Guide for contributors to the Australian Journal of Education in Chemistry

Introduction
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4. All chemistry structures, and schemes should follow the guidelines set for ACS publications. It is preferred that Schemes, Tables etc be arranged to fit in a column 7 cm wide, although full page width will be accepted.

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Editorial

Periodic Tables on the World Wide Web

The Periodic Table of the Chemical Elements (to give it its full title) is the principal organisational feature of Chemistry. It initially found its rightful place through its brilliant use as a predictive tool by Dmitri Mendeleev (1869) and was brought to its present scientific condition as a sequence in atomic number (rather than the earlier choice of atomic mass) through the spectroscopic investigations of Henry Moseley (1913). Books about the Periodic Table abound. The Wikipedia article (http://en.wikipedia.org/wiki/Periodic_table) mentions a few of the more recent ones. But pride of place should go to Primo Levi’s *The Periodic Table* (1984) which contains a series of short essays, each titled with the name of a chemical element, based on incidents in Levi’s tragic life (briefly reviewed in http://dannyreviews.com/h/Periodic_Table.html).

However, the main concern in this brief review is to present a number of the more interesting interactive or unusual periodic tables which are available for inspection on the Web. A very informative example of a straightforward presentation which was early in the field and yet remains current, with much additional information such as the Chemdex “directory of chemistry” which links to chemical sites around the world, is Web Elements (http://www.webelements.com/ from the University of Sheffield and Mark Winter). The major chemical societies have their own sites, of course. The American Chemical Society (ACS) has a Table in a half-dozen or so languages (http://acswebcontent.acs.org/games/pt.html) while the UK Royal Society of Chemistry (RSC) features the interactive Visual Elements Periodic Table (http://www.rsc.org/periodic-table/) with an artistic representation of each element. For the 2011 International Year of Chemistry (IYC), the Royal Australian Chemical Institute (RACI) produced an artistic “Periodic Table on Show” (Figure 1, http://www.raci.org.au/periodic-table-on-show) developed by a number of local printmakers. A beautiful version is the “Photographic Periodic Table of the Elements” (http://periodictable.com/) which displays photographs of samples of the elements. An unusual Periodic Table (http://www.colorado.edu/physics/2000/applets/a2.html) shows the atomic emission spectra of many of the elements together with the associated filling of the energy levels (but don’t read too much into the pictures of the ‘whizzing’ electrons and nuclei!)

Among the more entertaining versions is the song by Tom Lehrer listing the chemical elements set to music, with a clever cartoon version (http://www.youtube.com/watch?v=SmwlzwGMMw&feature=related) and a very creditable version by Daniel Radcliffe (the “Harry Potter” star http://www.youtube.com/watch?v=rSAaiYKF0cs&feature=related). Every chemist should be familiar with the quite exceptional Periodic Table of Videos (http://www.periodicvideos.com/) from the University of Nottingham, which has short videos related to each of the chemical elements - and much, much else. (The videos are often narrated by the engaging Prof. Martyn Poliakoff, FRS, who recently visited Australia in connection with IYC. See also an essay in http://www.sciencemag.org/content/332/6033/1046.full).

Many have recognised that the Periodic Table provides an excellent organising principle which can be applied well beyond chemistry. For instance, the website http://web.mit.edu/dryfoo/www/Info/condiments.html lists a “Table of Condiments That Periodically Go Bad” (which includes the ‘useful fact’ that Vegemite lasts 2 months after opening!). Mathematicians are reported to be in the process of creating a periodic table of shapes (http://www.newscientist.com/article/dn201...
A striking resource is the Periodic Table in nearly 400 languages, including some which are extinct or have been constructed (in Czech, but quite clear: link to an extensive, and eclectic, set of Periodic Tables).

In this issue.....

An overview of problem-based learning, along with the criteria of a 'good' PBL activity, and integration of the outcomes into the curriculum, is presented by Llorens-Molina. Going beyond the generalities, Llorens-Molina describes in some detail a particular organic chemistry PBL laboratory activity based on searching for, and testing, some natural substances that control sprouting of potatoes during storage. In tracing out pathways through which students might be encouraged to pass, he clearly demonstrates that, apart from attaining chemical knowledge related to the stated problem, students can develop skills in the use of the literature; experimental design, conduct and interpretation; exposure to experimental situations in which the outcomes are not known; general aspects of the nature of science such as assumptions, approximations, simplifications, and experimental limitations; as well as affective aspects such as motivation, and development of student-teacher relationships.

Lim provides a brief overview of the origin of chirality in molecules of various structural types. In the focus of the paper, information about chirality, stereocentres, \( R \) and \( S \) configurations, and the Cahn-Ingold-Prelog classification rules is encoded in the form of a song as a learning aid.

To estimate the vapour pressures above concentrated aqueous solutions of electrolytes, we usually calculate the activity coefficients of the ions by use of equations that contain empirically derived parameters. These parameters have little physical significance. De Berg describes the Heyrovská predictive model which makes a distinction between the surface and the bulk solution, with the water vapour pressure proportional to the mole fraction of unbound water molecules at the surface which, in turn, can be estimated from the hydration numbers of the ions in the surface as well as the degree of dissociation of the solute. De Berg uses the vapour pressures of 1.0 M solutions of LiCl, NaCl, KCl, RbCl and CsCl to compare the hydrations numbers of the cations at the surfaces, and the degree of dissociation of the salts. The trends allow powerful insights into the interactions in the solutions, consistent with interpretations based on the charge-to-radius ratios of the cations.

Determination of the point group of a molecule traditionally involves identification of its symmetry elements. To check that no symmetry operations have been overlooked, it is useful to know the order of the group, and Curnow's rules give a simple process for deciding this. General proofs of Curnow's rules to date involve mathematics rather too abstract and sophisticated for many undergraduate chemistry students. Williamson presents a proof, using simple geometric concepts and elementary group theory, that is more accessible to students and their teachers.

Xiao et al describe the chemistry and optics underlying the 'development' of latent fingerprint deposits, which are a complex matrix of substances. The techniques that can be used depend on the properties of the underlying substrate. This paper describes how students can be given experience in development of latent fingerprints in a problem-solving context. Such experiences can be useful vehicles for the introduction of students to a body of knowledge and principles of chemistry and optics.

Harrison et al describe an e-learning resource designed to prepare students for practical work at the bench. The LabSkills resources, for example, give students an interactive introduction to common techniques and experiments, best practice, safety, videos, and calculations. Simulations provide opportunities to explore techniques through trial and error, addressing common student mistakes, as well as correct equipment setup, optimisation of experimental conditions, and visualisation of molecular behaviour during instrumental analysis. The focus is on development of student understanding of the methodology of the practical work they will encounter, through practice, testing and feedback.

Driven by a belief that chemistry and chemical engineering students should experience more modern instrumentation and application software, Khaleel describes in detail the real-time monitoring of a heterogeneous catalytic reaction using FTIR spectroscopy. The experiment involves qualitative and quantitative monitoring of the products of dehydration of methanol in the vapour phase over an alumina catalyst. Variables such as temperature and the flow rate of the carrier gas affect the reaction pathway and the products.
Letters to the editor

An ageing academic reflects.

It was forty year last October that I began at the University of Leeds as an undergraduate. At that time of course I had no idea that I was destined, six years later, to go to Australia to live and work for very many years. I was however aware that two of the lecturers who taught me in my very first term were Australian, having graduated from the University of Melbourne. They were N.N. Greenwood (1925-) and D.L. Baulch (1932-). There was another Melbourne graduate on the staff of the department although he did not ever teach me, A.T. Austin (circa 1918-1984). Greenwood and Austin had known each other in Melbourne. Greenwood and Baulch are both alumni of University High School.

It was not possible to do a PhD in Australia until the mid 20th Century. I am told that the first PhD from the University of Melbourne was Rupert Myers, a metallurgist, ultimately Vice-Chancellor of UNSW. That was in about 1949. Greenwood and Austin came to England as PhD students, the former with Emeleus at Cambridge and the latter with Ingold at London. Baulch did his PhD at Melbourne about a decade later under Jimmy Duncan, whose obituary appeared in Chemistry in Australia not very many years ago.

In the earlier post-war period there were many Australian chemistry graduates who wished to get a PhD and deserved the opportunity to do so. Often they were 30-ish by the time the ambition to do a PhD developed and so had others besides themselves to consider. At that time universities in Australia were expanding and New South Wales was just opening up its second university. Consequently a route to a PhD became possible whereby a lectureship was offered on the basis of a degree at Baccalaureate level on the understanding that work towards a PhD would be carried out during the first few years. When I entered Australian academia in 1978 men whose careers had developed that way were in their early to mid fifties so were still a good way from retiring. I can remember many.

It would require a much deeper study than these few hundred words to analyse in retrospect the contributions made by such academics. It was however my privilege to write for Chemistry in Australia an obituary of Ken Basden, who died late last year. Ken was very much an example of what I have attempted to describe in the previous paragraph and I develop this theme a little more in the obituary.

Returning to 1971 when I first went to Leeds, one of the most illustrious Australian chemists in the UK at that time was Sir Ronald Nyholm FRS. Having graduated from Sydney he did a PhD at the University of London where he was ultimately to become a professor. At the end of the Christmas term in 1971 Sir Ronald died in a car accident whilst driving to Cambridge to collect his son for the vacation. He was 54.


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Replace Band Theory

Band theory is used in introductory texts to explain conductivity and semiconductivity, but it is not adequate for this purpose. It does not explain what happens when an electron is excited to the conduction band or why it then assists conduction. It does not explain why insulators are in the top right of the periodic table. Band theory offers no explanation for the increase in conductivity when a substance is compressed. It also creates the impression that the electron is moved into the conduction band whereas no movement is actually implied – it merely acquires energy. It also implies that the conduction band has some reality beyond a modeling abstraction.

The Mott-Hubbard model succeeds where band theory fails. When semiconductors receive energy as heat or light, some of the energy causes electrons to dissociate from their parent atoms and simultaneously combine with dissociated electrons of other atoms, forming a non-localized system. The delocalization releases some energy helping the dissociation. This delocalization contributes to conductivity in the same way that the delocalized electrons of graphite make it a conductor. More incidents of excitation cause more delocalizations and greater conductivity. Multiple dislocations lead to extensive non-localized systems making conduction easier and conductivity greater. Even more excitations create an “electron sea” as in a metal

This model also accounts for the existence of insulators and their position in the periodic table. Two conditions must be fulfilled for a substance to be a conductor. An electron must be easily dissociated (i.e. the substance must have a low ionization potential) and/or the atoms must be packed together closely enough – i.e. the density must be high enough - that the dissociated electron is in close contact with an electron of another atom and can combine with it. Sulfur for example, and other elements in the top right of the periodic table, have neither of these criteria under normal conditions, so they are insulators.

The “band gap” posited by band theory is the energy needed for this excitation of the electrons.

Band theory should be eliminated from introductory texts and replaced by the Mott-Hubbard model described here.


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Problem Based Learning in Introductory Organic Chemistry. A laboratory activity based on the anti-sprouting effect of essential oils

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Abstract

The application of a Problem Based Learning methodology to transform the organic chemistry laboratory activities in a 1st course of Agricultural Engineering is described in this paper. The goal is to put these activities in a meaningful context in order to promote inquiry learning strategies which take into account Science-Technology-Society-Environment relationships. The proposed activity is referred to the application of natural products as alternative phytosanitary treatments, in this case, the sprouting control of potatoes during their storage. This activity has been a good opportunity to develop competencies such as information search and selection, experimental design, results discussion, making generalizations, etc.

1. Introduction

1.1. PBL as a tool for methodological renovation in learning chemistry

The actual trends in teaching science are going towards learning models which enhance the main role of students’ activity and their engagement in tasks of high cognitive demand, in inquiry type learning environments. In the same way, reflection on the relationships of their own learning within social and technological contexts is also outlined as is their commitment with social values such as sustainability. Therefore, each time a greater attention is paid to metacognitive activity so autonomy and self-regulation are developed as key skills for lifelong learning. In this way, the creation of learning environments about problematic situations can provide students opportunities to build and to apply the scientific knowledge successfully and to consolidate their acquisition in cooperative and collaborative working contexts. In this educational model the teachers’ role as facilitator, creator and manager of learning environments acquires a greater significance. In summary, all these features configure a very coherent model with scientific work methods and, therefore, particularly useful in the training of future engineers. With regard to transversal competences development, several aims can be emphasized:

• To help students to manage in the information society, giving them opportunities to decide what he/she needs to learn to face a problematic situation and acquire searching, processing and information selection abilities.

• To develop characteristic abilities and skills of the engineer’s professional profiles, particularly the communicative ones and cooperative work skills. In this way, a participative view of assessment process must be introduced through self and peer evaluation, encouraging students to assess their own learning process and the educative resources.

