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Introduction of Gas Chromatography in the Sophomore-Level Organic Chemistry Lab by Solving an Arson Crime

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Abstract A laboratory experiment for the introduction of the use of Gas Chromatography (GC) is described. The lab introduces GC in the form of a "forensic style" investigation in which groups of students apply GC towards solving a fictitious arson crime. Students become familiar with how to use a GC, how to identify compounds in a mixture using retention times versus known compounds, and how to roughly calculate percentages of individual compounds in a mixture. This lab is suitable for a first-semester sophomore-level organic chemistry course.

Keywords Gas Chromatography, Forensic Chemistry, Arson, Compound Mixtures

1. Introduction

Gas chromatography (GC) is one of the most frequently used methods in the field of organic chemistry for the analysis of compound mixtures. It is important, therefore, that students in an organic chemistry course understand: i) the operating principles of a GC, ii) the meaning and importance of retention times and their application towards compound identification, iii) information provided by area integration , and iv) how to properly operate the instrument independently so they can apply the method in subsequent labs where suitable. In our experience we have found that student interest is piqued when lab experiments demonstrate how chemistry can be applied to "real-life" situations[1,2]. Given the recent interest in forensic chemistry as a result of several popular television shows, we decided to introduce GC in the form of a "forensic style" arson investigation laboratory. Several experiments have already been published in which GC or GCMS were applied to determining the identity of various accelerants that are often used in crimes of arson[3-7]. However, these labs generally focused on the extraction of accelerants from crime scene evidence (usually charred wood) and/or relied upon compound libraries for compound identification. Typically, the accelerants isolated were complex mixtures of compounds that were not actually analyzed, but instead the complicated chromatogram was simply compared to the complicated chromatogram of the "pure" accelerant. While such comparisons may well be closer to "real-life" situations (in that common accelerants used by arsonists are gasoline, kerosene, etc. which actually are complex mixtures) these labs did little to support the desired learning objectives (listed above) that we were interested in promoting. Furthermore, the previously published labs required extensive sample preparation by the instructor prior to the lab period that we wanted to avoid.

Therefore, we created a new GC lab that includes forensic analysis of an arson crime in which students: i) are provided with an actual crime investigation scenario that they must solve, ii) create their own library of "knowns" from which they can determine unknowns, and iii) apply area integrations to provide a rough percentage of compounds present in a mixture. Additionally, no extensive sample preparation is required for the experiment.

2. Results and Discussion

This introductory GC lab begins by requiring students to read background information on how a typical GC works and how compounds are separated on a GC column. This background information is provided below (see Section 3, Background Information on GC). Students were also required to read a fictitious "Police Crime Report" that describes the particulars of the arson crime, informs them where the investigation stands, and provides directions as to how they are to proceed. The "Police Crime Report" is provided in its entirety below (see Section 4, Police Crime Report). In short, however, the Report describes that there are 4 potential compounds implicated as accelerants in an arson crime: toluene, acetone, ethyl acetate, and octane. Three of the four compounds have been used in the accelerant mixture. Furthermore, a sample of the mixture

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was isolated from the crime scene and awaits analysis. The task of each group of lab students is to determine the retention times for each of the known compounds and then determine which of the knowns are present in the accelerant mixture. This will determine which of the story's characters are responsible for the crime. Also, they are expected to calculate an approximate composition of the mixture using the integrated signal areas.

2.1. Student Preparation for the Laboratory Experiment

Before beginning any of our Organic Chemistry lab experiments, students are required to submit a "prelab" report for grading. The prelab requires that they read the laboratory (and associated information) and answer specific questions regarding the techniques and/or procedure relevant to that experiment. For this lab, as discussed above, students prepare for the lab by reading the background information on GC and the Police Crime Report. Thus, students were made familiar with how the column we used in this particular lab (column B, 20% DC-710 on Chromosorb P 80/100 mesh) separates compounds based primarily on boiling points (i.e., higher boiling compounds have higher retention times). The other column (column A) available on the GCs (Gow Mac) is a 20% Carbowax 20M on Chromosorb P 80/100 mesh that separates compounds primarily on differences in polarity. The students are asked to complete the following questions as part of their prelab assignment:

1. Two mixtures are provided below. For each mixture, would you expect better separation on column A or column B?

Mixture 1: hexane and 1-hexanol

Mixture 2: cyclopentane and octane

2. Look up the boiling point values for acetone, ethyl acetate, toluene and octane. Cite your source(s).

3. We will be injecting onto column B of the GC for the experiment this week. Predict the relative retention times for the four known compounds. Explain your answer.

