

GC/MS Analysis of Kerosene

PURPOSE

This experiment introduces the basic concepts of mass spectrometry and the hyphenated technique gas chromatography-mass spectrometry (GC/MS). You will use GC/MS as a tool for qualitative and quantitative analysis of a kerosene sample.

THEORY

A brief introduction to mass spectroscopy with an emphasis on alkanes is provided on the Chem 4243 website. The discussion here applies specifically to the main features of the GC/MS experiment using electron-impact mass spectrometric detection. See your instrumental analysis text for a general introduction to this topic.

In a GC/MS analysis, the GC generally utilizes a small-bore open-tubular column and a splitless injector. The column outlet is connected directly to the mass spectrometer so that the effluent is introduced into the ion source of the mass spectrometer, typically an electron-impact source. The sample is injected into the splitless injector as a dilute solution in a volatile solvent, and the GC column oven is operated in the programmed temperature mode. During the initial low temperature portion of the run, the injection solvent vaporizes and elutes from the column while the higher boiling sample components are retained at the head of the column. In order to avoid overheating the source components, the ion source is maintained in a standby mode and no data is collected while the relatively large amount of solvent elutes from the column (**Samples should always be diluted in a solvent. Injecting concentrated sample will cause the MS detector to shut down and may cause serious damage**). After essentially all of the solvent has eluted the column temperature is increased steadily, the ion source is activated and the MS detector signal is monitored. As the sample components elute from the column outlet, they are ionized in the source by electron impact and are accelerated through the mass filter (quadrupoles) to the ion detector.

When used as a chromatographic detector, the mass spectrometer is often referred to as a mass-selective detector (MSD). The MSD can be operated in several modes and several types of data can be generated. In the standard mode mass spectral scans are repeated continuously during data collection at a user-determined rate, typically about 10 Hz (ten scans/second). The simplest form of the output in this mode is a total ion chromatogram (TIC), which represents the total ion current as a function of time. A TIC looks like any other chromatogram produced by a simple one-dimensional GC detector (e.g., flame ionization or thermal conductivity), in which each component has a characteristic retention time and peak areas are related to the quantity injected on the column. However, the data for every MS scan during the run is stored in a file that includes the time each scan was done. It is a simple matter then to examine the mass spectrum of the component(s) eluting at a specific retention time. The mass spectrum can be used to either identify or confirm the presence of a substance in several ways.

- To determine the identity of an eluting component
 - If the parent peak is present, molecular weight is known

- The fragmentation pattern can be used to provide structural information. This approach can be especially powerful for advanced users.
- A computerized library search can be performed, based on the mass spectrum, to provide one or more candidate structures. Fragmentation patterns for electron-impact (EI) mass spectra obtained under carefully controlled conditions, usually at 70 eV, are highly reproducible. For this reason, the EI technique lends itself well to computerized library searching.
- The following information can be used to confirm the presence of a known component.
 - The presence of the parent ion peak.
 - The fragmentation pattern. In particular, the intensity ratios of specific daughter ion peaks can be used as supporting evidence. This is especially useful to confirm peak purity (i.e., no coeluting substances).

In addition to the standard mode, the MSD can be used for selected-ion monitoring (SIM). In this approach, which is used primarily to determine specific components in a sample, full spectral scans are not performed, but the MSD is set to monitor only specific ions, such as the parent ion and one or more daughter ions. The intensities of these peaks are used for quantitation, and the intensity ratios for confirmation of peak purity. Because more time is spent collecting data on the peaks of interest, this approach can provide significant improvements in signal-to-noise ratio and lower detection limits.

In this experiment you will operate the MSD in the standard mode to obtain retention time and mass spectral information on a series of n-alkanes. You will then use both the retention time data and mass spectral data to identify the presence and amounts of the major n-alkanes present in a kerosene sample. In addition to the parent ion peaks, you should select specific daughter ion peaks for each n-alkane and provide confirming evidence for their presence based on the intensity ratios. Additional information on the interpretation of mass spectra of n-alkanes is provided in the introduction to mass spectrometry on the Chem4243 website.

APPARATUS

- HP 5890 Series II GC with 30-m x 0.25-mm x 0.25 μm film thickness HP-5MS column (crosslinked 5% phenyl polydimethylsiloxane)
- HP 5971A quadrupole mass-selective detector (MSD)
- HP Chemstation software (G1034C VersionC.03.00)

GC/MS Conditions

Inlet:	splitless
Initial Temp:	60 °C
Initial Temp Hold:	3 min
Temp Ramp 1:	8 °C/min
Final Temp 1:	180 °C
Temp Ramp 2:	30 °C/min
Final Temp 2:	320 °C
Final Temp 2 Hold:	2 min
Low mass cutoff:	29

High mass cutoff: 300

Method saved as: 4243

Set the ChemStation integration parameters to include peaks that have an area percent (that is, peak area as a percent of total area for all peaks detected) of 0.5 % or greater.

