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# Contribution of benchtop NMR spectroscopy to the identification of unknown liquids separated by fractional distillation

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## ABSTRACT

Fractional distillation is part of the essential experimental techniques taught to first-year chemistry students, especially during practical organic chemistry work. The characterization of the distillate generally involves measuring the boiling temperature, the refractive index or the infrared spectrum. In this paper, an unknown mixture composed of two organic solvents is given to the students in order to be separated by fractional distillation and characterized. To perform this task, the benchtop <sup>1</sup>H NMR spectroscopy was introduced to complement other analytical methods and to familiarize students with this technique while implementing their reasoning abilities.

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## GRAPHICAL ABSTRACT

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## KEYWORDS

First-Year Undergraduate / General; Analytical Chemistry; Organic Chemistry; Hands-On Learning / Manipulatives; Problem Solving / Decision Making; IR Spectroscopy; NMR Spectroscopy; Qualitative Analysis

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## 30 INTRODUCTION

Among the purification techniques available for organic compounds (i.e. recrystallisation, liquid-liquid extraction, silica gel flash column chromatography), fractional distillation is commonly taught in undergraduate practical work sessions<sup>1,2</sup>. It allows students to experience the purification of liquids<sup>3</sup>, the separation of unknown mixtures<sup>1,4,5</sup> and even the understanding of the Le Châtelier principle through reactive distillation<sup>6</sup>. Advanced structural characterization techniques like GC-MS or high field NMR spectroscopy are sometimes employed to characterize the distillate<sup>4-6</sup>. However, these techniques are not commonly available in the teaching laboratory for obvious cost reasons.

Today, the recording and analysis of NMR data during practical work can be achieved thanks to the emergence of benchtop NMR<sup>7</sup>. This technique was successfully used for instance in quantitative analysis<sup>8,9</sup> and as a major characterization tool for the synthesis of ester<sup>10</sup>, ether<sup>11</sup>, brominated compounds<sup>12</sup> and cis/trans product in Wittig reaction<sup>13</sup>. It was also used to teach structure elucidation of unknown liquids<sup>14</sup>.

Teaching the identification of unknown organic compounds can be a challenge since it mobilizes the students' deductive and reasoning skill<sup>5,15</sup>. To help them, web-based activities<sup>16</sup>, or games<sup>17</sup> were developed. In most cases, clean spectroscopic data were provided to students which then had to collect information from spectra to elucidate the structures of the unknown compounds. Nevertheless, those activities do not involve laboratory skills, i.e. students don't record the data themselves on IR or NMR spectrometer for example.

Paralleled to previous work<sup>14</sup>, we have developed at the Université du Littoral Côte d'Opale (France) a laboratory experiment for first year students combining fractional distillation and structure elucidation of distilled compounds. This experiment involves the separation of a mixture containing two unknown organic solvents by fractional distillation followed by their identification using physical and spectroscopic data including <sup>1</sup>H NMR from benchtop NMR. Instructors are encouraged to use this experiment in order to implement benchtop <sup>1</sup>H NMR into their own distillation laboratory activities.

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## LEARNING OUTOCOME

At the end of this 3-hour lab session, students are able to

- (1) Explain how to separate a liquid mixture using a Vigreux column
- (2) Assemble the fractional distillation apparatus
- (3) Measure the refractive index and density
- (4) Record spectroscopic data (IR and  $^1\text{H}$  NMR)
- (5) Combine multiple data to identify unknown compounds in a mixture

## MATERIALS AND METHODS

The unknown organic liquids constituting the mixtures are: dichloromethane, propanone (acetone), ethyl acetate, butanone (MEK), toluene and o-xylene. Hexane, water, chlorobenzene, and cyclooctane were added to the potential liquids list as "dummy" compounds. The students have at their disposal the common laboratory glassware, an infrared spectrometer, a refractometer and a benchtop NMR (picoSpin 45, ThermoScientific).

## HAZARDS

The "unknown" nature of the solutions requires students to take all necessary precautions when handling hazardous solvents. Thus, wearing individual protective equipment such as labcoats, gloves and goggles is mandatory throughout the session. Distillation assemblies must be carried out under a fume hood. All the solvents are flammable (GHS02) and harmful (GHS07). Dichloromethane, toluene and o-xylene present health hazards (GHS08). Waste should be disposed according to local legislation.

## EXPERIMENTAL PROCEDURE

In a 100 mL round bottomed flask, place 50 mL of unknown solution (containing two components) and a few grains of pumice stone or a stir bar. Set up a distillation apparatus and start heating the solution gently. Collect the distillate in a graduated cylinder and record the temperature every 1-2 mL. For both components, when the temperature is stable, collect a few milliliters of distillate in a previously tared 10 mL glass cylinder. Identify the two components of the mixture by measuring their boiling point, density, refractive index, infrared and  $^1\text{H}$  NMR spectra.