• To stimulate the use of tutorial activities, as a privileged tool to change the teachers’ role and the relationship between teachers and students.

• To guide the curriculum from the Science-Technique-Society-Environmental perspective, as a way to give an answer to the challenges which the social context outlines to the future engineers. Likewise, this real-life view must also be related to the business world and, concretely, in rural productive sectors

• To perform a deeper transformation in the role of laboratory work, according to all the mentioned aims above. This should change its traditional understanding as merely testing of theoretical knowledge or introduction of certain laboratory skills, towards an inquiry-type approach. Such has been stated by Hofstein: "Inquiry-type laboratories have the potential to develop student’s abilities and skills such as: posing scientifically oriented questions..., forming hypothesis, designing and conducting scientific investigations, formulating and revising scientific explanations, and communicating and defending scientific arguments"; However, from a realistic view of our educative context, a higher effort must be made to put in context the laboratory work with regard to the rest of curriculum as the social, technological and professional framework.

To face these challenges, PBL is a suitable and well established methodology. Besides its implementation as a comprehensive curricular approach as it is developed in universities like McMaster, Aalborg, Delaware, etc., the application of PBL as a strategy to introduce active methodologies has been the object of a great deal of researchers. In relation to PBL contribution to conventional learning improvement, there is empirical evidence of PBL contribution not only to develop new competences but also to improve the persistence and solidity of acquired knowledge. On the other hand, PBL has shown a great adaptability to its use in information and communication technology contexts by means of educational resources such as webquests and collaborative work tools.

With regard to learning chemistry, there are numerous and varied proposals similar to PBL, usually in an experimental way. In many contributions, PBL is proposed as strategy for methodological change dealing with its curricular integration. Likewise, the
PBL contribution to high order cognitive skills development is also justified.\textsuperscript{19} From a whole point of view, Duch\textsuperscript{20} describes accurately a framework to apply PBL in learning chemistry including the course model, the learning cycle, cooperative work management and assessment. Other contributions are related to concrete activities\textsuperscript{1,22} close to case studies\textsuperscript{23,24} or centred in socioeconomic and professional issues.\textsuperscript{25} In organic chemistry, the Lehman handbook of experimental activities\textsuperscript{26} can be mentioned, the same way as the active methodologies introduction through PBL activities.\textsuperscript{27} Most recently\textsuperscript{28} an attempt for introducing PBL as a strategy for methodological change in conventional learning environments related to an introductory organic chemistry course has been proposed. One of the developed activities is the one described in this paper.

1.2. Proposed PBL activity

1.2.1. A “good problem” features.

According to Duch\textsuperscript{20} the problem nature is a key factor to successful development of PBL. Their main features are the following:

1. A good problem must engage students' interest, and motivate them to delve deeper into its conceptual understanding. Its subject should be related to the real world, particularly, to students’ professional profile.

2. It must demand the making of decisions or judgements based on the available information. Also, the students should be asked to justify all decisions and reasoning based on the principles being learned. In this way, a good problem should demand students to define what assumptions are needed (and why), to distinguish the relevant information.

3. A problem should be designed in such a way that it requires cooperation from all members so that the simple compilation of individual efforts not is an effective strategy.

4. The starting of the activity is a key issue for good problem development. The initial questions must be proposed accurately in such a way that they must be connected to previously learned knowledge and, usually, show an explicit anchorage in everyday knowledge. Furthermore, their design must contribute the students’ engagement and participation in discussion. To reach this goal the questions must comply the following requirements:

(i) They must be open-ended, not limited to one correct answer, and to generate controversial issues which lead to the diverse opinions elicitation.

(ii) The difficulty level must be placed in the Vygotsky Proximal Zone Development\textsuperscript{28}, in such a way that their solution are neither obvious nor will take them to a feeling of failure. The students must have the sense of goal achievement, although this may not be too successful.

5. An effective problem must be clearly linked to content course objectives and, at the same time, to connect the new knowledge to other disciplines.

1.2.2. Problem anchorage in the syllabus

Taking into account these guidelines, an example of a performed activity in an introductory course in organic chemistry in the 1\textsuperscript{st} year of Agricultural Engineering (Polytechnic University of Valencia, Spain) is presented. In the course planning, a set of PBL type activities as complementary tasks are proposed to students cooperative groups with three-four members. They are developed throughout the four month form in such a way that these activities were integrated accurately in a coherent sequence of theoretical and experimental contents. Mainly, they were carried out during the six hours weekly period assigned to tutorial support. The aim was to lead students to develop generic competences such as self-regulation and metacognitive abilities, communicative skills, information searching and management, collaborative work, etc., integrating laboratory work into the subject matter content.

From the syllabus point of view, the curricular topics related to the exemplified problem are the following:

\textit{From the conceptual point of view:}

- Optical isomerism, chirality and biological activity.
- Terpenes and terpenoids
- Solubility of organic compounds. Emulsifiers.

\textit{From a methodological point of view:}

- Application of experimental techniques, use and management of laboratory equipment: mass and volume measurements, solution preparation and hydrodistillation.
- Experimental designs: variable control, definition of parameters, etc.
- Data expression, tables, charts and graph making, etc.
- Development of communicative skills such as the making of slide presentations, the carrying out of a well structured oral exposure.

\textit{From the social and professional point of view:}

- Importance of post-harvest treatments. Tuber storage.
- Environmental sensibility regarding with the use of natural products as alternative to conventional chemical treatments.
- Paying attention to relationship between concepts and models about the structure of matter and observable reality facts.

Regarding to laboratory methods, obtaining essential oils from aromatic plants through hydrodistillation with a Clavenger apparatus has been one of the ordinary experimental activities in the introductory organic chemistry course mentioned. During these laboratory sessions the physical and chemical basis are introduced, just like its assembly and use. Related to this activity, some rudiments about gas-chromatography analysis are introduced, particularly, the identification of substances.
from the testing with pure standards and the calculation of Kovats retention index.

1.2.3. The problem as it was delivered to students. Some reflections.
This activity has been carried out during a four month term. It is designed in such a way that the mentioned ordinary laboratory activities come up to formative needs which have been identified by students to develop PBL activities.

In this way, the students’ cooperative work begins establishing the PBL scenario: a farm requires their contribution to plan the potatoes post-harvest treatment to avoid the sprouting, an important problem related to tuber storage which reduces its quality noticeably. Some chemicals applied usually in post-harvest treatment are profam and chlorprofam, represented in Figure 1, but, nowadays, there is an increasing trend towards the use of non-environmentally harmful chemicals. What alternatives can be applied based in natural substances? How can their effects be assessed?

A first approach to literature concerned to biological activity of essential oils shows that most of them (lavender, thymus, sage, etc.) have a lot of applications in pest control, food conservation, etc. Regarding to potatoes sprouting, a quick check of literature leads students to an active principle: carvone. This is a terpenic ketone with optical activity, whose enantiomeric forms R and S are plentiful in essential oils of spearmint and of caraway seeds, respectively. Once these substances are identified, there is a good opportunity to explore deeper into the specific biological activity of enantiomeric forms. For instance, the teratogenic effect of (S)-thalidomide can be mentioned as a social and relevant historic case about this matter.

From this information, the following hypothesis was proposed: A specific anti-sprouting activity of the essential oil of caraway seeds will be observed in domestic potatoes storage conditions.

![Figure 1. Chemical structures of profam and chlorprofam.](image)

A previous reflection must be taken into account: the relationship between a real research and a guided inquiry-type activity. Obviously, in the last one, it is about a fictitious research which is asked for the students, because we reconstruct a process whose development and results are well known. Likewise, this process is carried out in a very limited conceptual and experimental framework. However, as the inquiry-type activity is developed in a very particular context, a certain degree of open-ended and uncertainty may occur which makes it more similar to the real investigation. This is more frequent when the problem subject is more related with natural and everyday facts due to their higher variability.

Some more reflections about the relationship between real research and inquiry-type activity can be argued. Mainly, it is necessary to have enough previous rigorous and updated information to design a meaningful and sound PBL activity, avoiding vagueness, mistakes and superficial approach. Sometimes, the study of phenomena is a bulk approach, where the higher and more noticeable changes and relationships can be analysed. In this way, the development of experimentation must be oriented accurately to obtain relevant and clear results from the students’ perception.

1.2.4. Proposed work hypothesis. Inquiry process aims and contextual limitations.
At the beginning, the students consider the need of looking for natural products which have biological effects on sprouting. This search leads easily to essential oils of aromatic plants as suitable natural products.

The design of an experiment to evaluate comparatively the efficiency of both enantiomeric forms of carvone poses several problems which configure a guided inquiry process:

- How do we obtain the essential oil and check its chemical composition?
- How can the essential oil be applied? To what concentration must the essential oil be diluted, and with what?
- How can the tuber sprouting be quantified?
- How many times should the treatment be applied?

In the course of running work group sessions, through interviews with the teacher, these problems are dealt with. Successive decisions are being adopted to make the working method with the information at the same time in which the information is being obtained. The time planning is controlled in such a way that the information obtained from ordinary laboratory work satisfies the expectations generated by the inquiry process. In this way, the experimental methods are not recipe laboratory work; on the contrary, the hydrodistillation process and gas chromatography analysis are methodological resources for solving a previously identified meaningful problem.

The most conflictive issue was decisions about the statistical significance of sprouting quantitative data. The need of confining the activity into suitable boundaries of first year syllabus leads to considerable restrictions in experimental design. That should not prevent discussion of these limitations with students so they can become aware of experimental data significance.
2. Experimental methods

2.1. Essential oils obtaining and GC analysis

The essential oil was obtained from air dried, at room temperature, vegetable material from a university experimental crop and a specialized shop for spearmint and caraway seeds, respectively. To obtain and separate the essential oils a Clavenger apparatus was used with a rate of 1 g of dried vegetable material per 10 mL of distilled water with 1.5 hours distillation time.

The GC analysis was performed in the following way:

- **Sample preparation:** 1 mL essential oil was dissolved in 10 mL of dichloromethane for GC residue analysis (Scharlau), then, 1 µL from this dissolution was injected in GC equipment.
- **GC system features:** HP3398A GC Chemstation equipment with a FID detector. The capillary column was a ZB-5 (5% phenyl-95% dimethylpolisiloxane; 30 meter x 0.25 mm x 1.00 df (μm)).
- **Operating conditions**
  - Carrier gas: N₂ (20 mL/min flow)
  - Split relation: 1:25
  - Injector temperature: 210°C
  - Detector temperature: 250°C.

Initial oven temperature: 50 °C, maintained for 3 minutes, then it was raised to 250°C at the rate of 10°C/min. This temperature was maintained for 10 minutes.

The figures 3, 4 show the performed GC analysis with essential oil samples. The labelled peaks match with Kovats R.I. of carvone and the other main components (checked by GC-MS analysis performed by the teacher). Their % was estimated by peak normalization areas.

From the literature data, the students were able to assign each one of the enantiomeric forms of this compound.

2.2. Potatoes treatment. Experimental design and complementary data

With regard to the way of diluting the essential oil, the aqueous media is previously selected as a consequence of environmental considerations. For this reason, an emulsifier solution composed of 5 % propyleneglycol in water is used, the same way in which is proposed by Ricci, M. et al. Likewise, the concentration of essential oil (1 %) is selected from the usual range used in this sort of essential oil applications.

From this information, an experiment is designed in the following way: thirty potatoes bought in a shop, with a very homogeneous size without any developed sprouts are selected. They are treated with aqueous detergent and then, washed again with abundant water for ten minutes to eliminate possible applied chemicals. Once they get dried, ten potatoes are immersed instantaneously in each one of the following treatments, where the concentrations have been selected to apply the same quantity of carvone, aproximately:

- Propyleneglycol (Probus (CG) min 99 %) in distilled water 5 % (v/v) (blank)
- 1,75 % (m/m) essential oil of *Mentha spicata* L. (46,6 % of (R)-(–)-carvone) in propyleneglycol (5 % in water)
- 1,00 % (m/m) essential oil of *Carum carvi* L. (82,2 % of (S)-(–)-carvone) in propyleneglycol (5 % in water)

After this treatment, the potatoes are dried in air and then, are placed on the three trays (ten on each one) and stored in darkness, at 20°C practically constant temperature with enough ventilation (similar conditions to the domestic storage in the time of year in which the experiment was carried out). Every week (168 h) from the start of the experiment the length of the sprouts is measured and the total length of sprouts is calculated ($\sum L_{i}$, where $L_{i}$ is the length of all and each one of the observed sprouts).
Figure 5: Sprouts formation in stored potatoes

During a later course, other teamwork took over these results and proposed a new way for testing caraway oil effect comparing the direct influence of essential oil vapours and its emulsion in a tensioactive agent - aqueous tween-20, 1 % (w/w) (propyleneglycol was replaced by tween-20 as consequence of its better emulsifier power). Furthermore, the possibility of finding similar effects with other essential oils was also proposed. This way, the rosemary essential oil was also tested according the following experimental design (Table 1).