4. Do some research online and answer the following question: What is the most often used accelerant in arson crimes? Cite your source.

2.2. Progression of the Laboratory Experiment

Prior to lab, a set of samples is prepared for each group of students (typically four to five students per group). The set includes four vials containing ~1 mL of each of the known suspected accelerants (acetone, toluene, octane and ethyl acetate) and a vial containing the sample isolated from the carpet of the crime scene. The carpet sample is a random mixture of three of the known accelerants. A key is made to keep track of the contents of each of the unique carpet samples. An approximate ratio of each of the knowns within the carpet sample is also recorded (e.g., a 1:2:1 mixture of acetone, ethyl acetate and octane). Four such sets of samples are made (for the four groups in the lab). These sets can be reused for other sections of the course (we typically have 7 sections of Organic Chemistry I in the same semester).

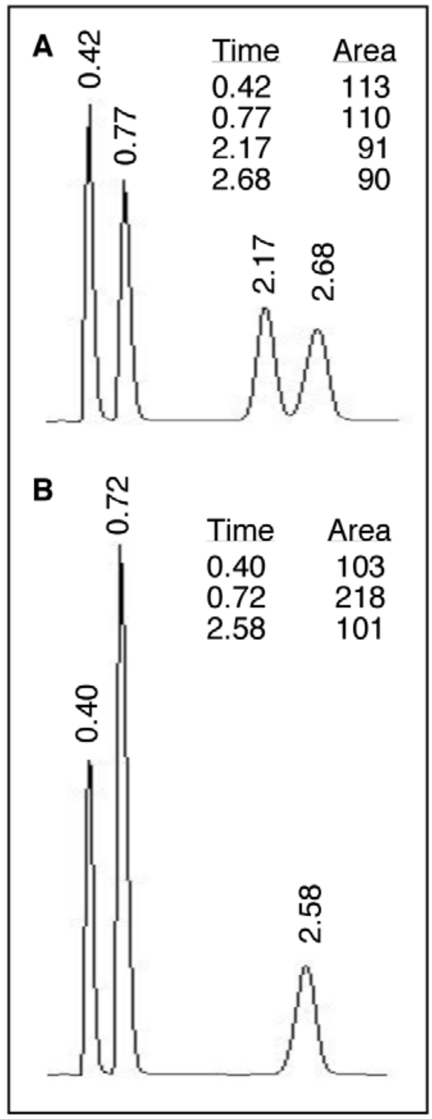

Figure 1. GC traces of mixtures of the known suspected accelerants. (**A**) A 1:1:1:1 mixture of acetone (rt = 0.42), ethyl acetate (rt = 0.77), toluene (rt = 2.17) and octane (rt = 2.68). (**B**) A 1:2:1 mixture of acetone, ethyl acetate, and octane

Students collected their chromatograms on Gow-Mac 350 or 400 GCs interfaced to PCs running PeakSimple™ software. Each GC provides slightly different results (i.e., retention times) therefore it is imperative that all of the data for a group be collected on a single GC for analysis. A group begins by running each of the individual known compounds (typically 5 μL injections) and determining the retention time for the pure compounds. The importance of cleaning the syringe between each run is stressed in order to avoid contamination of successive runs. A GC trace for a 1:1:1:1 mixture of the four known suspected accelerants is provided in Figure 1A. The group then compiles this data by preparing a table containing retention times for each of the known compounds. In effect, the students have created their own "library" from which to identify these known compounds in a mixture. Each student is responsible for running the GC on two of the "known" suspected accelerants on their own. By conducting two chromatograms in succession, they become comfortable with the technique of GC injection and the use of the software for data analysis.

Finally, each student then runs the "accelerant mixture". A typical "mixture" GC trace is provided in Figure 1B. By comparison of the retention times of the signals in the mixture with those of the known compounds, the identity of the compounds in the mixture was readily assessed. Generally the retention times for the known compounds and the mixture signals agreed within a few tenths of a minute (see Figure 1). Once the compounds in the mixture were identified, the persons responsible for the arson crime were also readily determined.

2.3. Student Analysis of Data

After completion of the lab, each student is responsible for preparing a "postlab" report to be submitted for grading. In particular, students are asked the following questions:

1. Create a table listing all of the known suspected accelerants and their retention times.

2. What were the retention times of the accelerants found in the carpet sample? What are the identities of these compounds? Explain how you arrived at your answer using specific data.