## RESULTS AND DISCUSSION

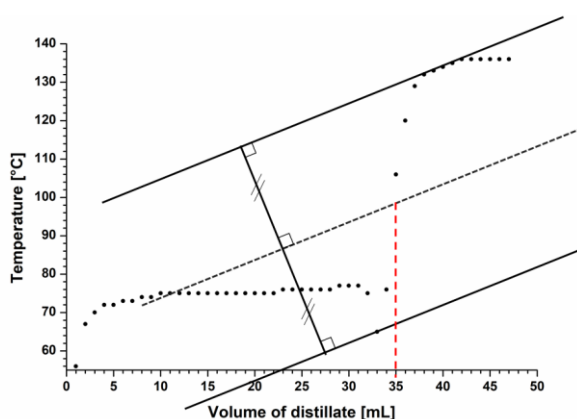
85 The experiment was performed with about 180 undergraduate students (divided into 12 groups of 10-16 students) since 2017 as part of their second semester organic chemistry course. It was found that one benchtop NMR device was sufficient for such small groups.

At the beginning of the practical session, each pair of students is assigned one of the four unknown solutions consisting of a mixture of 2 organic solvents (Table 1). They are then asked to  
90 measure the refractive index of the mixture as well as an IR and NMR spectrum and to separate the two constituents by fractional distillation. It should be noted that analyses on the unknown mixture can be performed during the distillation time.

	Solvent 1	Solvent 2	Proportion (v/v)
<b>Solution A</b>	Ethyl acetate	Toluene	50/50
<b>Solution B</b>	Ethyl acetate	o-Xylene	70/30
<b>Solution C</b>	Dichloromethane	Butanone	60/40
<b>Solution D</b>	Acetone	Toluene	30/70

Table 1 : Constitution of unknown binary mixtures

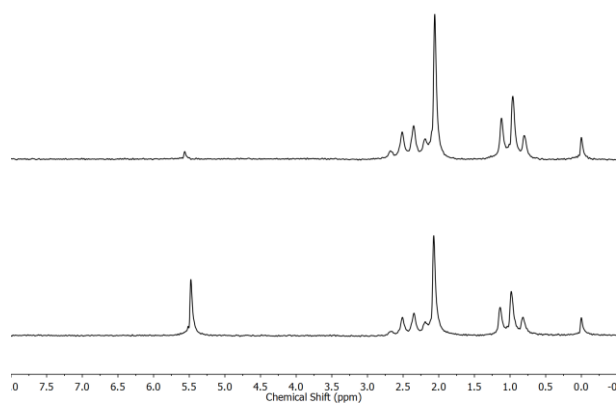
95 During distillation, students should report the temperature at the top of the column according to the volume of distillate obtained and then transfer the points to graph paper or a spreadsheet. This graph will be used to determine the boiling temperature of each of the compounds and the proportion of each component by applying the tangent method to the temperature jump as illustrated in Figure 1.



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Figure 1 : Illustration of a typical plot of temperature vs volume obtained for mixture B (Ethyl acetate / o-xylene 70:30 v/v) with the application of the tangent method.

It should be noted that boiling temperatures may be inaccurate depending on the position of the thermometer at the head of the column or on the glassware/thermometer used. On each temperature plate, students collect a pure sample which was then used to record physical and spectroscopic data. Students are encouraged to formulate hypothesis for the identification of their compounds based on their analytical data (boiling point, refractive index and IR) prior to recording NMR spectra using the built-in interface of the benchtop spectrometer. The recording of NMR spectra during the lab session also makes it possible to assess the purity of the collected samples and as a matter of fact, to explain why some data could be different from the data found in literature (pure compounds). As an illustration, if students heat the solution too quickly, the separation between the 2 compounds is not well achieved and no pure compounds were obtained as illustrated on  $^1\text{H}$  NMR spectra presented on Figure 2. On those spectra, one can observe that dichloromethane (bottom) is contaminated by butanone and vice versa. In this case, the infrared spectra of the most volatile compound (dichloromethane) indicate the presence of a carbonyl group only due to the contamination by butanone preventing students from correctly identifying the compound. Boiling point, refractive index and density cannot be used to identify the compounds either, highlighting the usefulness of NMR spectroscopy.