Table 1. Experimental design to compare anti-sprouting activity for rosemary and caraway vapours and emulsions

<table>
<thead>
<tr>
<th>Controls (sprouts number and length)</th>
<th>Treatments</th>
<th>Initial 15 days</th>
<th>30 days</th>
<th>45 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Initial</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Blank (aqueous tween-20, 1 % (w/w))</td>
<td>Initial</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Rosemary essential oil emulsion in aqueous tween-20 (1000 ppm)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Caraway essential oil emulsion in aqueous tween-20 (1000 ppm)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Caraway essential oil vapours from vials</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

Ten potatoes were placed into a carton box for each experiment. A chromatographic vial (1.5 mL) filled with 1 mL of caraway essential oil was introduced into the box attached to its internal wall. The evaporated essential oil was replaced each two weeks. Relative humidity and temperature were registered with a HOBO U12 data logger. Statistical data for both variables are shown in Table 2.

Table 2. Relative humidity and temperature values over the experimental period

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Maximum value</th>
<th>Minimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>17.89</td>
<td>1.51</td>
<td>21.70</td>
<td>14.29</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>46.80</td>
<td>7.95</td>
<td>68.07</td>
<td>25.80</td>
</tr>
</tbody>
</table>

Rosemary and caraway essential oils for this experiment were purchased in a specialist shop. Their composition was determined in the same way as caraway and spearmint essential oil in the 1st experiment. The caraway oil composition was practically the same. Rosemary essential oil composition is reflected in Table 3.

Table 3. Essential oil composition for Rosmarinus officinalis L

<table>
<thead>
<tr>
<th>Retention time</th>
<th>Compound</th>
<th>Kovats’ index</th>
<th>% peaks areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.627</td>
<td>α-pinene</td>
<td>941</td>
<td>20.19</td>
</tr>
<tr>
<td>8.935</td>
<td>camphene</td>
<td>956</td>
<td>10.49</td>
</tr>
<tr>
<td>9.514</td>
<td>sabinene</td>
<td>976</td>
<td>6.25</td>
</tr>
<tr>
<td>10.623</td>
<td>1,8-cineol</td>
<td>1040</td>
<td>28.23</td>
</tr>
<tr>
<td>12.760</td>
<td>camphor</td>
<td>1157</td>
<td>19.19</td>
</tr>
<tr>
<td>15.006</td>
<td>bornyl acetate</td>
<td>1295</td>
<td>2.04</td>
</tr>
<tr>
<td>13.084</td>
<td>borneol</td>
<td>1175</td>
<td>1.74</td>
</tr>
<tr>
<td>17.145</td>
<td>β-caryophyllene</td>
<td>1441</td>
<td>1.66</td>
</tr>
</tbody>
</table>

The number and length of sprouts was measured at 15, 30 and 45 days after treatment application. The most meaningful results are shown in the Figure 7.

3. Results of anti-sprouting activity

In the experiment 1, the effect of singular application after the treatments is observed throughout four weeks. Typical obtained results are shown in the Figure 6:

Figure 6: Evolution of potatoes sprouting for propilenglicol emulsions of caraway and spearmint essential oils

Figure 7: Effect of caraway and rosemary oil vapours and tween-20 emulsions on the potatoes sprouting


Regarding the students’ perception of this activity, it was studied within the whole research mentioned. From a qualitative point of view, some students’ opinions about the developed activities may be very illustrative:

I only have thankful words about these tasks since they made the teacher-student relationship closer; from the beginning, they helped to establish a closer linkage...
which is necessary to become self-confident, not to be afraid of asking questions, to talk with the teacher in a natural way, etc. In my particular case, I’m very proud because these tasks which we carried out since, as you know, I’m just doing my Final Project about the same subject...

I think that the task was quite interesting for me, I remember that I had to carry out the one related to beewax. Besides, I think it is one of the first tasks of this type which I have done at my university and, at least, I enjoyed it and, whether you like it or not, it is already a way for starting in laboratory work, making reports and power-points, be able to do a speech, etc.; Apart from all these issues, the fact that this task counted for my final mark in the subject is very good, taking into account that it was voluntary. I hope that my opinion has been helpful for you.

Personally, I think it was interesting for me and, moreover, I learnt a lot. My work consisted of detecting how much caffeine a decaffeinated tea by would contain means of murexida test. I think that the proposed subjects were quite interesting and useful, like that referred to essential oils extraction, the biodiesel obtaining, which I carried out, etc. In summary, to do tasks concerning such a frequent issues in everyday life is nice.

5. Concluding remarks

From the experiment point of view itself, the results confirm the posed hypothesis, although a noticeable activity was also found with the spearmint essential oil treatment. This is an open-ended result as a consequence of the greater complexity of this oil and the possible anti-sprouting effect of other compounds.

The subsequent classroom discussion aimed to relate the experiment with this trend research, posing the numerous problems which remain without any response in the PBL activity: approximations, simplifications, experimental limitations, etc., related to storage conditions, calculation of real quantities of active principles, influence of the way in which the treatment is applied, suitability of emulsifier solution, etc.32. From the science nature point of view, all these sort of activities can reinforce a most realistic and suitable point of view about the nature of science. Indeed, the students can appreciate the complexity of any research in a real context and become aware of the developed work value as a way to achieve better competency levels and the subject-matter knowledge. Likewise the fact of designing PBL activities taking as starting point the results of the ones developed in previous years allows the students to see science work as a cumulative and collective task. In summary, the students have learnt mainly that: (1) Synthetic phytosanitary chemicals may be replaced by natural products in order to reduce the amount of wastes, (2) the analytical chemistry methods are necessary to characterize substances whose biological activity is being tested, (3) any experiment must be designed carefully by means of a careful variables definition, taking into account the different factors which may have influence on the studied process.

From a general point of view, the main achievement of these activities is, undoubtedly, the great increase of the student-teacher and student-student interactions as encouraged in the tutorial activities, which extended to other aspects of the subject. Also, taking into account the high density of theoretical contents, the PBL activities become the only opportunity for the students to develop important competences related to cooperative work, etc.

With regard to laboratory work approach, the PBL activities have been able to create a framework for them. They can convert a recipe in a meaningful activity, in such a way that the students take awareness of agricultural (technological, in general) applications of curricular contents.

From the teacher’s point of view, the greatest challenge is probably to define the problem correctly, to adjust its status accurately as an open ended activity and to achieve a good enouncement. Besides, all this effort it must become an appropriate transmission in the context of the initial activity (interview or webquest type activity).

Another key issue is the most or least experimental nature of the outlined problems. To provide an organizational framework for laboratory management which allows us to perform experimental work adapted to the students’ proposals is not simple. This way, the PBL model proposed in this paper can be valued as highly satisfactory since in most of the problems which implied experiments, could be carried out correctly. Nevertheless, it is necessary to point out that the teachers overload work may end up being very high. For this reason, it may be necessary to adjust the level of experimental implication of the outlined problems accurately. In the same way, incorporate other ones whose resolution can be carried out with other didactic resources.

A lot of attention should also be paid to the improvement of strategies to search information. A greater effort must be made to provide students opportunities to work with databases, wikis, etc., and, generally, to get a reflexive and critical use of the web, since certain tendency has been observed to appeal to materials not excessively rigorous.

Lastly, it is necessary to highlight the capacity of PBL activities to integrate the students in the subject and encouraging them to participate. Nevertheless, PBL development requires deep changes in educational organization and management, with more flexible timetables and administration of educational resources like laboratories. On the other hand, these resources must be adapted to new demands outlined by methodologies like PBL, mainly, in all aspects related with the information searching and management, cooperative and collaborative work promotion, self-learning materials development, making virtual environments, etc. This way, the incorporation of
information and communication technologies can constitute an important performance perspective.

6. References

Amazing shapes: Chirality

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Abstract

The use of songs to help learning of content is consistent with multi-sensory models of learning. Here, a song to the tune of “Amazing Grace” can be used in the classroom to enhance the learning of chirality and the Cahn-Ingold-Prelog priority rules.

Amazing shapes: chirality
(Sung to the tune of Amazing Grace)

Amazing shapes: chir-al-i-ty,
That makes both left and right! 
Carvone does have e-nan-tio-mers 
Diff’rent tastes do delight.

One will be dill and caraway, 
Spear-mint is the mir-ror! 
Tetrahe-dral stereo-cen-tres, 
Four groups: no less, or more.

Pri-or-i-tise from 1 to 4, 
By “Z”, the high-est led! 
I-so-topes have same Z number 
So use the mass instead.

Put lowest group away a-far 
Which way it turns, to see 
Turn left is “S”, turn right is “R”, 
Carbon chir-al-i-ty.

Amazing shapes: chir-al-i-ty, 
That makes both R and S! 
Tetrahe-dral stereo-cen-tres, 
Four groups: no more, or less.

Notes and Discussion

The fact that molecules have 3-dimensional shapes is a key concept in chemistry, giving rise to differences in physical and chemical properties when interacting when molecules interact with each other or with light. Chirality refers to that property where some molecules are different from their mirror images. For example, the enantiomers of carvone (Figure 1) have different smells and tastes.

Chirality can arise from particular combinations of stereocentres, or in some cases from the overall molecular shape in the absence of stereocentres (Figure 2). In another example, poly-glycine has no stereocentres, but can form left- and right-handed helices. The possibility of chirality without stereocentres is usually not emphasised in introductory chemistry.

Figure 1 Enantiomers of carvone. Left: S-(+)-carvone, smells like caraway; it is found in caraway and dill. Right: R-(−)-carvone smells like spearmint; it is found in spearmint and peppermint.

Figure 2 Examples of chiral molecules (enantiomers) that have no stereocentres.

Figure 3 Berry pseudo-rotation (†) scrambles and racemises the positions for 5-coordinate trigonal bipyramidal geometry, which therefore cannot have simple enantiomeric isomerisation.
Five- and 6-coordinate atoms cannot be simple stereocentres as shown in Figures 3 and 4. For 5-coordinate trigonal bipyramidal geometry, Berry pseudo-rotation interchanges the axial positions with two of the equatorial positions (1). Hence 5-coordinate atoms cannot have simple enantiomeric isomerisation since a series of Berry pseudo-rotations will scramble and racemise all positions. Six-coordinate atoms in an octahedral geometry, do not have simple enantiomeric isomerisation since there are several types of isomerisation, some of which are shown in Figure 6. As a result, simple stereocentres are 4-coordinate atoms with four different substituents in a tetrahedral (sp³) arrangement.

Stereocentres are classified as R and S configurations, through use of the Cahn-Ingold-Prelog priority rules (2-4) as indicated in Table 1 and Figure 5.

Table 1 Cahn-Ingold-Prelog priority rules (2-4).

<table>
<thead>
<tr>
<th>Rule</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Atoms directly attached to the double bond or stereocentre are ranked according to the atomic number (Z), with the highest atomic number having highest ranking;</td>
</tr>
<tr>
<td>2.</td>
<td>If two atoms differ only by being isotopes, then the atomic mass is used for the ranking;</td>
</tr>
<tr>
<td>3.</td>
<td>If two or more groups have the same ranking, then rank the atoms in those groups, that are two bonds from the double bond or stereocentre (see Refs (2-4) for more details);</td>
</tr>
<tr>
<td>4.</td>
<td>If groups still have equal ranking, then atoms that are three bonds from the double bond or stereocentre are ranked; then atoms four bonds distant, etc, until the groups are either ranked or determined to have identical ranking.</td>
</tr>
</tbody>
</table>

The use of songs in chemistry is not new, but it is also not common. The use of mnemonics can help the memorisation, learning and recall (5) of chemical information, which are necessary first steps before the ultimate goal of chemical education, for students to learn, understand and apply chemical principles, can be achieved. Songs use rhyme, rhythm, text, melody and fun to engage learners, using multiple modes of learning. Here, information about chirality, stereocentres, the Cahn-Ingold-Prelog priority rules (2-4), and R and S configurations, have been encoded in the form of song as a learning aid.

Acknowledgments

The author acknowledges the inspiration of Mr Philip Ponder (Penleigh and Essendon Grammar School), Professor Brian Yates (University of Tasmania), Dr Dawn Joseph (School of Education, Deakin University), Professor Phanstiel’s students (University of Central Florida) and helpful discussions with Dr Stephen Moran.

References

Raoult’s Law: A Reinterpretation for Concentrated Strong 1:1 Electrolyte Solutions

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Abstract
Chemistry textbooks typically mention that Raoult’s Law is strictly applicable only for ideal solutions which usually also means very dilute solutions. Non-ideal behaviour for electrolytes is normally accounted for using activity coefficient data. It has recently been shown that for strong 1:1 electrolytes departure from ideal behaviour is best interpreted through the Arrhenius model of partial dissociation and the Armstrong model of ionic hydration. The new model of strong electrolytes, first proposed by Raja Heyrovska, distinguishes between free and bound molecules of water at the surface and bulk of a solution and involves the calculation of fractional dissociation values (a) and hydration numbers (n_a, n_b) for solute species at the surface and bulk of a solution. Raoult’s Law is shown to apply to concentrated strong 1:1 electrolytes if it is reinterpreted in terms of the Heyrovska model of an electrolyte solution. Examples are discussed here for the alkali chlorides with some important implications for the teaching of thermodynamics.

