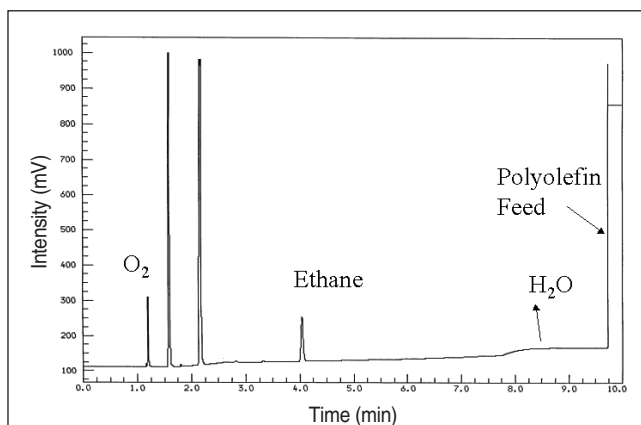


Figure 8. Typical chromatogram of polyolefin feed sample.

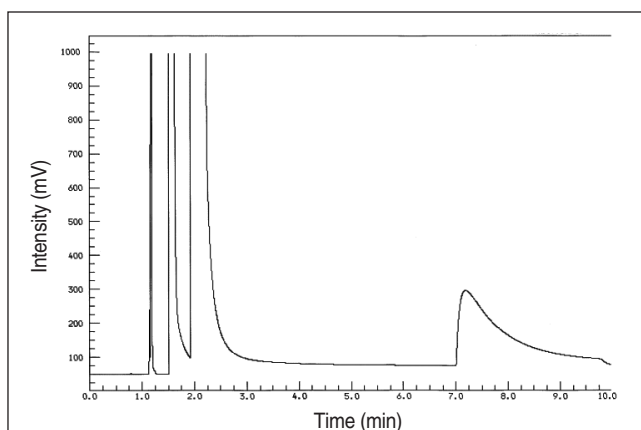


Figure 9. Chromatogram for nitrogen feed stream when proper sampling care was not taken.

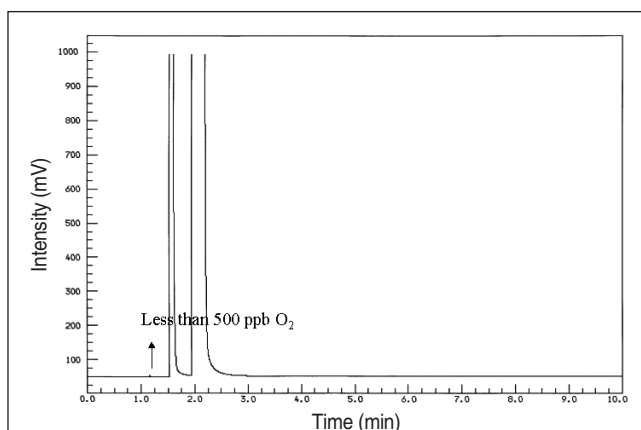


Figure 10. Chromatogram of nitrogen feed stream when care was taken during the sampling process.

attributed to air contamination. Spiking of a sample with ethane and comparison of retention times revealed that the peak at 4 min was ethane, an innocuous constituent of the sample. Although extreme care was taken during subsequent samplings of the propylene feed, there was always several ppm of oxygen present. It could not be unambiguously determined if this was caused by sampling issues or if there was in fact this level of oxygen in the sample. This method is capable of determining trace ppm  $O_2$  in process streams, but sampling is no doubt the limiting factor in determining low levels of oxygen in conventional cylinder samples.

Production nitrogen and hydrogen feed streams were also analyzed in the same manner as was the propylene feed. Figure 9 shows a chromatogram for the first set of nitrogen samples that were received. Because the nitrogen is supposed to be ultrahigh purity, the huge peaks for oxygen (1.1 min) and water (7 min) immediately indicated that the sample was possibly contaminated with outside air. A second round of samples for which much more care was taken during the sampling process revealed that there was less than 500 ppb of oxygen in the nitrogen stream, as shown in Figure 10. No other contaminants were detected. This ruled out the nitrogen stream as a source of contamination. Figure 11 shows a chromatogram for the hydrogen feed stream. Again, oxygen and water were shown to be present in the sample in large quantities. Poor sampling was probably the reason for this, as well.

## Conclusion

A GC method employing PPD for the analysis of polyolefin feed streams was presented. The detection limits for the catalyst poisons CO,  $CO_2$ , and  $O_2$  were between 50–250 ppb, with relative standard deviations of 2–8%. Standards using helium as a fill gas were clearly superior to standards using nitrogen when the PPD was used. Interpretation of oxygen present in the feed streams was ultimately limited by sampling techniques, with large amounts of air contamination probably contributing to most of the oxygen and water present in the samples.

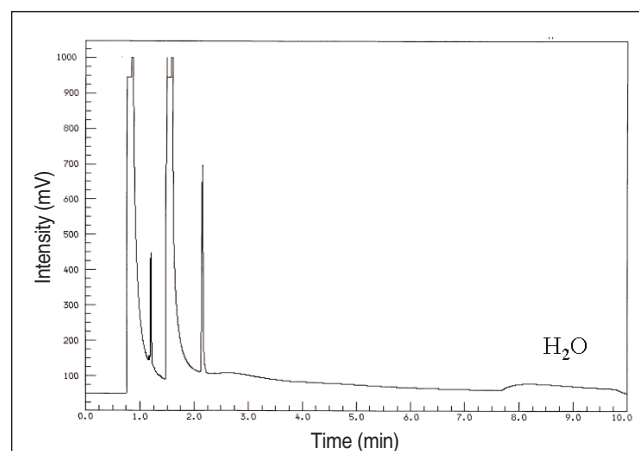


Figure 11. Chromatogram of hydrogen feed stream.

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