120 **Figure 2** : $^1\text{H}$  NMR spectra (neat, 45MHz, RT) of contaminated dichloromethane (bottom) and contaminated butanone (top)

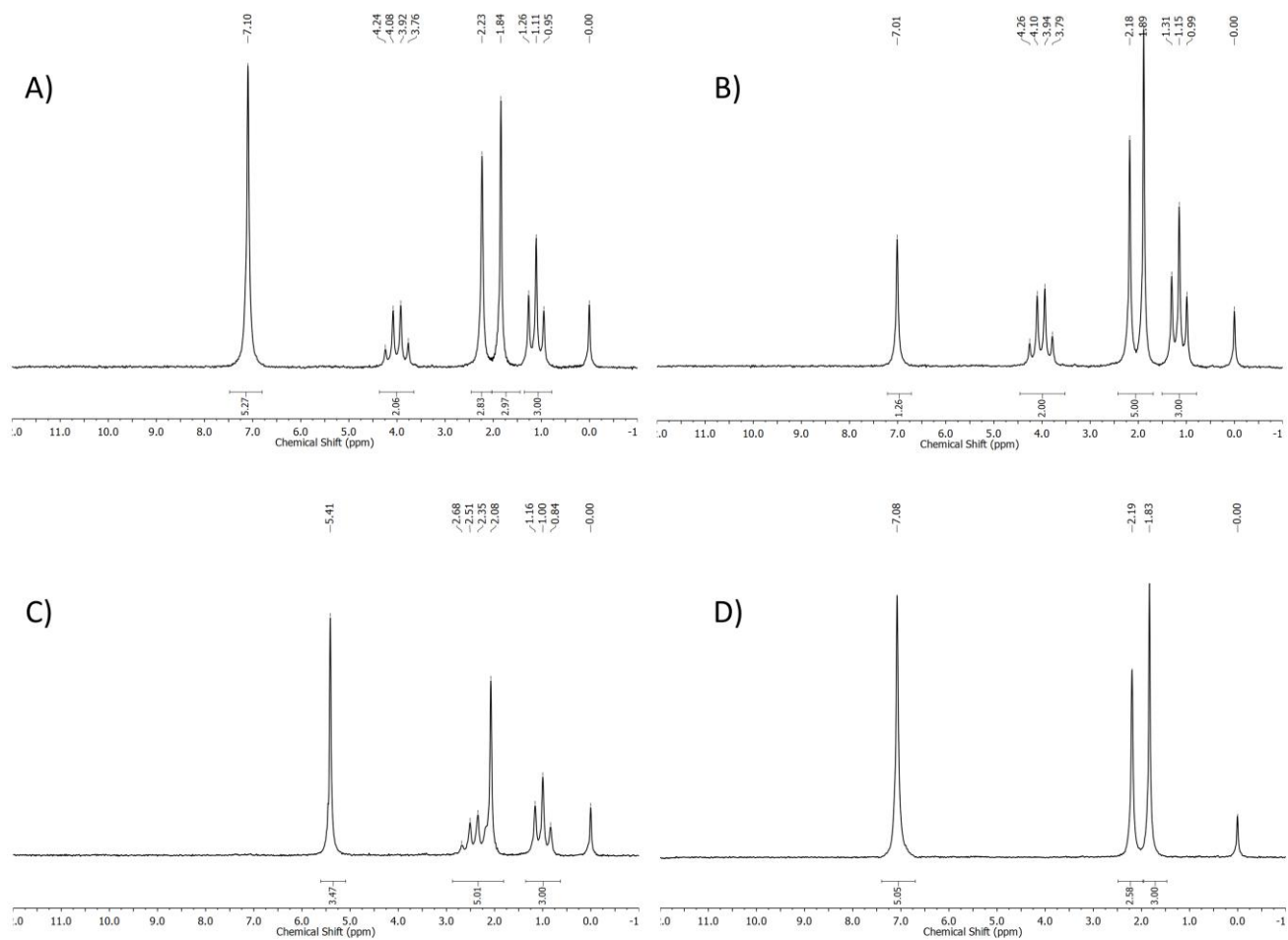
Historically, during this lab session only refractive index and density were measured in addition to boiling temperature. However, in view of the inaccuracy of temperature measurement and the difficulty for students to correctly identify solvents with refractive index as sole data (especially if the sample is

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125 not pure), and in order to increase their skills, it was decided to introduce spectroscopic measurements via infrared and then benchtop NMR.

The solvents used in this experiment were chosen to be easily identified by infrared spectroscopy and NMR without the use of high field instruments<sup>5,18</sup> (Figure 3). Thus, among the low-boiling constituents, dichloromethane and acetone, both have a single singlet in NMR but can be distinguished on the basis of the presence or absence of the C=O band in IR. Ethyl acetate and  
130 butanone have the same NMR pattern with a singlet, a triplet and a quadruplet. Toluene and xylene were chosen in order to obtain aromatic signal around 7 ppm and can be spotted owing to integration of aromatic and methyl signals.