Introduction:
Raoult’s Law was first proposed by the French chemist Francois Marie Raoult (1886) in papers published between 1886 and 1888. The law is commonly featured in physical chemistry and general chemistry textbooks in the section dealing with the properties of solutions. The law can be applied to mixtures of volatile solvents and to non-volatile solutes dissolved in volatile solvents. This paper focuses on solutions of the latter category and in particular to 1:1 salts dissolved in water. There are at least four different ways in which the law which is typically presented as shown below for 1:1 salts dissolved in water.

(i) \( p_o = p_x \), where \( p_o \) represents the equilibrium water vapour pressure above the solution and \( x \) represents the mole fraction of water in the solution.

(ii) \( \frac{(p_o - p_x)}{p_o} = \frac{x}{1-x} \), where \( p_o \) represents the equilibrium water vapour pressure above pure liquid water and \( x \) represents the mole fraction of salt dissolved in the solution.

(iii) \( \frac{(p_o - p_x)}{p_o} = 2x \), where \( (p_o - p_x)/p_o \) represents the relative water vapour pressure lowering. The factor, ‘2’, is consistent with the Arrhenius idea (1887) of the electrolytic dissociation of a 1:1 salt into two ions (de Berg, 2003). Raoult (1891, p.297) agreed with this assessment when he noted that, “The exceptions in aqueous (salt) solutions (compared with non-electrolytes) are explained by the theory of electrolytic dissociation”.

(iv) \( \frac{(p_o - p_x)}{mp^o} = \) a constant, regardless of concentration and the 1:1 salt dissolved in water. Each solvent has a characteristic value for this constant and in the case of water the constant has a value around 3.4 x 10^-2 for 1:1 salts. In the expression, \( (p_o - p_x)/mp^o \), \( m \) is the molality and the expression thus refers to the relative molal water vapour pressure lowering.

What is limiting about Raoult’s Law is that the four relationships outlined above only strictly apply to very dilute solutions. In the case of more concentrated solutions deviations from the so-called ideal behaviour represented in the previous four equations have been typically accounted for by the use of activity coefficients whose values are dependent on the concept of ionic strength through a range of equations developed initially by Debye, Hückel, and Onsager. In addition, electrolytes like NaCl in water are considered to be completely dissociated into its ions, a condition Arrhenius always believed was only achieved at infinite dilution. In the 1990’s the Debye-Hückel-Onsager approach, including the large range of equations subsequently developed for determining activity coefficients, was severely criticised (Darvell & Leung, 1991; Franks, 1991; Wright, 1991) because the expressions containing correction coefficients were becoming so complicated that they lacked any physical significance as far as the molecular properties of a solution were concerned. For example, Hamer and Wu (1972, p.1050) give the following expression for the activity coefficient, \( \gamma \):

\[
\log \gamma = \pm z.a.z. [A/I/(1+B^*I) + \beta I + CI^2 + DI^3 + ...]
\]

where \( z_a \) and \( z_c \) are charge numbers on the cation and anion respectively, \( I \) is the ionic strength, \( A \) is a constant for a particular medium, and \( B^* \), \( \beta \), \( C \) and \( D \) are empirical correction factors. These authors comment that, “The constants C, D, etc as well as B^* and \( \beta \) are taken as empirical and are not considered to have physical significance.”. Heyrovska (1991, 2006) responded to the criticisms referring to the lack of physical significance of the parameters in the various equations by suggesting that the properties of over one hundred strong electrolytes are better described by using the original Arrhenius concept of partial dissociation and the concept of ionic hydration. No theoretical or empirical correction coefficients were required under these conditions. A deeper physical
understanding of the molecular properties of the solution was thus possible. In this paper we wish to focus on Raoult’s Law and how the Heyrovska model enhances the significance of this law and other thermodynamic properties for 1:1 concentrated alkali chloride solutions.

**Principle of the Heyrovska Technique**

The Heyrovska technique revolves around six equations which can be used to treat published osmotic coefficient data (Robinson & Stokes, 2002, p.476; Hamer & Wu, 1972, pp.1047-1099) in order to determine hydration numbers in the bulk ($n_b$) and surface ($n_s$) of the solution and the degree of dissociation ($\alpha$) of the salt into its ions. The osmotic coefficient, $\varphi$, functions like the activity coefficient in that it is a correction factor accounting for non-ideal solution behaviour. The hydration numbers give one some idea as to how many water molecules are bound to the cation and anion in a way which prevents them from behaving freely as in pure water. The hydration numbers and the degree of dissociation of the salt enable one to then calculate the mole fraction of water molecules that are free at the surface. The six equations, shown in Box 1, and their derivations, where applicable, are discussed in some detail in Heyrovska (1997). See the Appendix for an example of how the six equations can be applied to NaCl data. Spreadsheet calculations for all the alkali metal chlorides can be obtained on request from the author. Data for the alkali chlorides from 0.001 molal up to saturation or near saturation show conclusively that water vapour partial pressure ($p_v$) is directly proportional to the mole fraction of free water molecules at the surface ($N_{fs}$). For the 1:1 alkali chlorides it is now possible to replace the four equations for Raoult’s Law described in the introduction and applicable only for very dilute solutions with the following four equations applicable up to saturation or near saturation.

(i) $p_v$ is proportional to $N_{fs}$, the mole fraction of free water molecules at the solution.

(ii) $(p^2 - p_v)$ is proportional to $N_{sats}$, the mole fraction of salt particles at the surface of the solution.

(iii) $(p^2 - p_v)/p^0 = N_{sats}$

(iv) $(p^2 - p_v)/mp^0 = 0.03356$

This is truly a remarkable advance for Raoult’s Law made possible by focusing on the properties of the solution’s surface, the hydration of the ions, and the partial dissociation of the salt in solution.

**Significance for Chemistry Educators**

The quantities calculated by the Heyrovska approach and used to reinterpret Raoult’s Law for concentrated 1:1 salt solutions have a great applicability in enhancing one’s understanding of the thermodynamics of such solutions. Calculated data for the alkali chlorides are shown in Table 1. Equilibrium water vapour partial pressures ($p_v$) were obtained from Hamer and Wu (1972, pp.1047-1099); the hydration numbers at the solution of the surface ($n_s$), the molality of free water molecules at the surface ($n_{fs}$), and the degrees of dissociation ($\alpha$) were calculated using the Heyrovska equations (1997) and data from Hamer and Wu (1972). The $\Delta H^o$ and $S^o$ values for the processes shown were calculated using the data from Aylward and Findlay (2008).

**Table 1. Thermodynamic trends for the series of alkali chlorides, LiCl to CsCl at 25°C. $p^0$ (equilibrium vapour pressure for pure water) is 23.753 mm Hg.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>RbCl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_v$ (1.0 molal) in mm Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl</td>
<td>22.8959</td>
<td>22.9653</td>
<td>22.9968</td>
<td>23.0067</td>
<td>23.0275</td>
</tr>
<tr>
<td>NaCl</td>
<td>6.12</td>
<td>3.35</td>
<td>1.99</td>
<td>1.75</td>
<td>1.71</td>
</tr>
<tr>
<td>KCl</td>
<td>49.39</td>
<td>52.16</td>
<td>53.52</td>
<td>53.76</td>
<td>53.8</td>
</tr>
<tr>
<td>RbCl</td>
<td>0.8489</td>
<td>0.7890</td>
<td>0.7598</td>
<td>0.7437</td>
<td>0.6947</td>
</tr>
<tr>
<td>CsCl</td>
<td>-519</td>
<td>-406</td>
<td>-322</td>
<td>-301</td>
<td>-276</td>
</tr>
<tr>
<td>$\Delta H^o$ [M$^+(g) + \delta$] in kJ mol$^{-1}$</td>
<td>12</td>
<td>58</td>
<td>101</td>
<td>122</td>
<td>132</td>
</tr>
<tr>
<td>$S^o$ [M$^{+}$ (aq)] in J K$^{-1}$ mol$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The data in Table 1 are very informative as far as the molecular properties of solutions are concerned. The surface hydration number ($n_s$) is a measure of the average number of water molecules attracted and bound to an alkali metal ion and a chloride ion at the surface of...
the solution. A naked lithium ion, Li\(^+\), is smaller than a corresponding caesium ion, Cs\(^+\), and therefore the electric field around Li\(^+\) is stronger than around Cs\(^+\). It is no surprise therefore that the surface hydration number \(n_s\) increases from CsCl to LiCl (1.71 to 6.12). This means, as one might now expect, that the molality of free water molecules at the surface \((n_{sw})\) decreases from CsCl to LiCl (53.8 to 49.39) with the natural result that the partial pressure of water vapour (mm Hg) also decreases from CsCl to LiCl (23.03 to 22.90). The stronger interaction between a smaller cation and surrounding water molecules compared to a larger cation also leads to an increasing negative enthalpy (kJ mol\(^{-1}\)) of solution \([M^+(g) \rightarrow M^{(aq)}]\) from CsCl to LiCl (-276 to -519). The entropy \((J K^{-1} mol^{-1})\) of the aqueous cation decreases from CsCl to LiCl (132 to 12) due to the stronger hydration. Another way of looking at the entropy changes is that as the number of free water molecules increases from LiCl to CsCl so does the entropy (12 to 132 J K\(^{-1}\) mol\(^{-1}\)). Such deductions as these were not possible with the traditional form of Raoult’s Law.

Traditionally all the alkali chlorides would have been regarded as 100% dissociated into their ions. In the technique reported here the salts are only partially dissociated as shown by the \(\alpha\) values in Table 1. One way of interpreting the trend in the \(\alpha\) values is that ion-pairing is more likely to occur with a less hydrated metal ion leading to a smaller \(\alpha\) value which is the case with CsCl (0.6947) compared to LiCl (0.8489) in Table 1. Ohtaki and Fukushima (1992) detected ion-pairs in concentrated NaCl and KCl solutions using X-Ray diffraction so the notion of ion-pairing (or conversely, partial dissociation) in alkali chlorides has some experimental support in addition to its theoretical value.

It is interesting that in the Heyrovská approach to Raoult’s Law, the insights of two bitter enemies of 19th century/20th century chemistry have been united. The two insights are those of Svante Arrhenius’ partial dissociation model of electrolytes and Henry Armstrong’s emphasis on the role of the solvent in the properties of solutions and in particular his suggesting (1978) that water vapour pressure was related to the number of free ‘hydron’ \((H_2O)\) molecules present. The scientific controversy between Arrhenius (salts dissociate in water) and Armstrong (salts associate with water) has been elaborated elsewhere (de Berg, 2003; Brock, 1992) and it has been shown (de Berg, 2006) how the two ideas, dissociation and association, can be used to introduce students to the importance of argument and counter argument in scientific epistemology. What is an amazing feature in the study elaborated in this article is how two seemingly antagonistic ideas came to serve one another in providing a new insight into Raoult’s Law and ultimately the properties of electrolytes.

References
Darvell, B.W. & Leung, V.W-H. (1991). RIP ionic strength 1921-1991. Chemistry in Britain, January, 29-30. [This article argues that the concept of ionic strength has outlived its usefulness in solution chemistry and should no longer feature in physical chemistry courses. Thus it should rest in peace]
Franks, F. (1991). Old habits die hard-Letters to the editor. Chemistry in Britain, April, 315. [This article also argues against the usefulness of concepts like ionic strength and observes that it still features as a concept in physical chemistry in spite of arguments for its demise]
Heyrovská, R. (1991). Ionic concentration outlives ionic strength-Letters to the editor. Chemistry in Britain, December, 1114. [This article proposes that there already exists a procedure for understanding the properties of solutions that does not invoke the concept of ionic strength. This procedure is basically that outlined in this paper]
APPENDIX-NaCl EXAMPLE

Molality (m) and Osmotic Coefficient Data (ϕ) for NaCl are given on page 1067 of Hamer and Wu (1972). The following steps are now followed.

Step 1: Calculation of the activity of water (a_A) using equation (1) in Box 1.

Step 2: Calculation of \( R_{df} \) from \( a_A \) using equation (3) in Box 1.

Step 3: It follows from equations (3), (4), and (5) in Box 1 that \( \frac{(55.51-mn_s)}{R_{df}} \) should equal \( 55.51-mn_b \), the equation of a straight line. So \( \frac{(55.51-mn_s)}{R_{df}} \) is plotted against \( m \), and the value of \( n_s \) changed until a straight line with the highest correlation coefficient is obtained. The plot below shows the result for NaCl for which the hydration numbers, \( n_s = 3.35 \) and \( n_b = 2.46 \), apply.