3. Calculate the rough percentage of each of the components in the accelerant mixture.

4. Who should be arrested for the crime of arson in this case? Explain how you arrived at your answer.

In regards to question 3, note that in Figure 1A the areas for the four accelerants in a 1:1:1:1 mixture are roughly equivalent. In figure 1B, however, a percent area calculation suggests these compounds are present in a 24:52:24 ratio. This is roughly equivalent to the actual 1:2:1 ratio of the composed sample. It should be noted that students are warned that calculation of the percentage of components in the accelerant mixture is a rough calculation. Actual percentage calculations requires obtaining detector-dependent response factors for each of the pure compounds relative to a common standard.

2.4. Typical Results, Potential Problems, and Other Comments

We have been conducting this lab for over 6 years in conjunction with our Organic Chemistry lab. The lab is suitable for the first-semester of Organic Chemistry since students by this time are familiar with typical classes of organic compounds and understand how structure relates to boiling points. Generally we do not delve into mass spectrometry until the second semester of the course. However, substituting a GCMS for the Gow Macs would allow for additional compound identification via retention time *and* MS. Generally, however, we tend to limit access to our sensitive GCMS to students in upper-level chemistry courses and research students. The Gow Macs are sturdy instruments that can take some abuse by students initially unfamiliar with their use.

One problem often encountered during the lab experiment is the tendency of students to make slow injections of their sample onto the GC. This of course broadens the signals and creates problems with the retention times. Students need to be warned (and reminded) that injections should be a nearly single-motion action in which the needle pierces the injector septum, the needle is slid into the injector, and the syringe barrel plunged without hesitation, followed by quick withdrawal.

Generally, students have little problem understanding how to identify the components of the accelerant mixture using the retention times of the individual known compounds. Furthermore, the calculation of the rough percentage of each of the compounds in the mixture provides little challenge. This introduction to GC proves useful in subsequent laboratory experiments when we expect students to be able to: i) run GCs with no additional help from the instructor, ii) determine the identities of the components from a reaction mixture, and iii) calculate ratios of isomeric products. An example of this application occurs during the dehydration reaction of an alcohol to provide a mixture of alkenes from which they are able to confirm Zaitsev's rule[8].

Overwhelmingly, this laboratory experiment has been a success. The results have often spurned much interest in how GCs are used in real crime labs. Further questions about how conditions affect GCs have also arisen. For example, many times we have had students ask if they could run the same mixture on Column A to see what difference in the chromatograms the two columns make. This sort of interest is of course encouraged!

3. Background Information on GC

The following is a short description of gas chromatography that is provided for students to read prior to the laboratory experiment:

Suppose we have a mixture of compounds in a bottle. How can we go about determining the identity of the components that make up the mixture? Gas chromatography provides a simple, straight-forward, method of analysis for simple as well as quite complex product mixtures.

A sample is introduced into the injection port of the gas chromatograph using a syringe. The injection port is typically heated to a temperature above the boiling point of the sample to be analyzed. The sample is therefore immediately vaporized. The resulting vapor is swept onto the column by a stream of helium gas that continuously flows through the column. This gaseous "solution" rapidly comes into contact with a solid "support" that fills a copper or stainless steel column. The gaseous compounds are attracted to the support by various intermolecular forces. Different compounds are attracted to the same support to different degrees, however. Thus, from the original mixture of compounds, some compounds will be strongly attracted to the support, others will be only weakly attracted and others will be attracted to a degree somewhere between these two extremes. In all cases, however, the flowing helium keeps ALL compounds moving down the column toward the exit. The compounds that are attracted the greatest to the column move the slowest are said to be "retained" the longest. These compounds exit ("elute") from the column last and have longer "retention times". Those compounds that are only weakly attracted are retained the least, and elute from the column early. Thus, as shown in Figure 2, whereas all compounds are together at the beginning of the column, they have been separated by the time they reach the end of the column, and elute as individual "peaks" in the chromatogram.

