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Laboratory Experiment

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Introducing High School Students to NMR Spectroscopy through Percent Composition Determination Using Low-Field Spectrometers

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Supporting Information

ABSTRACT: Mole to gram conversions, density, and percent composition are fundamental concepts in first year chemistry at the high school or undergraduate level; however, students often find it difficult to engage with these concepts. We present a simple laboratory experiment utilizing portable nuclear magnetic resonance spectroscopy (NMR) to determine the percent composition in a series of household solutions explored with high school honors chemistry students. Students engage with the science by using a portable NMR spectrometer to acquire and process their own proton spectrum of rubbing alcohol. From the acquired data, students then used the aforementioned concepts and calculations to determine the percent composition of the mixture in wt/wt, and v/v percents. Students and teachers both expressed excitement with getting to work with "advanced" techniques and a better understanding of the relevance of stoichiometry, density, and percent composition.

KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Laboratory Instruction, Instrumental Methods, Laboratory Equipment/Apparatus, NMR Spectroscopy, Hands-On Learning/Manipulatives*

Mole to gram conversions, density, and percent composition are fundamental concepts in first year chemistry courses at both the high school and undergraduate level; however, students often find it difficult to engage with these concepts. Hands-on activities and laboratory experiments have been shown to enhance student engagement and understanding of scientific concepts.[1] Nuclear magnetic resonance (NMR) spectroscopy is similarly a fundamental technique within organic chemistry.

Recently, there are an increased number of high schools offering a second or third year of chemistry that partially, if not fully, focuses on organic chemistry. Some of these courses may also include NMR spectroscopy.[2,3] However, organic chemistry is a course that tends to intimidate and challenge even gifted students. One study done to determine why premedical students change majors found that, of the students who indicated low grades were the reason, 78% of them named organic chemistry as the single course that caused them to change their plans.[4] The early introduction to common organic chemistry techniques and instrumentation such as NMR and IR spectroscopies in first year chemistry courses may provide lower level students a means to engage with the science while simultaneously exposing them to the material they will encounter as they continue their chemistry education. Although an in-depth coverage of NMR theory is not necessary at the high school level, a basic description of how the instrument works can help students understand the NMR process. Teachers can find a significant amount of information on the Internet to refresh their memories and possibly provide an introduction to the theory to their students. A few examples can be found in the references.[5−7]

Although it is nearly impossible for high schools to have direct access to a high field NMR spectrometer in their schools, it is possible to have collaborations with local universities with NMR instrumentation.[8] These collaborations are limited by the high schools' ability to transport their students to the university campus as well as scheduling by supervising university faculty. However, recent advances in low-field NMR instrumentation have made robust, low cost, portable NMR spectrometers commercially available, increasing access to a broader range of institutions, including high schools. Although these instruments are "low cost", this is obviously relative to the cost of a high field instrument. Low field instruments are likely still out of the budget range of high schools unless they are able to obtain a grant. Again, collaborations with local universities becomes ideal. The portability of the instruments allows for the instruments to be brought to the high school students rather than the students coming to the instrument.

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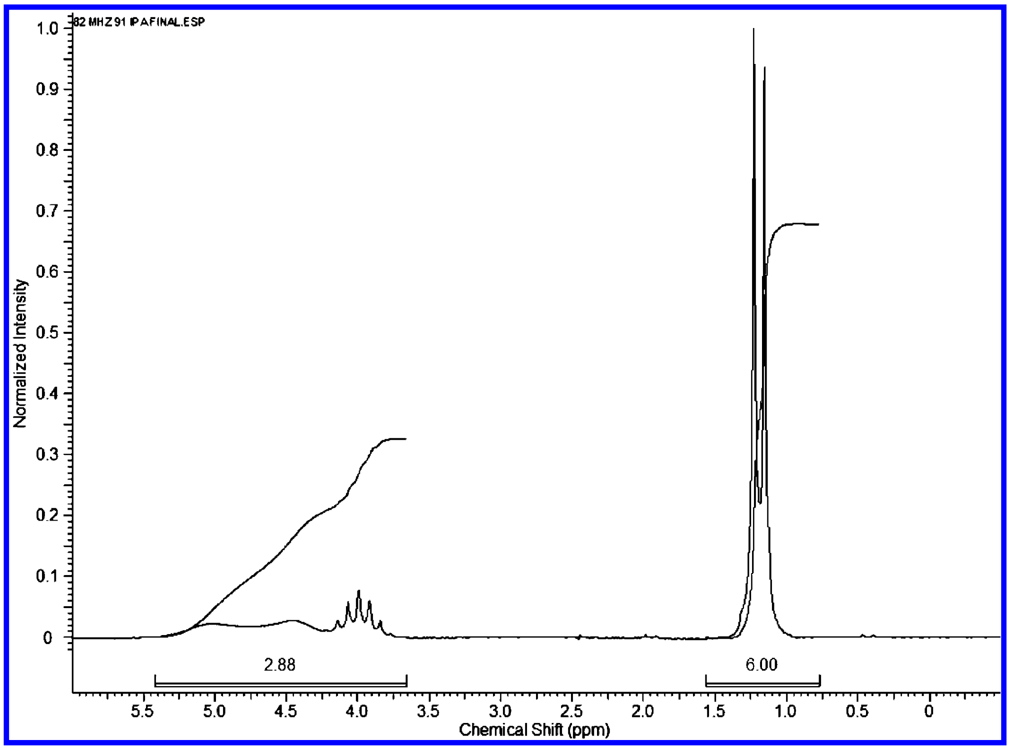