CHEMICALS

- C11-C14 n-alkane standard, 1 mg/mL in iso-octane. This standard is prepared from a neat mixture containing roughly equal masses of the four normal alkanes C₁₁H₂₄, C₁₂H₂₆, C₁₃H₂₈, C₁₄H₂₈. Refer to the analysis sheet supplied with the neat standard for the exact composition.
- Kerosene, 1 mg/mL in iso-octane

PROCEDURES

Your objective in this experiment is to identify each n-alkane present at 1 % or greater (mass basis). Provide documentation such as MS and t_r data. Report the distribution of *n*-alkanes as mass percent relative to the total mass of sample in the original kerosene sample.

A. Standards

Chromatograms and Reports

Inject 1 μ L of the C11-C14 n-alkane standard. When the run is complete, generate the following reports for data analysis.

- Total ion chromatogram with a table of retention times and peak areas.
- Mass spectra for each of the four solutes.

Data Treatment

For a typical programmed temperature run of an homologous series, there is a nearly linear relationship between retention time and molar mass. Generate a plot and equation that you can use to predict the retention times of neighboring *n*-alkanes that might be present in the kerosene sample.

From the mass spectrum of each component, identify the parent ion peak and two or more daughter ion peaks to be used in the calculation of intensity ratios. Two good daughter ion candidates are the propyl and butyl fragments (C₃H₇, C₄H₉), which are fairly intense peaks and can provide highly reproducible intensity ratios.

B. Kerosene sample

Chromatograms and Reports

Inject 1 μ L of the kerosene sample. When the run is complete, generate the following reports for data analysis.

- Total ion chromatogram with a table of retention times and peak areas. Adjust the software settings to report all peaks that have an area of 0.5 % or greater relative to the major component.
- Mass spectra and retention time data for all *n*-alkanes that are present at 1% or greater relative to the major component.

Data Treatment

Use the retention time data for the standards you obtained in part A to provide initial identification the corresponding components in the kerosene sample. Examine the mass spectrum for each peak and provide confirming evidence on the presence of the parent ion peak and daughter ion peaks, as well as the corresponding intensity ratios. The data for each component, for both the standard and kerosene sample, should be placed in a table in a format to facilitate comparison. Among other information for each *n*-alkane include the formula, the calculated molecular mass, and the observed mass of the parent ion.

In order to identify the presence of other *n*-alkanes in the kerosene, apply the regression data on retention time you obtained in part A to predict the retention times. For any candidate peaks, examine the mass spectra for the presence of the appropriate parent ion and daughter ion peaks, as the corresponding intensity ratios. Although you will not have standards data for these components, the information obtained for the C11-C14 standards can be used to make rational arguments. In addition, perform a qualitative examination of the mass spectrum for each *n*-alkane candidate and indicated in the table whether the fragmentation pattern is consistent with what you expect for a normal alkane, and also note if there are any irregularities.

After confirming the presence of the various *n*-alkanes, estimate the mass percent of each using the following approach. This approach ignores quantitative data on minor components (less than 0.5 % of the principal component), which limits the accuracy, but can yield good estimates.

Based on your data from part A, use the relative peak areas of the four standard solutes to calculate the corresponding response factors to convert relative peak areas to relative masses. The normalized response factor (relative detector response) for component *x* can be computed using the following relation.

$$R_x = \frac{\left(\frac{A_x}{m_x} \right)}{\left(\frac{A_x}{m_x} \right)_{\max}}$$

where the term in the denominator represents the largest value of area (A_x) per mass injected (m_x). Since these are relative numbers, it is not necessary to know the exact mass of each standard injected, but you must compute the exact relative masses. For this purpose, you can assume that the volume of sample injected is exactly 1.00 μL , and apply the data for composition of the standard mixture to compute the relative masses.

Plot the response factor vs retention time to include all detected components and perform a 2nd order polynomial fit to the data. Use this fit to estimate the response factors of all

the detected components (not just the n-alkanes!). Use these estimated response factors to calculate the reduced areas A_{Rx} for each component.

$$A_{Rx} = \frac{A_x}{R_x}$$

The mass percent of each component is then

$$mass\% x = \frac{A_{Rx}}{\sum A_{Rx}}$$

Include in your calculations all components present at 0.5 mass% or greater. List the n-alkanes separately in a table with their retention times and mass spectral data (parent peak, daughter-ion peaks and intensity ratios) from the mass spectrum, and the amount of each present expressed as mass percent relative to the total mass of the sample. Include all n-alkanes present at levels of at least 1 %. In your discussion, explain your choice of data for the table and make a case for your conclusions.