Step 4: Having obtained \( n_s \) and \( n_b \) from Step 3, \( n_{Afs}, n_{Afb}, i \) (and \( \alpha \) from \( i = 1+ \alpha \)), and \( N_{Afs} \) can now be calculated from equations (4), (5), (6), and (2), from Box 1.

Step 5: Water vapour partial pressures can be obtained by multiplying the equilibrium vapour pressure for pure water at 25°C (23.753 mm Hg) by \( a_A \), the activity of water.

The following table shows five entries for the important variables in Box 1 for NaCl.

<table>
<thead>
<tr>
<th>m</th>
<th>( \phi )</th>
<th>( a_A )</th>
<th>( R_{df} )</th>
<th>( n_{Afs} )</th>
<th>( n_{Afb} )</th>
<th>( i )</th>
<th>( \alpha )</th>
<th>( N_{Afs} )</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.99915</td>
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<td>0.983233</td>
<td>52.16</td>
<td>53.05</td>
<td>1.7890</td>
<td>0.7890</td>
<td>0.96839</td>
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</tr>
</tbody>
</table>
Determining the Order of a Molecular Point Group

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Abstract

Conventional methods of identifying the point group of a molecule require skills in finding symmetry elements and operations. A useful aid to error checking is an ability to determine the order of a group purely from its label. To this end, Curnow has promulgated a set of simple empirical rules. In this article, Curnow’s rules are substantiated using simple geometric considerations from the basis of point group generators. The proof is provided in a form that will be accessible to undergraduate chemistry students and their teachers.

Keywords: Symmetry, group theory, molecular structure

Introduction

Symmetry plays an important role in chemistry, particularly in respect to molecular structure, spectroscopy and crystallography. An elementary skill taught at the undergraduate level is identification of the symmetry elements of a molecule and the subsequent determination of its point group by using a decision-making flow diagram of the type found in many text books. A common problem with this process is that students are prone to missing whole classes of operations, particularly improper rotations (S3) and C2 operations in dihedral point groups; thus, for example, it is reasonable common for the chair form of cyclohexane to be misassigned to the C5 or C3 point group rather than to D3d.

A useful exercise in helping students to refine their skills in identifying symmetry operations is to give them a picture of a molecule, along with the correctly assigned point group, and then require them to identify all operations without reference to a character table (where the operations would be listed). As a check for missing operations, it is clearly useful to be able to determine their total number – the order of the group – simply from the point-group label. To this end, Curnow gave three simple, empirical rules:(1)

1. Assign 1 for C or S, 2 for D, 12 for T, 24 for O, or 60 for I.
2. Multiply by n for any numerical subscript.
3. Multiply by 2 for any letter subscript label (s, v, d, h, i).

The veracity of Curnow’s rules is readily established for a given point group, but it would obviously be better to have a general proof. In 1952, Weyl effectively provided such a proof as part of his demonstration that only certain point groups are permitted in three-dimensional space;(2) and more recently, a modified proof was presented by Kim.(3) Unfortunately, both Weyl’s and Kim’s proofs are of limited pedagogical utility in chemistry since they require levels of mathematics that are substantially in advance of what might normally be expected from an undergraduate chemistry student. Certainly, they are rather more abstract than would be ideal for presentation in an undergraduate chemistry text book.

This article presents a proof of Curnow’s rules using simple geometric concepts and elementary group theory. Though perhaps less mathematically elegant than those presented by the earlier workers,(2, 3) it should be more accessible to both undergraduate chemistry students and their teachers, and therefore more appropriate for incorporation into chemistry textbooks.

Point-group Generators

The proof starts from the concept of group generators;(3) small, usually minimal or near-minimal,3 subsets of symmetry operations from which all other operations of the group can be generated. Table 1 lists the molecular point groups (in a notation familiar to chemists) along with appropriate choice of group generators divided into two categories – principal and augmentary. For each group, G, one or two principal generators, α, define a principal subgroup, gα, of order hα. This is extended to the full group by the inclusion of Na (up to two) further augmentory generators, β.

Except for the simplest groups (C1, C2, C4 and C3) selection of generators is never unique and some of those listed in Table 1 are not minimal. For example, for Cdh point groups with odd values of n, S2n could have been chosen as an unaugmented principal generator; for odd and even n, respectively, the Ddh and D4d point groups can be generated by augmenting S2n with just C2(L); for Td and Td, the principal generators could have been chosen as C3 and C5, while selection of S4 and C3 for Td would have required no augmentory generators. However the choices in Table 1 are convenient for this article in that: (a) they conform to common chemistry conventions for point group nomenclature; (b) they accord with the implied scheme of Curnow’s rules; (c) they are efficient in the sense that the removal of any one generator would leave the group incomplete whereas inclusion of any other would lead to redundancies; and (d), important to the following derivation, the augmentory generators are all self-inverse (β = β−1).

‡ A minimal set of group generators is the smallest subset required to completely define the point group. No molecular point group requires more than three group generators.
In terms of the parameters used in Table 1, Curnow’s rules are more concisely expressed as

\[ h = h_0 \times 2^{N_p} \quad (1) \]

The first step in validating this equation is the determination of \( h_0 \). The second step is to show that the inclusion of \( N_p \) self-inverse augmentory generators expands the order by a factor of \( 2^{N_p} \).

**Table 1: Molecular point groups and their group generators**

<table>
<thead>
<tr>
<th>Point group</th>
<th>Principal generator(s) ( \alpha )</th>
<th>Augmentory generator(s) ( \beta )</th>
<th>( N_p )</th>
<th>Group order ( h = h_0 \times 2^{N_p} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_n )</td>
<td>( C_n )</td>
<td></td>
<td>0</td>
<td>( n )</td>
</tr>
<tr>
<td>( \text{C}_{nv} )</td>
<td>( C_n )</td>
<td>( \alpha )</td>
<td>1</td>
<td>( 2n )</td>
</tr>
<tr>
<td>( \text{C}_{nh} )</td>
<td>( C_n )</td>
<td>( \alpha )</td>
<td>1</td>
<td>( 2n )</td>
</tr>
<tr>
<td>( \text{S}_n )</td>
<td></td>
<td></td>
<td>0</td>
<td>( n )</td>
</tr>
<tr>
<td>( \text{D}_n )</td>
<td>( C_n )</td>
<td>( C_2(\perp) )</td>
<td>2</td>
<td>( 4n )</td>
</tr>
<tr>
<td>( \text{D}_{nd} )</td>
<td>( C_n )</td>
<td>( C_2(\perp), \alpha )</td>
<td>2</td>
<td>( 4n )</td>
</tr>
<tr>
<td>( \text{D}_{nh} )</td>
<td>( C_n )</td>
<td>( C_2(\perp), \alpha )</td>
<td>2</td>
<td>( 4n )</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>( C_i(a_i), C_i(b_i) )</td>
<td></td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>( T_h )</td>
<td>( C_i(a_i), C_i(b_i) )</td>
<td></td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>( O_h )</td>
<td>( C_{i}, C_i )</td>
<td></td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>( I_h )</td>
<td>( C_{i}, C_i )</td>
<td></td>
<td>60</td>
<td>120</td>
</tr>
</tbody>
</table>

* The non rotational groups are effectively included in this table as follows: \( \text{C}_1 = \text{C}_{nv} \); \( \text{C}_2 = \text{C}_{nh} \); \( \text{C}_3 = \text{S}_2 \).

For the uniaxial cyclic (C and S) and dihedral (D) groups, a single principal generator, \( \alpha = C_n \) or \( S_n \), defines the principle subgroup, \( \text{g}_0 = C_n \) or \( S_n \). The elements of \( \text{g}_0 \) are \( \gamma_i = \alpha^i (i = 1 \ldots n) \), where \( \alpha^n = 1 \) and \( \gamma_n = E \). Hence, \( h_0 = n \) for these groups (third column of Table 1).

The situation is more complicated for the poly-axial, T, O and I, groups, which each have two principal generators. The principal subgroup for each of these groups comprises the rotational symmetry operations of a regular convex polyhedron (Platonic solid) composed of identical \( n \)-fold regular polygons, \( m \) of which meet at each vertex (Table 2). The shape of the polyhedron is defined by \( (n, m) \). For example, a cube (Figure 1a) comprises six squares (4-fold polygons), three of which meet at each vertex, so \( (n, m) = (4, 3) \); for a regular tetrahedron (Figure 1b), three equilateral triangles (3-fold polygons) meet at each vertex, so \( (n, m) = (3, 3) \). Each rotational axis passes through the surface of the polyhedron at two antipodal symmetry points, which can be categorised as one of three types: vertices (filled circles in Figure 1), edge centres (open circles) and face centres (filled quadrilaterals or quadrilaterals). Each edge centre is associated with a \( C_3 \) axis and has another edge centre as its antipode (Figure 1). The symmetry operations \( C_0 \) and \( C_m \) are, respectively, associated with the face centres and vertices, and constitute the principal generators listed in Table 1. When \( n = m \) the two antipodal symmetry points of each principal generator must be of the same type, either both vertices or both face centres. This is illustrated for a cube in Figure 1a where the antipodes of the \( C_3 \) generate are both face centres while those for the \( C_1 \) generator are both vertices. However, in the case of a tetrahedron, where \( n = m = 3 \), the antipode of a vertex is a face centre, and vice versa, as illustrated for the \( C_3 \) generator in Figure 1b.

**Table 2: The principal sub groups of the poly-axial groups**

<table>
<thead>
<tr>
<th>( g_0 ) ( \text{Polyhedron} )</th>
<th>( (n, m) )</th>
<th>( \nu_e )</th>
<th>( \nu_i )</th>
<th>( \nu_f )</th>
<th>( h_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>tetrahedron</td>
<td>(3, 3)</td>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>O</td>
<td>octahedron</td>
<td>(3, 4)</td>
<td>12</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>I</td>
<td>dodecahedron</td>
<td>(5, 3)</td>
<td>30</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

\[ \nu_e = \frac{2m}{n} \quad (4) \]

Each vertex is at the intersection of \( m \) edges and each edge connects two vertices, so

\[ \nu_e = 2\nu_i/m \quad (5) \]

Simultaneous solution of equations 3 to 5 gives

\[ \nu_e = 2nm/(2n + 2m - nm) \quad (6a) \]

\[ \nu_i = 4n/(2n + 2m - nm) \quad (6b) \]

\[ \nu_f = 4m/(2n + 2m - nm) \quad (6c) \]

Substituting equations 6a-c into equation 2 then gives

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1 For \( S_n \) and \( S_m \) only even values of \( n \) are permitted.
\[ h_0 = 4nm/(2n + 2m - nm) \] (7)
The consequent values of \( h_0 \), listed in the right-most column of Table 2, are in accord with Curnow’s rule number 1. Furthermore, equation 7 is symmetric with respect to the interchange of \( n \) and \( m \), consistent with the fact that the symmetry is independent of the interchange of vertices and faces, for example when transforming a cube into an octahedron or a regular dodecahedron into an icosahedron.

Although \( g_0 \) for all poly-axial groups contains \( C_2 \) operations, this is not explicit in equation 7, where \( h_0 \) depends only on the two principal generators \( (\alpha_1 \text{ and } \alpha_2) \). Two (related) explanations can be offered for this. The first is that the number of \( C_2 \) operations is completely determined (via Euler’s polyhedral formula – equation 3) by the numbers of \( C_u \) and \( C_m \) operations. The second is that the product of the two principal generators is a \( C_2 \) operation: \( \alpha_1 \alpha_2 = C_2 \).

**Determination of \( h \)**
The inclusion of each self-inverse augmentor doubles the order of the group, as follows. If the operations of \( g_0 \) are \( \gamma_1, \gamma_2 \ldots \gamma_{h_0} \), then the inclusion of \( \beta \) results in \( h_0 \) new operations that can be represented as products of the type
\[ \gamma_{h_0+i} = \beta \gamma_i \quad (i = 1 \ldots h_0) \] (8)
(the right-hand side of which is to be read as application of operation \( \gamma_i \) followed by operation \( \beta \)). In fact, equation 8 represents all possible new operations, as can be demonstrated via the group-theoretical concept of similarity. For any arbitrary symmetry operation \( \phi \) that belongs to \( G \), the product \( \phi^{-1} \gamma_i \phi \) is “similar” to (belongs to the same class as) \( \gamma_i \); and if \( \gamma_i \) belongs to \( g_0 \) then so must \( \phi^{-1} \gamma_i \phi \). Consequently, since \( \beta \) is a self-inverse member of \( G \),
\[ \beta^{-1} \gamma_i \beta = \gamma_i \in g_0 \] (9)
Pre-multiplying equation 9 by \( \beta \) gives
\[ \gamma_i \beta = \beta \gamma_i \] (10)
Thus, every product in which \( \beta \) is a pre-multiplier (first operation) is identical to a product already included by equation 8 where \( \beta \) is a post-multiplier (second operation). The same argument applies for the inclusion of each of the \( N_e \) augmentory generators in the sequence of subgroups between \( g_0 \) and \( G \). Hence equation 1 is established and Curnow’s rules are vindicated.