Figure 1. 82 MHz NMR spectrum of 91% isopropyl alcohol.

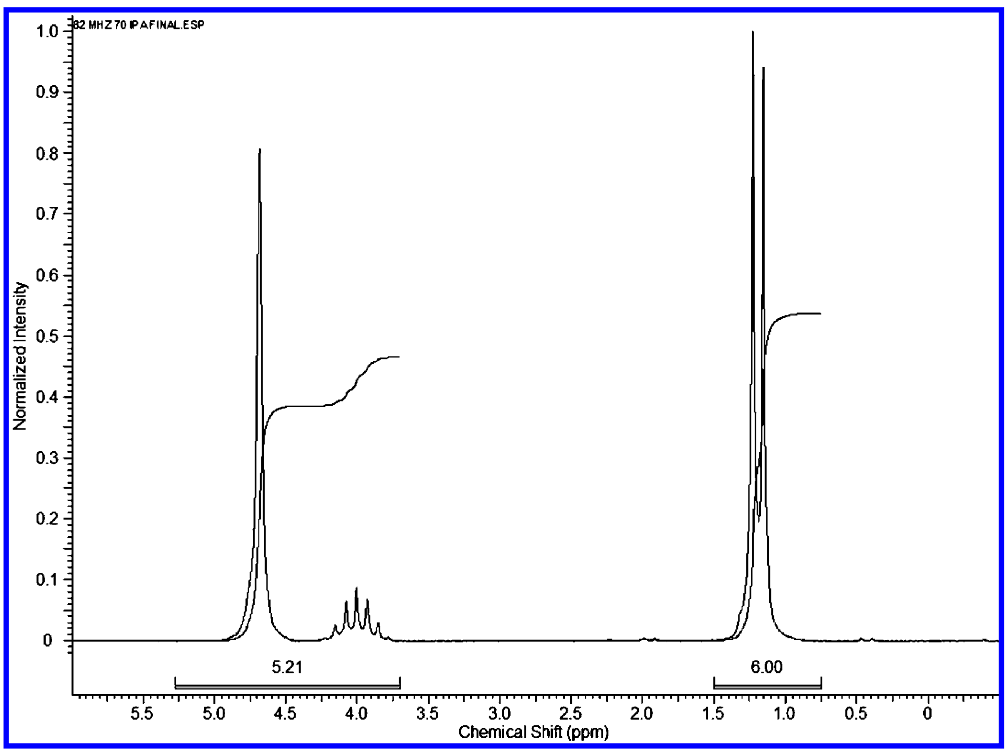

Figure 2. 82 MHz NMR spectrum of 70% isopropyl alcohol.

Since the introduction of the first benchtop NMR spectrometer in early 2011, the low-field NMR market has exploded. There are now several low-field "bench-top" NMR spectrometers available with field strengths from 42 to 82 MHz.[9] The various manufacturers offer systems that vary widely in size, cost, capability, and price. In addition to the reasonably high resolution all of these benchtop systems produce (typically <2 Hz, full width at half max (fwhm), some <1 Hz), some are capable of running samples in aqueous or other protonated solvents. The ability to run samples in standard nondeuterated solvents without complicated solvent suppression experiments or detector saturation is a unique advantage that can reduce costs and increase safety in an introductory laboratory. It also makes NMR a more appealing technique to investigate simple organic−aqueous mixtures such as the ones described in this experiment.

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The experiment discussed here has a simple, quick experimental procedure that does not overwhelm students and calls for the use of common household samples that require no prep and can be easily obtained by a high school teacher or college lab instructor. The spectrometer itself can be purchased, borrowed from a collaborating local college, or temporarily acquired through the Thermo Scientific classroom trial program. In the event that acquiring an instrument proves impractical, a less ideal but still effective option would be to convert this procedure to a "dry lab" and either provide students with a data file (see associated content) or a fully processed spectrum for analysis.