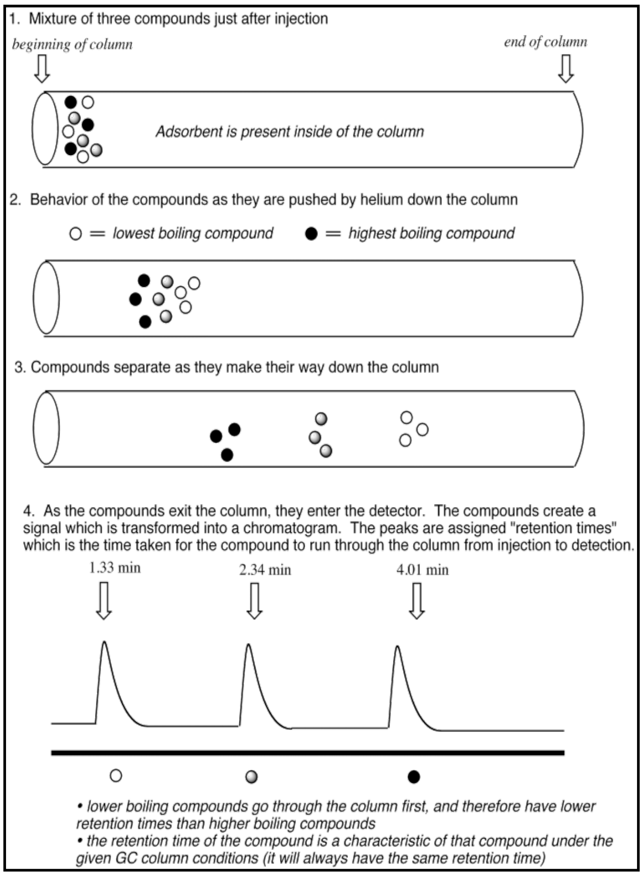

Figure 2. Visual description of the separation of mixtures of compounds as they move down a GC column

As the compounds elute from the end of the column they pass into a "detector" which registers their presence. There are many different types of detectors for gas chromatographs. We will be using a "thermal conductivity" detector on our GC's. This detector measures the ability of a gas stream to act as a thermal conductor. Helium is an excellent thermal conductor whereas organic compounds generally are not. As a compound elutes, therefore, the detector senses a decreased thermal conductivity of the gaseous stream and this registers as a peak on the chromatogram. Each eluting compound, therefore, gives rise to a separate peak in the chromatogram as it passes through the detector.

If a timer is started upon initial injection of sample, it will take each compound a certain amount of time to elute from the column and reach the detector (where it gives rise to a peak in the chromatogram). This time, called the "retention time", is a characteristic of the compound (on that particular column under those particular instrument conditions).

If there are two components in a mixture, one at 85% and one at 15%, the chromatogram will show two peaks. Since one is at much greater concentration than the other, we may expect that the larger peak corresponds to the component of greater percentage. This is usually correct. We can roughly determine relative amounts of compounds by analyzing the area under each of the peaks in a chromatogram. For a chromatogram in which there are several peaks we would determine the percentage contribution of each individual component to the mixture using the following equation:

$$\frac{\text{area of a \textbf{single} peak}}{\textbf{total}\text{ area of }\textbf{all}\text{ peaks}} \times 100\% = \text{percentage of that component in a mixture}$$

What factors influence when a compound elutes from a column (i.e., the compound's retention time)? SEVERAL:

1. *Nature of the support contained in the column*. Different support materials have different characteristics, and will therefore interact differently with the components of a mixture. It is not uncommon for three components to elute 1,2,3 on one type of column and 2,3,1 (for example) on another type. Thus, it is very important to specify the column that is used in a GC analysis. Our GC's are outfitted with two different types of columns:

Column A (i.e., injection port A): 20% Carbowax 20M on Chromosorb P 80/100 mesh —this is a polar column used primarily to separate compounds that differ greatly in polarity.

Column B (i.e., injection port B): 20% DC-710 on Chromosorb P 80/100 mesh —this is a non-polar column used primarily to separate compounds by boiling point. Higher boiling compounds generally come off later than lower boiling compounds.

2. *Rate of helium flow*. The rate of flow of helium is adjusted by means of a needle valve. This is carefully set by your instructor to give best results for each experiment. It should not be adjusted further by students!! Generally, the higher the flow of helium (measured in mL/min) the faster the compounds elute. So retention times are shortened with higher flow rates.

3. *Column temperature*. The columns are contained within an oven. The temperature of the oven can be manipulated by means of appropriate controls. Again, this is preset by the instructor and should be left alone! Generally, the higher the oven temperature, the shorter the retention times.

As a practical note: Since so many minor variations contribute to differences in retention times, people using different GC's will often get different retention times for the same compounds. However, if the same GC is used for the entire experiment, retention times should remain relatively constant. Thus it is important to select one GC and use it for the entire experiment.