**Summary**
Curnow’s rules for determining the order of a point group from its label can be considered as a product of two parts, as expressed by equation 1: the order \( (h_0) \) of a principal subgroup that is defined by the principal group generators; and a doubling of that order by the inclusion of each of up to two self-inverse augmentory generators. This result is affirmed by simple geometric considerations and elementary group theory.

As an interesting aside, equations 4–7 give the results that \( 2n \nu_s = m \nu_s = n \nu_t = h_0 \). In an early step of Weyl’s demonstration that the only possible proper (rotation-only) groups with less than spherical symmetry are \( C_m, D_n, T, O \) and \( I(2) \) he showed, quite generally for any polyhedron, that
\[ k \nu_s = N \] (11)
In equation 11, \( N \) is the total number of proper rotational operations (including the identity) of the polyhedron, \( k \) is one of the (up to two) types of symmetry points through which the \( C_i \) axis passes and \( \nu_s \) is the total number of points of type \( k \). After combining equation 11 with a more general form of equation 2 for any polyhedron with two or more rotational symmetry axes, he derived the equation
\[ 1 + 2/N = 1/n + 1/m + 1/2 \] (12)
Setting \( N = h_0 \), equation 12 is simply rearranged to give equation 7. Setting \( m = 2 \) and \( N = h \) gives the (correct) result of \( h = 2n \) for the \( D_n \) point groups.

**Acknowledgement**
I would like to thank Associate Professor Owen Curnow for setting me the challenge of finding a simple general proof of his rules.

**References**
Chemical Detection of Latent Fingermarks in the Classroom

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Abstract

Fingermarks provide important information during criminal investigations. Most people are familiar with fingermark as portrayed on news reports, television shows like CSI, Silent Witness and detective novels. There is a common image that crime scene investigators use powder “dusting” to detect fingermarks. Although this method of detection is still used, modern science and technology have provided a number of advanced techniques that can detect latent fingermarks with high sensitivity and selectivity. The purpose of the exercises discussed in this paper is to allow students to gain valuable experience with fingerprint techniques and apply their chemical skills for the detection and enhancement of fingermarks on a range of surfaces. These methods are similar to those used in real casework.

Keywords: Fingermark, chemical detection, ninhydrin, 1,2-indanedione, luminescence.

Background

Latent fingermarks can be considered as complex chemical mixtures deposited in a given pattern on smooth surfaces that are touched with bare hands. As a result, fingerprint detection methods rely heavily on organic chemistry, physical chemistry, physics and also draw on analytical chemistry. For this reason, they are ideal specimens to use for the teaching of chemistry and related disciplines. This article presents how this can be achieved.

Most fingermarks found in forensic science casework are “latent”, or invisible to the naked eye. In order for a latent fingerprint to be visualised, it must be enhanced or developed in a manner that produces a high degree of contrast, hence differentiation, between the fingerprint and substrate. Typical latent fingerprint deposits are a complex chemical matrix of various organic compounds, inorganic salts, cosmetics, drug and food metabolites, cellular detritus and biological macromolecules. Latent fingermarks are generally derived from a combination of secretions from eccrine glands, present on all skin surfaces including the palms and soles of the feet, and sebaceous glands associated with hair follicles [1]. Eccrine perspiration comprises the aqueous fraction of latent fingerprint deposits, which includes up to 2.59 mg/mL total amino acid concentration [2]. Sebaceous glands contribute the lipophilic, or non-water soluble, fraction of latent fingermarks, consisting mostly of volatile and long chain fats and fatty acids.

A variety of techniques have been used to enhance the visibility of latent fingermarks. The combination of optical methods (absorption, diffuse reflection, luminescence, UV absorption and reflection), physical methods (powdering, small particle reagents, vacuum metal deposition), physico-chemical methods (physical developer, multi-metal deposition, iodine, cyanoacrylate) and chemical methods (ninhydrin and its analogues, metal complexation after ninhydrin treatment, 1,8-diazafluoren-9-one, 1,2-indanedione and genipin) allows for the development of fingermarks deposited on various surfaces. The most effective approach is to use a sequence of techniques that are appropriate for the type of substrate such as porous or non-porous surface and environmental conditions that the fingermarks have been exposed to.

The properties of the substrate upon which the fingerprint is deposited also significantly affect the behaviour of the latent fingerprint components and the detection methods available. Substrates are generally placed into three categories:

- Porous, including cellulose-derived materials such as paper;
- Non-porous, including ceramic, metal and plastic; and
- Semi-porous, including polymer-coated papers or materials that exhibit properties of both porous and non-porous substrates.

The aqueous fraction of latent fingermarks placed on porous surfaces are rapidly absorbed into the cellulose matrix, with small ionic or highly polar constituents such as metal salts and urea diffusing from the point of deposition over time. The amino acids present in the aqueous fraction do not diffuse and are highly stable within the paper substrate, provided it is not exposed to moisture, making them ideal targets for chemical latent fingerprint enhancement. The non-aqueous or lipid fraction are slowly absorbed into the superficial layers of the substrate and do not migrate from the point of contact. Fingerprint secretions remain on the surface of non-porous substrates and can be easily disturbed by friction or microbial activity. The presence of reactive components in the substrate – such as trace metal ions present in copy paper or free silanol groups on the surface of glass – may also catalyse chemical enhancement reagents or accelerate background development, reducing the contrast between the fingerprint and the background.

Amino Acid Sensitive Reagents

Most methods involving the use of chemical reagents rely on a reaction between the reagent and amino acids produced by skin secretions. Among the most commonly used amino acid sensitive reagents are colorimetric and fluorogenic reagents [3-5]. Ninhydrin (2,2-dihydroxy-1,3-indandione) and some ninhydrin derivatives are the most widely used reagents for developing latent fingermarks on paper and other...
porous surfaces. Ninhydrin reacts with amino acids to give a dark purple product known as Ruhemann’s Purple. The addition of an ethanolic zinc chloride solution to Ruhemann’s purple results in the formation of a red or orange complex that exhibits fluorescence at cryogenic temperatures.

1,8-Diazafluoren-9-one (DFO) is another commonly used compound [6]. DFO reacts with amino acids and proteins to give a pale pink-purple coloured product that is highly photoluminescent at room temperature. It produces excellent results with sweaty latent fingerprints on porous and semi-porous surfaces, as well as with weak fingerprints in blood. 1,2-indanedione, the most recent ninhydrin analogue adopted for case work, reacts with amino acids to form a pink product (Joullié’s pink) that is highly luminescent at room temperature (Figure 1) [7][8]. More recently, the addition a 1:25 to 1:4 molar ratio of zinc chloride to 1,2-indanedione to the reagent solution has greatly increased the sensitivity of the reagent in arid climates by catalysing a rate-limiting hydrolysis step in the reaction [9].

Each of these reagents react with amino acids via the same basic mechanism: the amination of a carbonyl group via Strecker degradation, as shown in Figure 1 [9][10]. The slight differences in reaction kinetics, sensitivity to ambient laboratory humidity and the addition of metal salts to the reaction provide an excellent model to demonstrate the effect of various functional groups on reaction kinetics. While both ninhydrin and 1,2-indanedione produce greater yields and react at faster rates in high humidity environments, DFO does not exhibit the same degree of sensitivity to slight fluctuations in humidity [11]. Conversely, Ruhemann’s purple is the only product that has demonstrated complex formation with metal salts, with the addition of metal salts to DFO developed fingerprints or the DFO reagent demonstrating no significant difference to control samples. Recent research confirmed that the role of zinc chloride in the 1,2-indanedione reagent was solely as a Lewis acid catalyst [9].

Lipid-Sensitive Reagents
The development of latent fingerprints on non-porous and semi porous surfaces uses techniques that generally target the non-water soluble deposit. The most commonly used technique is cyanoacrylate fuming in a sealed cabinet, followed by enhancement with luminescent stains (Basic yellow 40 and Rhodamine 6G) and powders [12]. Other reagents that target sebaceous material in fingerprints include iodine/7,8-benzoflavone, physical developer and small particle reagents [13][14].

Cyanoacrylate fuming leads to fingerprint development via an anionic polymerisation reaction (Figure 2). Vapourised cyanoacrylate molecules are adsorbed to the sebaceous emulsion in the fingerprint deposit. The polymerisation is then catalysed by nucleophiles including Lewis bases, water and other hydrogen-bonding molecules. Until recently it was believed to be the bound water in the fingerprint deposit which was solely responsible for the reaction, as aged and dry fingerprints resulted in poor polymer formation. Recently published work by McLaren et al. [17] indicated that pretreatment of aged fingerprints with methylamine significantly enhanced polymer formation, resulting in results similar to those obtained with fresh fingerprints. Consequently, it appears a variety of nucleophiles are responsible for initiation of the cyanoacrylate polymerisation reaction on latent fingerprints, with the greatest results observed when the fingerprint emulsion contains high concentrations of water, amino acids and other volatile components [17].

The water is held in the fingerprint deposit as an emulsion on the surface of non-porous materials. The product of the fuming reaction is a white solid on the surface of the material, which is generally hard to visualise. The staining reagents are highly photoluminescent dyes which bind to the cyanoacrylate polymer by non-covalent interactions.

Physical developer is a technique for developing the lipid fraction of latent fingerprints on porous substrates, which relies on chemical processes similar to that of wet photography. Samples are placed in a redox solution containing silver nitrate and ferrous ammonium sulphate as the active redox components and slowly agitated until ridge detail appears (Equation 1). The deposition of elemental silver is accelerated on areas containing high concentrations of sebaceous materials, resulting in the formation of black ridge detail on a pale background.

\[ \text{Ag}^+ + \text{Fe}^{2+} \rightarrow \text{Ag}_{(s)} + \text{Fe}^{3+} \] (1)

Prior to development in the redox solution the samples are soaked in deionised water followed by a maleic acid wash to remove inorganic salts such as calcium carbonate that are commonly used as binding agents in commercially available paper stocks and trace metals also present in the paper substrate [18]. The removal of these salts is essential as the presence of calcium carbonate results in the formation and precipitation of silver oxide, which stains the paper substrate black. The presence of other interferences can also lead to the rapid precipitation of elemental silver or silver chloride,
resulting in severe background staining and reduced contrast between the fingerprint and the substrate [18].

**Visualisation**

Reflection or luminescence imaging is used to visualise the developed marks, depending on the fingerprint detection technique employed. Luminescent visualisation is preferred to reflection due to the high contrast obtainable. For luminescent imaging, the light source needs to be filtered and the imaging system requires long-pass filters. Typically, for the imaging of developed fingerprints in the luminescent mode, the incident light is filtered to provide a wavelength band in the range 500-555 nm, while the detection filter needs to be a long-pass or band-pass filter in the range 550-600 nm.

Once the fingerprint images have been obtained, they may be digitally enhanced to improve contrast or sharpness, while preserving the original image for verification. The enhanced images are then compared with a reference image of a “suspects’” fingerprint. The comparison process involves looking firstly at the general type of the fingerprint (radial loop, ulnar loop, arch, whorl), followed by a systematic comparison of the minutiae that are present (bifurcations, ridge endings, etc).

**Learning Objectives**

Practical experiments involving the development of latent fingerprints are an ideal carriage for the discussion and introduction of students to a variety of complex facets of chemistry and light theory. In particular, these experiments highlight:

- The detection and analysis of low concentration analytes in complex matrices without destruction of the matrix;
- The application of physical, organic and inorganic chemistry to an unusual solid-state environment;
- The effect of interferences, environment and substrates on chemical reactions;
- The use of controls and blanks for quality assurance purposes;
- The ability to use two or more fluorescent dyes to improve visualisation by increasing the signal or the Stokes shift (for example, using basic yellow 40 and rhodamine 6G in tandem);
- A comparison of the limits of detection that can be obtained using qualitative absorbance and fluorescence spectroscopy, through the coupling alternative light sources and digital photography; and
- The significance of using procedures in a correct order (sequencing).

The students are also encouraged to improve their problem solving skills through the use of various development schemes and adaptations to existing reagents or visualisation techniques in an attempt to enhance weak or poorly developed fingerprints, as well as the identification of any fingerprints recovered from the exhibits. Furthermore, their understanding of these concepts can be reinforced through the utilisation of classroom discussions and reporting of the results to both lay and scientific audiences.