Depending on the skill level of the students, the experiment can be tailored to provide the appropriate level of difficulty. Little-to-no guidance or step-by step guidance can be provided as necessary. Step-by-step guidance for the rubbing alcohol, vinegar, and mouthwash samples can be found in the Supporting Information.

EXPERIMENTAL SECTION

Materials and Instrumentation

As previously discussed, a variety of low-field NMR spectrometers are now on the market and are suitable for use with this experiment. Thermo Fisher Scientific picoSpin-45 and picoSpin-80 NMR spectrometers were used for the development of this experiment.[10] All NMR spectral processing was completed using the educational version of ACD/Laboratories 12.0 1D NMR Processor.[11]

Table 1. Data Based on the 91% Isopropyl Alcohol NMR Spectrum

Peak (ppm)	Integration	Number of Solvent Hydrogens	Number of Solute Hydrogens
1.0−1.3	6.00	6	0
3.75−5.5	2.88	2	0.88

Several different aqueous solutions can be used for this experiment depending on the NMR interpretation skill level of the students. Aqueous solutions with various concentrations can be prepared; however, there are some common household items that can be utilized that require no additional prep work. The real-world connection provides the students with additional context and helps pique their interest.

Vinegar provides the least complex spectrum and requires no understanding of multiplet splitting. Store-bought vinegar is approximately 5% (wt/wt %) acetic acid. The spectrum of this solution gives two singlets, one for the methyl group of acetic acid and a second for the water and acidic proton of acetic acid. Additional discussion can occur regarding the merger of the acidic proton from acetic acid and the water signals in the spectrum.

Some added complexity can be provided by using isopropyl ("rubbing") alcohol. Store-bought isopropyl alcohol can be purchased as 70 or 91% (v/v %). For these samples, students would also need to understand multiplet splitting patterns and chemical shifts to help determine which peaks belong to the isopropyl alcohol and which peaks belong to water. Although it does not affect the results, it should be noted that depending on the concentration of the isopropyl alcohol and the operating temperature of the magnet, the hydroxyl and water signals may appear as a single combined peak or as two broad, partially overlapping peaks. This is due to the availability and rate of exchange among the hydroxyl protons. In either case, at least one of the water/hydroxyl peaks will partially overlap with the methine hydrogen signal from the alcohol at field strengths at or below 82 MHz. The doublet resulting from the two methyl groups of isopropyl alcohol is fully resolved.

Table 3. Data Based on the 70% Isopropyl Alcohol NMR Spectrum

Peak (ppm)	Integration	Number of Solvent Hydrogens	Number of Solute Hydrogens
1.0−1.3	6.00	6	0
3.75−5.5	5.21	2	3.21

Another store-bought aqueous solution that can be tested is alcohol-containing mouth wash. These will typically have the concentration of alcohol listed on the back of the bottle as percent by volume. Again, students would benefit from understanding multiplet splitting patterns to assign the methyl triplet and the methylene quartet.

Spectra of each of the above-mentioned samples can be found in the Supporting Information. The rubbing alcohol sample was used with the students at Lakeland Union High school and will be discussed in detail below.

Prelab Exercise

Due to the household nature of the suggested solutions, students should be able to complete a basic Internet search to determine the chemical formula, molar mass, density, and Lewis structure of their components. This information will be useful for completing the calculations. Students can also find what the typical concentrations are, and if they are typically listed as volume percent (v/v %) or weight percent (wt/wt %). An example of the prelab assignment can be found in the Supporting Information.

Procedure

The procedure for this lab is quite simple. First, students obtain the sample of the solution under investigation from their instructor. A ^{1}H NMR spectrum is then acquired according to the operating instructions for the specific spectrometer being used. The students then process and integrate the spectrum using the NMR software that is available at their institution. Although there are many NMR processing packages available that will accomplish this task, we chose to utilize ACD Laboratories 12.0 1D NMR Processor. This software package was chosen for its relative ease of use and accessibility, which is free for academic use and, therefore, allows the students to process the data offline, in the computer lab, or at home. The key to the spectral processing is the integration, as all calculations are based on these values. All samples discussed will have at least one peak fully resolved. The other peaks may

Table 2. Calculated Values Based on the 91% Rubbing Isopropyl NMR Spectrum

	Number of Molecules	Number of Moles	Number of Grams	Weight Percent	Volume (mL)	Volume Percent	Percent Error (v/v)
Solvent	1	1	60.1	88.4	76.5	90.6	0.42
Solute	0.44	0.44	7.92	11.6	7.92	9.4	

