

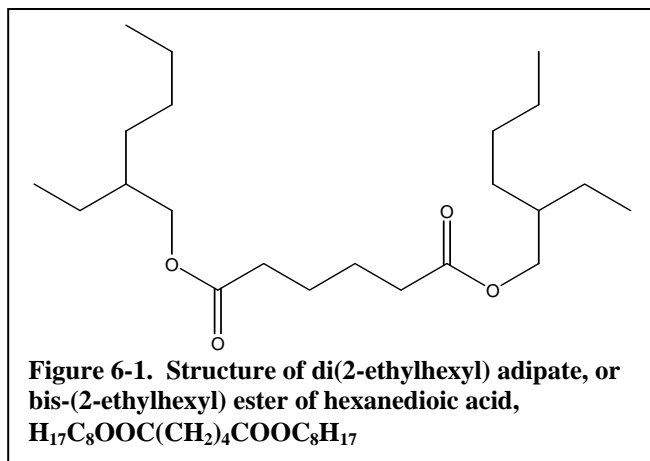
Laboratory 6

GC-MS Determination of Plasticizer in Commercial Plastic Wrap

In a recent experiment, you extracted a plasticizer from a commercial plastic wrap into a methylene chloride solution. This week you will use what is probably the most important “hyphenated technique,” gas chromatography-mass spectrometry (GC-MS), to separate and identify the plasticizer.

Introduction to Mass Spectrometry. Mass spectrometry determines the molecular weight of a compound by first ionizing the compound in the gas phase, accelerating the ions with a high voltage, and then using the physics of ion motion in electric or magnetic fields to determine the mass-to-charge ratio of the ion. Coupling a mass spectrometer to a gas chromatograph (GC) allows the analyte to be in the gas phase, and it separates the compound from large quantities of solvent that would otherwise overwhelm the detector and prevent detection of the signal of the compound of interest. We will use the GC to separate out the methylene chloride.

If the parent ion (usually designated **M**) of the compound undergoes fragmentation, as is almost always the case, there will be ions of lower mass present in the mass spectrum. The fragmentation pattern is often a good way to identify the compound because the pattern (i.e. the intensity of the peaks and their mass) depends on molecular structure. For the plasticizer to be studied here, there are two ester groups, and electron impact ionization (the method of ionization used most often, and the method to be used here) typically causes fragmentation of the single C-O bond of the ester group. The masses of the fragments would distinguish this compound from isomers.



In this lab, you will use the GC-MS instrument to separate the plasticizer from the methylene chloride, determine the mass spectra of methylene chloride and the plasticizer, and use information from a mass spectral library to confirm the identity of the plasticizer.

PRE-LAB ASSIGNMENT

1. Calculate the molecular weight of the plasticizer's parent peak **M** and the mass of the fragment $O=C(CH_2)_4C=O$. Predict the masses of the fragments obtained when one side group is lost ($-OC_8H_{17}$), and when two side groups are lost.
2. The National Institute of Standards and Technology, NIST, maintains accurate standard information such as mass spectra of standard compounds. Go to the NIST web site at <http://webbook.nist.gov/chemistry/> and look up the mass spectrum for this compound. Determine if the four masses predicted above are actually present in the mass spectrum of this compound, and examine the relative intensities of the observed peaks.

EXPERIMENTAL

Your TA will instruct you on how to operate the GC-MS instrument. As has been the case throughout this course, we are not focusing on what buttons to push and how to operate specific instruments, but rather on understanding how to analyze and interpret the data that the instruments produce.

Here are the parameters that are to be used for the elution of the plasticizer from methylene chloride: Oven temperature 100 °C; Initial column temperature 100 °C; Injection delay: 2 minutes; Column temperature ramp rate 15 °C/minute; Final time 3 minutes; Injection port A temperature 275 °C; Injection port B temperature 90 °C; Total run time 18 minutes; Final column temperature 300 °C. *You should not have to set these parameters, but they are listed here in case anything goes wrong. These parameters are programmed into a stored method.* The GC window displays the chromatogram as sensed by the total ion current, so both the methylene chloride and plasticizer are visible. Below is a sample gas chromatogram for this solution.