**Experimental Procedure**

The fingerprints were collected on various surfaces by requesting the donors (“suspects”) to handle specific substrates (exhibits) after lightly rubbing their fingers across their nose and forehead. Both porous and non-porous surfaces were used by the students in these experiments. Laser printer paper (white, 80gsm) and paper box packaging were used as porous surfaces, while plate glass, polyethylene bags and ceramics (coffee cups) were used as non-porous surfaces.

- The fingerprint investigation work was performed using two methods depending on the surfaces of the items:
- Using the reagent 1,2-indandione/zinc chloride which was found to provide superior results for porous surfaces such as paper. The reaction of 1,2-indanedione (Figure 1) with amino acids gives a highly photoluminescent pink product.
- A commercial cyanoacrylate fuming chamber (CynoFume FCC171 Forensic Cyanoacrylate Cabinet; Carter-Scott Design) was employed for this experiment on non-porous surfaces such as polyethylene. Exhibits were exposed to cyanoacrylate vapour in the enclosed chamber for 20 to 40 minutes depending on the degree of cyanoacrylate development observed on each exhibit. Rhodamine 6G is a very efficient photoluminescent stain that can be used as a general purpose stain for cyanoacrylate developed marks.

**Hazards**

Caution must be used when working with dichloromethane, ethyl acetate, ethanol, and cyanoacrylate/superglue. Dichloromethane is a toxic DG6 solvent, ethyl acetate, isopropanol, methyl ethyl ketone and ethanol are flammable solvents, while HFE7100 is a low toxic solvent. Cyanoacrylate (superglue) vapour is hazardous and should only be generated and used in an enclosed chamber. If a commercial chamber is not available in the laboratory, fuming can be performed in a sealed container – such as a fish tank – using an 80°C heat source to vapourise the cyanoacrylate monomer. These chemicals should be handled in a fume hood while wearing appropriate gloves, eye protection, and a laboratory coat.

**Procedure**

A clear plastic fruit and vegetable bag (polyethylene), containing several different items was sealed around the top with clear adhesive tape and presented to a group of students.

The students were required to give a detailed description of the evidence and to photograph it when it was initially received. Removal of the adhesive tape from the top of the plastic bag was done using tweezers without destroying either the bag or the adhesive tape. The contents were removed and each exhibit was documented and photographed.

Fingerprints from the donors - “suspects” - were requested by the students. The students obtained
fingerprints from the “suspects” using black ink and rolling each inked finger onto white paper. The inked prints were visualised using white light. The students were then instructed to invert the colour of either the developed fingerprint or reference fingerprint images so that the ridge colour appeared consistent across all images, allowing for easier comparison.

Porous surfaces: Paper box and printer paper
1.0 g of 1,2-indanedione was dissolved in 30 mL of dichloromethane, then 60 mL of ethyl acetate, 10 mL of acetic acid (glacial) and 1 mL of zinc chloride stock solution (8.0 g of zinc chloride dissolved in 200 mL of absolute ethanol) are added. This is then diluted with 900 mL of HFE7100 (Hydrofluoroether) carrier solvent [18]. The paper box was treated with IND-Zn solution by immersion and then development achieved in a dry heat press at 160° C for 10 seconds. Excellent strongly coloured visible fingerprints were obtained. Under luminescent detection conditions, the contrast was significantly better than using visible light reflection.

Non-porous surfaces: Ceramics, glass and polyethylene
The non-porous surfaces were initially treated by fuming with cyanoacrylate (superglue) according to the cabinet manufacturer’s standard operating procedures [13][19]. Cyanoacrylate vapour preferentially polymerises on greasy and moist latent fingerprint ridges to form a hard white polymer as seen in Figure 2. An initial ten minute cycle was performed with fresh fingermarks (“controls”) on substrates similar to each exhibit, after which the exhibits were examined. Having observed the development time was adequate (15 minutes in this case) the ceramic saucer was stained with a Rhodamine 6G photoluminescent staining solution [13][19]. The solution was prepared by dissolving 0.2 g of Rhodamine 6G in 200 mL of isopropanol, then adding 300 mL of methyl ethyl ketone and diluting with 1500 mL of water.

Digital imaging of fingermarks
Digital images were recorded using a Poliview IV CCD-based imaging system (Rofin Australia Pty Ltd) equipped with Polilight PL 500 forensic light source (Rofin Australia Pty Ltd). To record images in the luminescence mode, an appropriate monochromatic band was selected from the Polilight. A long-pass filter was placed in front of the Poliview camera for detection of luminescent fingermarks. Photographs can also be taken using a digital SLR camera with the Polilight as the illumination source. Appropriate filters on the camera lens were required for luminescence imaging.

Examples of reference fingerprints from a “suspect” are shown in Figure 3.

Porous surfaces
Porous surfaces were illuminated using the 505 nm band of the Polilight, and observed through a KV555 (555 nm) band-pass interference filter. Detected marks were captured individually by the Poliview CCD camera with 12 bit pixel depth resolution, 1/8 s exposure and the camera aperture was set to its maximum opening (F4). Three high-contrast prints (Prints 1-3), shown in Figure 4, were found on the inside surface of the opening flap. These marks were exploitable, exhibiting adequate ridge detail for identification purposes.

Non-porous surfaces
Non-porous surfaces were illuminated using the 530 nm band of the Polilight, and observed through a 610 nm long-pass filter. Five marks on the under rim were found, as shown in Figure 5 (print 4, 5). The marks showed contrast against the white reflective surface. While there appeared to be sufficient ridge detail for identification by an expert analyst, these fingermarks were particularly challenging for students learning the basics of fingermark identification. On the topside of the saucer, faint partial prints and smudges were present, but none were exploitable.

Comparing recovered fingermarks to reference inked fingerprints
Students were instructed to perform a manual comparison on a maximum of five fingermarks...
recovered from their exhibits to the reference inked fingerprints obtained from a named “suspect” using the Analysis, Comparison, Evaluation and Verification (ACE-V) methodology [20]. The verification step was performed by other members of their laboratory group, although ideally it should be performed by a student independent to the group. Firstly, primary level detail, or pattern, of the recovered fingermark was identified, followed by marking of the core and delta, ridge count between these points and a sufficient number of minutiae for comparison purposes (at the discretion of the analyst). These were then compared to the reference fingerprints and students were required to evaluate their evidence based on identification, insufficient information for comparison or exclusion of the “suspect”.

Print 4 – Underside of saucer Print 5 – Underside of saucer

Figure 5 Fingermarks on ceramic treated with cyanoacrylate, stained with rhodamine 6G, and visualised in the photoluminescence mode with excitation at 530 nm and observation using a KV610 (610 nm) long-pass barrier filter.

The success of each student in achieving identification was dependent on the quality of the developed fingermarks, the photographs recorded of each fingermark and their ability to identify a sufficient number of relevant minutiae.

Conclusion
This experimental work gave the students experience in the fundamentals of fingerprint detection and comparison. The techniques used are part of the standard sequence for porous and non-porous surfaces respectively, and the students carried out the full set of tasks required to enhance and identify a fingerprint, from chemical treatment to visualisation to comparison with reference inked prints. The exercises discussed in this paper allow students to gain valuable experience with fingerprint techniques and applied chemistry in a manner that mimics common casework scenarios.

Acknowledgments
We wish to thank the Forensic Science students at UTS who have trialled this exercise.

References
15. Services, AFP, Canberra, ACT.
Chemistry LabSkills: Software to Support Laboratory Skills from Schools’ Pre-University to University Foundation Courses

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Abstract
The UK’s Centre for Excellence in the Teaching and Learning of practical chemistry, Bristol ChemLabS, has completely rethought the way its practical chemistry course is delivered and has created an e-learning resource called the Dynamic Laboratory Manual (DLM) to support this. The emphasis on e-learning allows students to engage with the material as a pre-lab exercise. The concepts from the full undergraduate degree DLM have been adapted for the UK’s pre-university courses and for generic foundation chemistry courses at universities worldwide.

Keywords: Bristol ChemLabS, e-learning, pre-lab, LabSkills, practical, supported self-study

Introduction
Chemistry LabSkills is an unusual piece of software for several reasons [1, 2]. First it was produced by a university chemistry department who had developed a novel way of supporting its undergraduate practical skill development course as part of an honours degree program. Second it is software that is designed to aid practical work in chemistry and not to replace it by simulated experiments. Third it was produced in conjunction with an educational software company, Learning Science, whose staff have a strong science background themselves, particularly in Chemistry.

During the period 2005-8 the School of Chemistry at the University of Bristol, the home of Bristol ChemLabS, the UK’s Centre for Excellence in the Teaching and Learning of practical chemistry, totally revamped its traditional practical courses. It was replaced with a practical skills course that was divorced from the lecture program and from the false segregation of organic, inorganic and physical chemistry. This course was supported by a major investment in e-learning software (called the Dynamic Laboratory Manual or DLM) that also allowed formative and summative assessment of practical skills. One of the many innovations of the Bristol ChemLabS project was the establishment of the full-time post of School Teacher Fellow [3,4]. The STF is an experienced secondary school science teacher and the benefit in the ‘front loading’ of practical work to pre-university level chemistry was obvious to someone from that background. With a resident STF in post it was possible to develop a pre-university DLM called Chemistry LabSkills and from this, a university foundation level LabSkills package was also developed.

So what is LabSkills?
LabSkills is innovative software that helps chemistry students develop essential practical skills. It is made up of 50 chemistry modules, each containing a variety of activities for study that are both interactive and engaging. For many elements there are virtual experiments that students can explore, opening taps, adjusting heating and many more, that allow students to understand what is going on and why a practical may or may not work if certain things are done and in a certain sequence. Students learn quickly, gain confidence and perform better in practical work having used a resource whose activities are challenging and fun; being able to rehearse practicals beforehand in a virtual environment has been shown to have a marked impact on cognition [5,6].

The LabSkills resources include common techniques and experiments, best practice, safety, videos, calculations, tests, revision and exam practice questions. Each technique contains interactive simulations which are intuitive and media-rich. These provide multiple opportunities to explore techniques through trial and error, addressing all common student mistakes with questioning, hints and feedback. Setting up equipment correctly, optimising experimental conditions and visualising molecular behaviour during instrumental analysis is also covered and exam-style, multi-step questions are provided with optional interactive hints and feedback throughout.

There are in built elements of skills and competency training where there are questions and worked examples with interactive hints and feedback on topics such as the understanding of basic chemical tests and the appropriate choice of equipment, mathematics within chemistry covering errors, accuracy, precision and significant figures, and in balancing equations and calculating quantities, concentrations, reaction rates and equilibrium constants.

The Lab techniques modules are made up of several elements. There are simulations that allow the student to work out why a piece of apparatus is set up as it should be. These scenarios start from the point of view of the inexperienced student. Once the correct arrangement of the equipment has been mastered there is a video section. Here short sections of video clips show the latest equipment being used and provide a step-by-step breakdown of each technique with brief notes which McKelvey (2000) [7] notes is a very powerful aid to cognition. The notes are the sort of information that a teacher or demonstrator would give to a student if they were alongside them in a practical class; the sort of information that comes from experience and that is not found in a text book. There are a few self-test questions to reinforce and consolidate learning for each technique.
that may be printed out or uploaded to the VLE if required. This facility is not available on the teacher memory stick only version (see below). The Safety section has interactive images of apparatus with safety and good laboratory practice emphasised.

The software does have examples of experiments where the various practical techniques may be used with interactive images for each experiment broken down with information on background and context, health and safety, experimental procedure and observation opportunities.

Three versions are available for educators; the first is a version that runs on a virtual learning environment (VLE) and a second that runs on an individual computer for seminar work or individual self-study. A third version, with much less functionality for individual students is also available. Details of all products are available at http://www.labskills.co.uk/. In the VLE form, it can of course be used at the place of learning or at home where students can practice in a safe environment and develop skills by exploring simulations, answering questions and correcting mistakes and misconceptions.

Why is LabSkills effective?
The learning resources in LabSkills require students to actively participate in the learning process and to come into lab classes prepared for the practical to be undertaken. The high level of responsive interaction requires students to continually test their understanding of the science and learn from their successes and mistakes. Instant feedback is provided to formative and summative problems which supports students whatever their level of knowledge and understanding.

Using LabSkills, students can prepare for practical classes by exploring the techniques and experiments that they will then encounter in the laboratory itself. They can practice in a safe environment and receive directed and focused feedback on their performance at whatever pace they are working. Virtual glassware costs nothing to replace! The students then can recognise that laboratory classes are there to develop practical skills and are not simply a recipe following exercise.

Implementing LabSkills

The resource can be used in several ways. Before starting a practical (‘pre-lab’) students can be directed to work through specific sections in the lead up to practical work. This supported self study may be used as preparative work and will result in more effective use of valuable laboratory time. Students can submit printed test results if necessary. Being fully SCORM compliant LabSkills allows results to be viewed electronically through the institution’s learning platform. In seminars and tutorials the whiteboard option allows the screen size to be maximised so that interactive elements can be used for whole class reviews and group discussion.

