Oxygenates in Gasoline

A Versatile Experiment Using Gas Chromatography[1]

Linda C. Brazdil

Department of Chemistry, John Carroll University, University Heights, OH 44118-4581

The analysis of oxygenates in gasoline by extraction with water and subsequent analysis by gas chromatography provides a versatile experiment that can be used to teach topics ranging from the separation of physical mixtures to quantitative analysis. Extraction of oxygenates from gasoline prior to chromatography provides a simpler method for chromatographic detection of these compounds than previously reported, because only the oxygenates dissolve in the water (*1–3*). Since addition of oxygenates to gasoline is an issue of current environmental and political concern, students readily perceive the importance of this technique in analysis of real-world samples. It also allows for further discussion of scientific, political, and social issues surrounding the addition of oxygenates to gasoline.

Methods

Standard and Sample Preparation: Oxygenate Identification

For identification of the oxygenates in gasoline samples without quantification, prepare three standards, each containing one drop of methanol, ethanol, or methyl *tert*-butyl ether (MTBE) in 10 mL of distilled water. These quantities give readily observable peaks using the gas chromatograph settings described below, without overloading the megabore column. Adjustments may be necessary for specific gas chromatographs or if packed columns are used.

Samples of several brands of gasoline were obtained from local service stations, since different companies use different oxygenates and some do not add oxygenates. Any oxygenate is extracted by placing 1 mL of gasoline in 9 mL of distilled water, mixing well, and letting the sample stand until the gasoline is separated from the water. The water layer of this mixture is sampled by inserting a dropper pipet through the gasoline layer of the mixture while applying a slight positive pressure to the bulb to prevent any gasoline from entering the pipet. Once the tip is deep enough into the water layer, a sample of this layer is withdrawn.

Standard and Sample Preparation: Semiquantitative Analysis

A semiquantitative determination of the amount of oxygenate present in gasoline can be carried out simultaneously with oxygenate identification. Three standards, each containing methanol, ethanol, and MTBE, are prepared. Low, medium, and high concentrations of each oxygenate are calculated based on the highest con-

centration likely to be found in the aqueous phase of extracted gasoline samples. Standards are prepared following the scheme in Table 1. Appropriate amounts of each oxygenate are weighed into a previously weighed volume of water to avoid their evaporation after weighing. Between 25 and 75 µL (0.015–0.06 g) of each component added to 10 mL of water provides a good range of concentrations for the experimental conditions given here.

Gasoline samples are prepared by weighing a 9-mL sample of water, adding about 1 mL of gasoline, and determining the weight of gasoline added. Extraction and sampling are carried out as described in the section above.

Gas Chromatography

Separation is carried out using Perkin Elmer Autosystem III capillary gas chromatographs equipped with flame ionization and thermal conductivity detectors. A 25-m Carbowax 20M column with an inner diameter of 0.53 mm and a film thickness of 1.0 µm is used. Flow of the carrier gas, helium, is regulated at about 7 mL/min. The sample injector is kept at 250 °C, and the oven is programmed beginning at 40 °C for 1 min, ramping at 15 °C/min to 70 °C, and then at 30 °C/min to 100 °C. This program gives excellent separation of methanol (RT = 1.87 min), ethanol (RT = 2.13 min), and MTBE (RT = 0.98 min), as shown in Figure 1, and provides for removal of excess water from the column. This ensures reproducibility of retention times and peak areas. Detection of components is carried out using a flame ionization detector at 250 °C, with a range setting of 1 and a sensitivity setting of 0. Each sample is injected twice.

Data Analysis

Identification of oxygenates is accomplished by a straightforward comparison of the retention times of the standards with the peak(s) observed in the water used for oxygenate extraction from gasoline. If standards for semiquantitative analysis are prepared, observed changes in the areas of peaks at the same retention time, but in different standards, are used to determine the re-

Table 1. Scheme for Standard Preparation[a]

	Standard 1	Standard 2	Standard 3
Methanol	low	medium	high
Ethanol	medium	high	low
MTBE	high	low	medium

[a]Concentration levels listed.
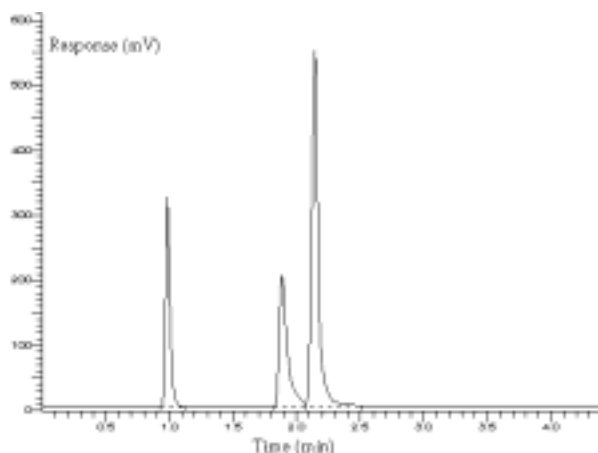
Figure 1. Chromatogram of methanol, ethanol, MTBE standard.