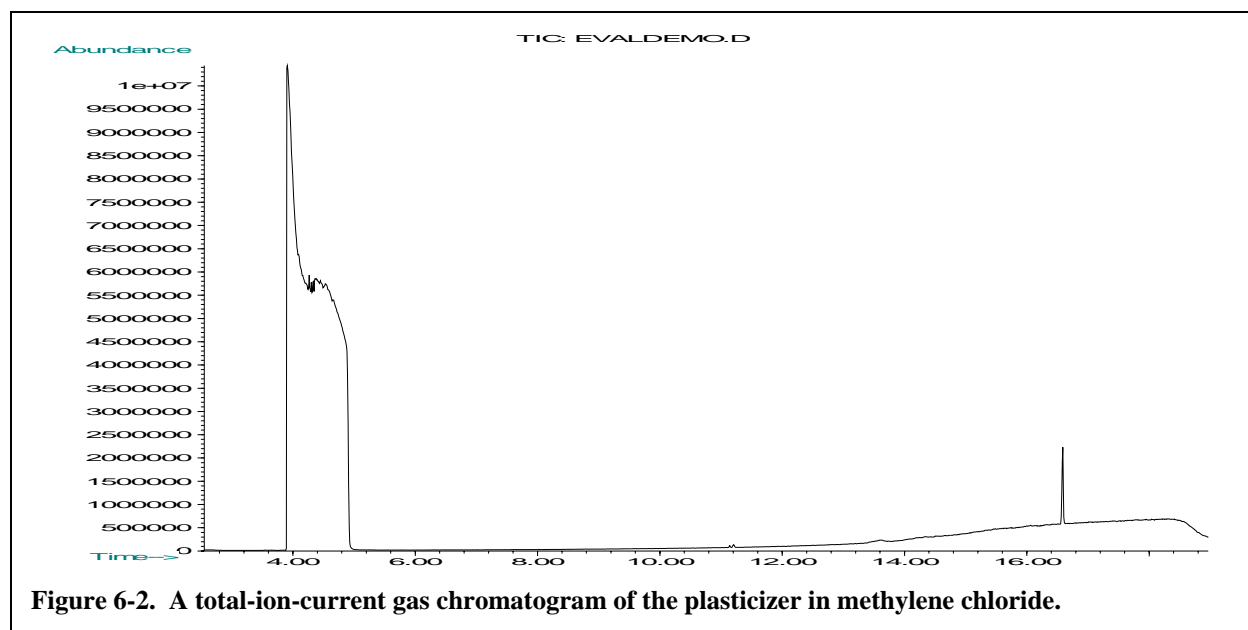


Figure 6-2. A total-ion-current gas chromatogram of the plasticizer in methylene chloride.

The large broad peak from ~4 to 5 minutes is due to methylene chloride. The reason it is so broad is that the capillary column is overloaded by the large amount of methylene chloride. The peak at 16.58 min is from the plasticizer. The software will allow you to choose each peak in the total-ion chromatogram with the mouse to display its mass spectrum. You can adjust the sensitivity of the vertical axis to find small peaks. Select a desired peak by using the left mouse button to draw a box around it to enlarge it. If you then put the cursor in the middle of the peak and double-right-click, the mass spectrum of the selected peak will be displayed. Make a printout of the mass spectrum for each observed peak in the GC. Using the software, determine the abundances (i.e. peak intensities) of the peaks at each of the four molecular weights you had predicted for the plasticizer in your pre-lab assignment.

Using the Mass Spectral Library. Your TA will help you do the database search, but here are helpful instructions. Once you have obtained your experimental chromatogram, you can load this file into the data analysis software. To do this, begin by left clicking on the FILE tab at the top of the window, and selecting your file. This will open your experimental data in the software. To enable a computer search for peak identification, left click on the SPECTRUM tab located at the top of the window and select the heading SELECT LIBRARY. Type over the current entry with the following library, **NBS75K.L** and hit ok. (To view the other possible libraries, it is useful to use the EDIT LIBRARY heading located in the SPECTRUM tab, and then repeat the last step.) Go back now to your experimental chromatogram. Hold down the left mouse button and drag/draw a box around the peak whose mass spectrum you wish to view from your experimental chromatogram. Once you are zoomed in on this peak, double right click on the maximum of the peak, this will display the mass spectrum for your sample. Once the mass spectrum has opened, you can double-right-click on the mass spectrum and the computer will search the selected library (**NBS75K.L**) to look for a match. The results will give many possible compounds. Therefore, you will have to select which mass spectrum corresponds to the compound you are analyzing. Both the experimental and library spectra will appear on the screen to make a direct comparison simple. You can then print out the two spectra as a comparison of your data to that found in the library. Print out the comparisons between experimental and library mass spectra for both methylene chloride and the plasticizer.

WRITTEN REPORT

Show the chromatogram and the mass spectra for the two components in your sample, and show the library spectrum for the two components.

1. Speculate about the reason for any differences in relative abundances (i.e. peak intensities) of methylene chloride and plasticizer in your chromatogram compared to the chromatogram shown in Figure 6-2.
2. In the mass spectrum of methylene chloride, what are the formulae for the two peaks with masses 84 and 86?
3. In the mass spectrum for the plasticizer, go back the NIST web site and record the abundances of each of the four ions of the plasticizer and compare them with what you determined experimentally for your sample. Decide if the library spectrum is different from the experimental spectrum and the NIST spectrum. Speculate about the reasons for any significant differences in mass spectra of the plasticizer for the NIST spectrum, the on-line library spectrum and the experimental spectrum.

This lab was created by graduate student Ms. Stuti Christie and Professor Mary J. Wirth in Spring, 2003. It was revised by Professor Thomas P. Beebe, Jr., October, 2003. We welcome your comments on how to improve the learning experience of this lab. The best time to communicate these comments is when you are working on the lab.