In the early development of this laboratory, it was not possible to exploit the chemical shift  
135 information due to the lack of reference signal. Indeed, in classical NMR, spectra are often calibrated with residual signal from deuterated solvent. To overcome this drawback, 50  $\mu$ L of tetramethylsilane (TMS) was added to 1 mL of unknown solvent prior to benchtop NMR experiment (Figure 4) highlighting for students the need of calibration.



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Figure 3 :<sup>1</sup>H NMR spectra (neat, 45MHz, RT) of A-D mixtures calibrated using TMS.



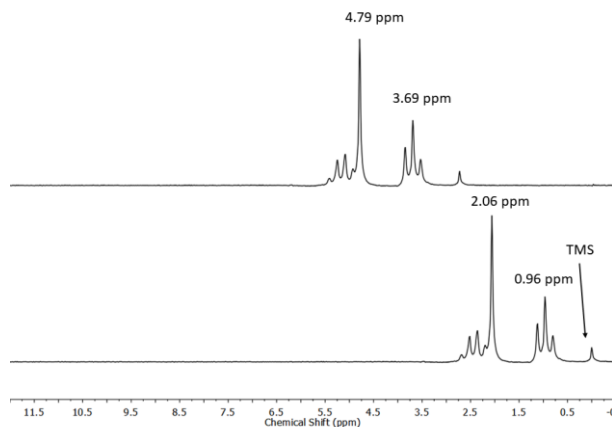


Figure 4 :  $^1\text{H}$  NMR spectra (neat, 45 MHz, RT) of butanone. Top : raw data. Bottom : calibrated using TMS

If students were not able to obtain one of their compounds, a pure sample was provided by the instructors in order to help them achieve by themselves all the characterization process. This can occur for example if the solvent was accidentally discarded, spilled on the bench or if there are leaks in the distillation apparatus.

In order to evaluate the relevance of the incorporation of benchtop NMR in complement of other analytical methods, students (N=37) were asked to answer questionnaires before and after the lab session. From the pre-lab questionnaire, it was found that only 73% of students were able to explain what is the purpose of fractional distillation. Concerning their background, 73% of students stated that they have already had an introductory course to NMR spectroscopy and 65% an introductory course to infrared spectroscopy from high school. However, only 35% can explain briefly what NMR is used for (structure elucidation) and 8% what IR is used for (bond identification). At the end of the lab session, students were asked i) to rate between 1 and 10 (1=not useful; 10=very useful) the usefulness of data obtained for unknown compounds identification and ii) to indicate the 2 most useful techniques to identify compounds. Results are summarized in table 2 below:

	Density	Boiling point	Refractive index	IR	NMR
Average score obtained from question 1 <sup>a</sup>	4.49	6.05	6.16	7.89	8.83
Percentage of citations from question 2 <sup>b</sup>	8.3%	27.8%	16.7%	66.7%	80.5%

<sup>a</sup> question 1: On a scale of 1 to 10 (1 = not useful, 10 = very useful) rate the usefulness of the following data for identifying compounds

<sup>b</sup> question 2: Indicate the two techniques that were most useful for you in the identification of the unknown compounds

Table 2: Responses of students (N=37) on the usefulness of techniques regarding compound identification obtained from post-lab questionnaire.

As expected, NMR and IR spectroscopies obtained the highest score (8.83 and 7.89 respectively) among the proposed techniques for their usefulness in compounds identification and were the two most cited techniques that help students identify compounds (80.5% and 66.7% respectively). Those results highlight that student have acquired skill in spectroscopy.

170 Furthermore, it was noticed by the instructors that the number of students misidentifying one or both of the compounds is much lower with the use of benchtop NMR. Misidentifying compounds was estimated at 50% without benchtop NMR and dropped to only 20% with benchtop NMR (some errors were due to the confusion between ethyl acetate and butanone which possess the same NMR pattern) Moreover, this incorporation of benchtop NMR made students realize the importance of this analytical  
175 technique taught in high school<sup>19</sup>.

## CONCLUSION

Benchtop NMR spectroscopy was successfully introduced in an existing 3-hour laboratory experiment designed for first year chemistry students. Fundamental concept and practice of fractional  
180 distillation were acquired by students through the separation of a binary mixture of organic solvents. Students also acquire skills in analytical chemistry, especially in structural identification of unknown compounds, by recording a set of physical (boiling point, refractive index, density) and spectroscopic (IR and benchtop NMR) data. This experiment made use of the students' knowledge in spectroscopy as well as their deductive reasoning abilities to identify both compounds in an unknown mixture.

## 185 ASSOCIATED CONTENT

Supporting Information

Instructions for students

Note for instructor

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