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Table 4. Calculated Values Based on the 70% Isopropyl Alcohol NMR Spectrum

	Number Of Molecules	Number Of Moles	Number Of Grams	Weight Percent	Volume (mL)	Volume Percent	Percent Error (v/v)
Solvent	1	1	60.1	67.5	76.5	72.6	3.7
Solute	1.61	1.61	28.89	32.5	28.89	27.4	

or may not be fully resolved based on the sample and frequency of the instrument. For consistency sake, all other peaks are integrated together. The lab procedure and data analysis in the Supporting Information are set up to handle the peaks integrated together. Integration values can be normalized to the correct number of hydrogens for resolved signals, but it is not necessary and can provide an additional level of complexity for advanced classes. Figures 1 and 2 show typical isopropyl alcohol spectra acquired and processed for this experiment.

Data Analysis

Using the integration values from their spectra, students complete the calculations and data analysis to determine the percent composition of the solution. If signals are overlapped, they will need to determine how much of the integration is due to the solvent and how much is due to the solute. They should then recognize that this ratio is identical regardless of whether it is expressed as molecules of solvent to molecules of solute or as moles of solvent to moles of solute. With the number of moles in hand, the molar mass of each can be used to calculate the weight percent of the components. To calculate volume percent, an additional conversion using the component's density will be necessary. Tables 1 and 2 show the data collected from Figure 1 and Tables 3 and 4 show the data collected from Figure 2 and the resulting weight and volume percentages. The experiments provided in the Supporting Information provide a walkthrough of the calculations for students with leading questions to get them from step to step.

In the case of the isopropyl alcohol, the added complexity of water being the solute and isopropyl alcohol being the solvent is an interesting twist that forces the students to follow the data and not make assumptions. Students tend to recognize water as the "universal solvent"; however, because water is the smaller component in this case, it is actually the solute.

It should also be noted that although useful concentration information can be obtained from most NMR spectra, accurate and repeatable quantitation of a sample is dependent upon many factors including experimental design and careful data processing, which are beyond the scope of this experiment. The reader should therefore understand that although quantitative NMR, or "qNMR", is capable of producing accurate measurements with standard deviations of less than 1%, standard deviations of 5% or more should be expected. The authors encourage instructors to focus their assessments more on student understanding of the material and the ability to properly work the calculations than on the end result.

Implementation

The lab described here was used by two instructors at Lakeland Union High School in three sections of Honors Chemistry and one section of Organic Chemistry for a total of 71 students. Three 40 min class periods were spent on NMR spectroscopy in each section. One class period was spent on an introductory lecture of NMR spectroscopy and examining example spectra for practice. A second class period was used to run the lab, and a third class period was used for groups to work on the calculations, although it was later agreed by the instructors that this could have been done in a half period or outside of class. A total of 71 students participated as either groups of two or three. Groups were given unknown samples of either 70% or 90% isopropyl alcohol prepared from reagent grade isopropyl alcohol. Prepared samples can be purchased at most local pharmacies and drug stores in 70% and 91% isopropyl alcohol. Although this experiment was tested in high school courses, it is the authors' opinion that it would also fit well in an undergraduate general chemistry experiment.

■ HAZARDS

Safety glasses should be worn during the use of the instrument. As all components used are household items, they may be disposed of down the sink. No additional hazards are known.

■ RESULTS

From the 71 students involved in the testing of this experiment, 33 groups were formed. Of these 33 groups, 4 groups had significant calculation errors throughout the process. For the remaining 29 groups with correct calculations, the average experimental percent error was 4.0% ($\sigma \approx 4.1\%$). This distribution of results is likely the result of small spectral processing errors that can affect the integration of the spectrum. Feedback received from the high school students and teachers was generally positive. They felt the exposure to NMR spectra and instrumentation was worth the class time spent. The teachers indicated that when the experiment is repeated, they intend to only use 2.5 days of class time rather than 3 with just a half class period for data analysis. Specific comments and suggestions regarding the lab instructions and handouts have been incorporated into the Supporting Information.

■ EXPANSION

As NMR spectroscopy is typically used as a qualitative tool to identify compounds, students could also be provided with various samples of alcohols such as ethyl alcohol, *n*-propanol, and isopropanol. The spectra of these samples can be compared to those of rubbing alcohol or mouthwash to identify the alcohol that is present in the solutions.

■ ASSOCIATED CONTENT

Supporting Information

Prelab and experimental instructions for students; notes for instructors, including representative spectra of each of the mentioned solutions, tables of associated data, and calculations. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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