Figure 2. Oxygenate calibration curves.

tention time of each oxygenate. For example, the second peak to elute from the column has an area in standard 1 lower than in standard 2 or 3, and its highest peak area is found in standard 3; so it can be identified from Table 1 as methanol. The peak corresponding to ethanol has its lowest area in standard 3 and its highest in standard 2.

A calibration curve for peak area vs. oxygenate concentration is constructed for each oxygenate. A typical plot is shown in Figure 2. Weight percent (g oxygenate/100 g solution) is a convenient unit of concentration for this experiment. The appropriate calibration curve, as determined by retention time, is used to determine the concentration of this oxygenate in the aqueous extraction solution.

Once this concentration is known, the actual weight of oxygenate extracted can be calculated and used to determine the original concentration of the oxygenate in the gasoline. The aqueous layer consists of the original amount of water plus any extracted oxygenate. Therefore, the amount of oxygenate in the aqueous extraction solution can be expressed as:

$$\text{wt oxygenate} = (\text{wt oxygenate} + \text{wt } H_2O) \times \text{wt \% oxygenate}$$

All the terms of this equation are known except the weight of the oxygenate, which can readily be calculated. The original weight percent of oxygenate in the gasoline sample can be determined by dividing the weight of oxygenate extracted by the weight of gasoline from which the oxygenate was extracted and multiplying by 100.

For example, for a sample in which 8.8187 g water was used to extract the oxygenate from 0.7167 g gasoline, a peak area of 1492088 μV s at a retention time of 2.13 was obtained. From Figure 2, it can be seen that this corresponds to 0.44 wt % ethanol in the aqueous solution. Therefore, the weight of ethanol is 0.069 g. Dividing this value by the weight of gasoline used gives 9.7% ethanol in the gasoline.

Results

Laboratory Techniques

The careful laboratory work needed for construction of good calibration curves quickly dispels the misconception some students have that when an instrument is collecting data, the laboratory results automatically will be accurate and precise. Additionally, extraction
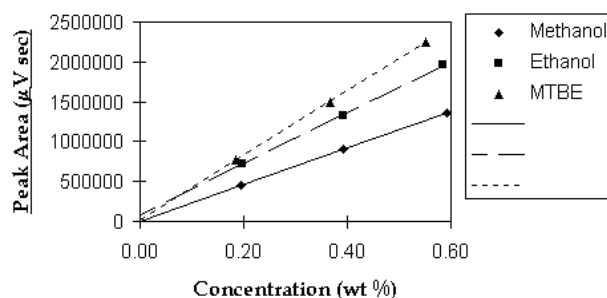
greatly simplifies the identification and quantification of oxygenates in gasoline. A chromatogram of gasoline readily displays the difficulty of this by chromatography alone (2).

Chromatography

The principles of separation due to differential adsorption by the stationary phase are discussed with the students. The improvement obtained in using capillary columns to replace packed columns and the trade-off made in amount of sample that can be injected are also discussed. Operation of flame ionization and thermal conductivity detectors is described at length. Emphasis is placed on the fact that samples leaving the column are detected as they reach the detector. They are either destroyed (FID) or pass through the detector into the atmosphere (TCD).

Quantitative Analysis

Because students in general chemistry are often unfamiliar with calibration curves, strong emphasis is placed on the proportionality of peak area and peak height to the concentration of components. Comparison of a sample of unknown concentration to those of known concentrations through a calibration curve in order to determine the concentration of the unknown is also emphasized.

Error Analysis

One of the major, and possibly most questionable, assumptions in this experiment is that all of the oxygenate in a gasoline sample is extracted by the water. Students are asked to discuss the effect on their calculated weight percent of oxygenate in gasoline if this assumption is not correct and to consider possible experiments, particularly chromatography experiments, by which this assumption could be tested.

A discussion of the precision of the peak areas is beneficial. While the values for the duplicate injections are not identical, they are usually within 2% of each other, reflecting the precision of the technique.

Conclusion

The identification and quantification of oxygenates in gasoline provides a challenging and interesting laboratory experience for general chemistry students while demonstrating the principles of chromatography and the

construction and use of calibration curves. Emphasis on sample preparation and extraction techniques enables students to appreciate multistep separations in the analysis of complex mixtures.

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Note

1. Presented at the Cleveland Section, American Chemical Society, Meeting-in-Miniature, March 15, 1995.

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