4. Police Crime Report

The following is a copy of the Police Crime Report that students are required to read prior to beginning the laboratory experiment:

TO: Criminal Forensics Investigation Lab

CASE: Cheese-Whiz factory arson crime

CASE DETECTIVE: Lt. Ima Gonnagettem

SUMMARY

Update 1. The newly hired manager, Bill M Twice, fired four long-term employees of the Cheese-Whiz factory when he found them playing poker at the back of the building rather than performing their jobs. Maya Headhurts, Ura Loser, Celia Tomorrow, and Davis Whacko all left that day disgruntled with the decision and vowing revenge.

Update 2. Headhurts, Loser, Tomorrow and Whacko devised a plan to burn down the Cheese-Whiz factory the following weekend. They drew straws on who would actually commit the crime. The person that drew the short straw was selected as the one to carry out the arson. All four went to the local Homestead Depot store and purchased different cans of common flammable solvents to use as fire accelerants. They also purchased an unmarked empty metal container. The idea was that they would make a cocktail mixture of all of the solvents to create a "super accelerant" to start the fire at the factory. They each took a turn pouring various amounts of their particular solvent into the empty metal container. At the last minute, one of the four apparently got cold feet and decided that he/she could not carry out the crime after all, and would have "nothing more to do with it". He/she also refused to pour any of their particular solvent into the solvent cocktail mixture. The other three harassed the "chicken" for not participating, but could not convince the person to contribute any of their particular solvent. However, the others threatened the "chicken" that it would be "all over for them" if they ratted out the other three. All four of the disgruntled employees then poured the remainder of the contents of their can of solvent down the sewer drain and threw the empty cans into a nearby dumpster that they knew would be emptied by morning. The person that drew the short straw took home the container containing the cocktail mixture of solvents.

Update 3. That Saturday night, the former employee that drew the short straw entered the closed Cheese-Whiz factory through a window that was often left unlocked. The person was dressed in such a manner that it was impossible to tell their identity. The person dumped the contents of the solvent mixture onto the carpet in the office of Bill M Twice, and tossed in a match. The mixture of solvents ignited so quickly and ferociously that the person dropped the solvent container and scurried out of the building to avoid the flames. After leaving the building, the person bundled their disguise into a plastic bag, tied a few big stones to the bag and dropped it into the local lake, never to be seen again. The Cheese-Whiz building engulfed in flames before the local fire department arrived to extinguish the building. A security camera in the building was found to have survived. It showed a single person present in the building holding a metal container but it was impossible to determine the identity of the arsonist because of the disguise.

Update 4. Detective Ima Gonnagettem questioned the building manager Bill M Twice who immediately reported the firing of the four disgruntled employees and their threats against him. With search warrants in hand, the police rounded up the four and searched their houses for evidence. However, no evidence was found at their residences. The four suspects were gathered into a room and questioned by Detective Gonnagettem about their involvement with the arson. All four decried their innocence, and—when presented with the video camera footage—laughed that there was no way that anyone could be identified underneath that disguise. The suspects then demanded to be released. The detective, realizing that there was nothing at that point that warranted holding them further, allowed them to leave. From there the four suspects went to a local Waffle Haven for pecan waffles, thinking they had safely carried out the intended crime.

Update 5. The next day, additional evidence came to light. The crime lab examined the dropped solvent container found in Twice's office and noticed a partially burned Homestead Depot label on the bottom of the can. Lt. Gonnagettem obtained a warrant to review purchases made at the Homestead Depot store over the previous few days. It was discovered that each of the four suspects purchased their individual cans of solvent with a separate credit card. They were able to determine that Loser bought a can of acetone, Tomorrow purchased ethyl acetate, Headhurts bought octane, and Whacko purchased a can of toluene. Later that day, the crime lab notified Gonnagettem that some of the accelerant used in the arson had been isolated from underneath the burned carpet in Twice's office. The carpet was so completely saturated with the solvent at the point where it was poured out that some remained unburned underneath the carpet pad. The crime scene investigators were able to recover some of the solvent by simply sucking it out from the carpet using a mini-vacuum. The solvent was then emptied into a vial, sealed and retained as evidence.

CASE STATUS

The solvent sample isolated from the carpet, and samples of each of the purchased canned solvents are sent to you in the forensic crime lab. It is up to your group to identify what mixture of solvents was used in the arson utilizing the gas chromatograph and thereby determine which three of the four disgruntled employees were directly responsible for the crime.

5. Conclusions

This laboratory experiment on the introduction to gas chromatography has been immensely successful for over 6 years. Not only do students learn the essentials of GC but their imaginations and interests are sparked by housing the learning experience in the form of solving an arson crime via forensic style analysis.

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