During the practical class the software may be run on PCs and whiteboards in the laboratory as an aide memoire. Where needed LabSkills provides an effective way for students to actively revise practical work away from the laboratory when repeating the experiment is not possible.

LabSkills also has a number of reference resources; the equipment glossary with descriptions of commonly used equipment, reagent glossary with descriptions of reagents commonly used at this level, lab health and safety comments, a scientific calculator and of course a periodic table.

There are fourteen self-contained modules covering the main lab techniques commonly used at this level shown in Table 1. Each module contains a mix of simulations, videos, safety resources and multiple choice tests.

<table>
<thead>
<tr>
<th>Table 1. Preparation and purification techniques covered.</th>
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<tr>
<td><strong>Filtration</strong></td>
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<td><strong>Recrystallisation</strong></td>
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<td><strong>Melting point</strong></td>
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<td><strong>Thin layer chromatography</strong></td>
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<td><strong>Colorimetry</strong></td>
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<td><strong>Enthalpy change of combustion</strong></td>
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<td><strong>Enthalpy change in solution</strong></td>
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</tbody>
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Added to this are sixteen additional modules consider core laboratory competencies covering basic skills, lab calculations, and chemical tests shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Chemical tests, basic laboratory skills, chemistry calculations and instrumental techniques.</th>
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</thead>
<tbody>
<tr>
<td><strong>Tests and Observations</strong></td>
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<tr>
<td>Tests for inorganic compounds</td>
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<td>Tests for organic compounds</td>
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<td>Transition metal compounds</td>
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<td>Reaction rates</td>
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<td>Equilibrium constants</td>
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Twenty widely performed experiments covering preparative, qualitative and quantitative practicals are also included to augment the institutions own practical scripts.

Other Uses and Development of LabSkills

Foundation Chemistry LabSkills is already being used in a number of universities in South Africa and Canada with interest being shown in Australia and the United States. Feedback indicates that a major strength is in the training of the postgraduate demonstrators/teaching assistants so that gaps in their understanding of practical procedure are overcome and a more unified approach to
work can be developed. The schools and colleges pre-university version, A-Level LabSkills is already in use in schools in countries from Mongolia to South Africa as well as widely within the UK.

LabSkills also provides highly effective support for trainee and newly qualified teachers. In partnership with the Royal Society of Chemistry it has been used in over 50 universities in the UK and was available to up skill 1100 postgraduate trainee chemistry teachers through the Discover LabSkills project www.rsc.org/labskills in the last two years. The first year of this programme was evaluated by the National Foundation for Education Research NFER) an external body [9].

Within the School of Chemistry at the University of Bristol the Dynamic Laboratory Manual methodology is already being developed and implemented in two Doctoral Training Centres (DTCs), one in Chemical Synthesis and the other in Functional Nanoscience. DTCs are EPRSC-funded four-year PhD programmes in which the first year focuses on advanced training in research methods.

Acknowledgments

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References


Developing an FTIR method to monitor heterogeneous catalytic reactions

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Abstract

This experiment aims at enhancing students experience in utilizing FTIR spectroscopy in monitoring reactions over solid surfaces and characterizing products in the vapor phase. It employs FTIR spectroscopy to study a heterogeneous catalytic reaction where the products are qualitatively and quantitatively monitored as a function of time. Besides demonstrating the importance of FTIR spectroscopy in quantitative evaluation of a reaction, the experiment involves areas that are not commonly covered in chemistry laboratory courses including heterogeneous catalysis, solid surfaces, and solid-gas interactions. In addition, the experiment allows students to vary reaction conditions, observe associated changes, and propose possible explanations.

Keywords: FTIR spectroscopy, heterogeneous catalysis, methanol, dehydration, dimethy ether.

1. Introduction and objectives

It is necessary to improve chemistry and chemical engineering teaching programs by incorporating more experiments that enhance the utilization of modern instruments and application software. Students should be taught to utilize as many functions and facilities as possible of the modern instruments so that they can better understand and present results and withdraw conclusions. One of the basic instruments in almost every chemistry laboratory is the FTIR spectrometer. Most of the experiments designed for basic and even advanced chemistry laboratory courses are based on qualitative measurements of solid or liquid samples. Measurements on gas samples using FTIR spectroscopy are very rarely involved in undergraduate courses. Moreover, experiments rarely utilize FTIR spectroscopy for quantitative evaluation of reaction products which becomes very useful when using typical analytical methods is difficult. In addition, students are rarely taught to obtain the text files of the spectra for further manipulation by a spreadsheet program which allows them to compare several spectra in one graph and look at selected regions of the spectra more closely. Better utilization of functions and facilities available with FTIR spectroscopy enhances students’ appreciation of the technique. Therefore, the first objective of the present experiment is to utilize FTIR spectroscopy in qualitative and quantitative monitoring of a reaction in real time.

The second objective of the present experiment is to introduce students to concepts related to heterogeneous catalysis and its applications in industrially important processes, especially in relation to environment friendly fuel alternatives. Although heterogeneous catalysis is behind the production of > 80% of chemicals including petroleum and petrochemicals, it has not received enough attention in theoretical as well as practical chemistry courses.

In addition to the above discussed objectives, the experiment provides students with a chance to deal with gases, gas controllers, and gas-solid reactions under continuous flow conditions. It also shows students how slight changes in the experimental conditions may affect the reaction pathways and hence the nature of products significantly.

In this experiment, a commercially available γ-alumina will be employed as a catalyst for the dehydration of methanol to DME in the vapor phase. The reaction will be conducted under continuous flow conditions and will be monitored in real time using FTIR spectroscopy. The effect of the reaction temperature and the feed gas flow rate will also be studied.

2. Background

Infrared spectroscopy has been widely used for qualitative and quantitative analyses of chemicals and chemical reactions. Infrared spectroscopy is based on the interaction of radiation in the middle infrared region, 2.5-50 μm, with molecular vibrations. A molecule is infrared active if its molecular vibrations are associated with a change in the dipole moment. Therefore, homonuclear diatomic molecules do not absorb infrared radiation due to the fact that they do not have a dipole moment. Molecules containing heteroatoms have vibrations and rotations that are infrared active. Large molecules usually have a large number of vibrations and rotations that generally complicate their infrared spectra. However, such spectra usually have some unique fingerprints that represent common functional groups. The fact that infrared absorbance is directly related to the concentration of a component in a mixture allows one to use FTIR methods to identify and quantify components of a mixture including gas mixtures.

Heterogeneous catalysis plays a key role in various environmentally important applications, especially in the area of clean fuel alternatives. Along this line, the conversion of natural gas and other natural-gas-based chemicals into more efficient fuel alternatives is attracting a great attention from researchers and industries as a promising approach to reduce the dependency on petroleum oil which is currently associated with serious economical and environmental problems. One of these promising conversion routes is the dehydration of methanol to dimethyl ether, DME. Besides its various industrial applications as an
intermediate for the production of a range of fine chemicals. DME has been recognized as a very promising fuel alternative that could potentially reduce the dependence on petroleum-based fuels. The increasing interest in DME as an alternative fuel is due to several unique physical and chemical properties that DME possesses [1-2]. It is a colorless, nontoxic, noncorrosive, noncarcinogenic and environmentally friendly substance with a boiling point of -25 °C. Hence, it is usually handled as a liquid in pressurized tanks, just like liquefied petroleum gas, LPG. DME has a high cetane rating of 55-60 which is much higher than that of methanol and even higher than that of conventional diesel, 40-55. In addition, DME is an environmentally friendly fuel as it is a clean-burning chemical without the emission of black smoke or SO2. Besides its promising application as fuel for diesel engines, DME can be used as a source of hydrogen for fuel cells through partial oxidation or steam reforming [3]. Since DME can be obtained from methanol, it can be produced from various feed-stocks including coal, natural gas, biomass, etc.

The most widely studied catalysts for the methanol to DME conversion are based on zeolites [4] and γ-Al2O3 [5]. Alumina is a cost-efficient material that can be tailored to possess unique textural properties including high surface areas. It has been widely used as a catalyst support and as a catalyst due, mainly, to its surface strong Lewis acidity.

3. Experiment Description

3.1 Time requirement
- In the laboratory: 4 hours are needed to complete the experimental work.
- After the laboratory session: 1-2 hours to plot and discuss the results and complete the report.

3.2 Materials and equipment
- γ-Al2O3: can be obtained from SASOL North America Inc or from Aldrich.
- Methanol (> 99.5% pure).
- FTIR spectrometer (the reported results in this experiment were recorded on an IRAffinity-1 FTIR spectrometer from Shimadzu by averaging 16 scans at 4 cm⁻¹ spectral resolution).
- Reactor system as described in the next section. Note: The reactor setup should be prepared by laboratory staff before the laboratory session.

3.3 Experimental apparatus and procedure
The catalytic dehydration of methanol in the vapor phase was studied using a continuous-flow fixed-bed reactor and FTIR spectrometer for the analysis of the gaseous products as shown schematically in Figure 1. The reactor was made of a stainless steel U-shaped tube of 4 mm inside diameter and was heated using a tube furnace equipped with a temperature controller and a K-type thermocouple, positioned in the proximity of the catalyst bed. An IR cell, equipped with an inlet and an outlet for gases, was connected to the exit of the reactor and was housed in the spectrometer chamber during the whole experiment allowing for continuous measurement of the gaseous products exiting the reactor. The cell, purchased from Pike Technologies, USA, was made of a 15-cm long stainless steel tube (25 mm inside diameter) and was equipped with two KBr windows. The cell was also equipped with a furnace and a temperature controller with an ability of heating at temperatures as high as 350 °C. Methanol was introduced to the reactor by bubbling N2 as a carrier gas through a methanol saturator that was kept at a constant temperature in an ice bath to control the partial pressure and hence the composition of the feed. The flow rate of the carrier gas was 15 ml/min and was monitored by a mass flow controller. The FTIR cell and the transfer line between the reactor and the cell were heated at ~150 °C, using heating tape, to prevent any condensation. The transfer line and all connections were made of stainless steal. In all experiments 0.125 g of 120-180 mesh particles of the catalyst was packed in the reactor between glass wool plugs. Before each reaction, the catalyst was heated for 30 minutes under N2 flow (15 ml/min) at 350 °C, and the reactor was then cooled down to the reaction temperature, 200 °C. Once a stable reaction temperature was obtained, a background spectrum was collected for the cell with He flow before starting the reaction. The carrier gas was then allowed to bubble through the methanol saturator. FTIR spectra of the eluting products were recorded every 5 minutes for the first 15 minutes then every 15 minutes for another 45 minutes on stream. The reaction temperature was then raised to 300 °C and an FTIR spectrum was recorded for the products after a stable temperature was obtained. The flow rate was then raised to 30 ml/min and an FTIR spectrum was recorded after 5 minutes. For catalytic activity calculations, as described below, a blank experiment was conducted separately under the same conditions (200 °C) following the same procedure using an empty reactor, without a catalyst, where 4 spectra were recorded during a period of 10 minutes. All spectra were saved as text files for further manipulation.

4. Results and discussion

4.1 FTIR spectra of the products
Using Microcal Origin program, the FTIR spectra were plotted from their text files. The spectra from the blank experiment and for the reaction products at 200 °C are shown in Figure 2 and Figure 3 respectively. Figure 4 shows the spectral region 800-1250 of the spectra in Figure 3. The spectra of the products at 300 °C at flow rates of 15 ml/min and at a higher flow rate, 30 ml/min, are shown in Figure 5.
4.2 Calculations

The catalytic activity was expressed in terms of % conversion of methanol, plotted in Figure 6, which was calculated based on comparisons with the spectra recorded in the blank experiments. The absorbance of methanol at 1030 cm$^{-1}$, averaged from 4 blank spectra, was determined. The ratio between the absorbance at the same wavenumber in each spectrum of the products and the absorbance in the blank spectra was used to calculate the % conversion of methanol. DME was quantified based on its characteristic absorbance at 1175 cm$^{-1}$. Baseline corrections were done for the absorbance at 1030 cm$^{-1}$ and the absorbance at 1175 cm$^{-1}$ by selecting starting and ending points at 1025 to 1036 cm$^{-1}$ and 1140 to 1220 cm$^{-1}$, respectively. The absorbance that corresponds to the theoretical yield of DME was calculated based on the absorbance and the % conversion in selected spectra where 100% DME selectivity was obtained. The % yield of DME was then calculated using the absorbance at the same wavenumber in each spectrum of the products and the one that corresponds to the theoretical yield. The % selectivity to DME was calculated as follows:

$$\% \text{ selectivity} = \frac{\% \text{ yield of DME}}{\% \text{ conversion of CH}_3\text{OH}}$$

Methanol and DME were quantitatively evaluated to determine the % conversion, which relates to the catalytic activity, and the % yield of DME which reflects the selectivity to the desired product. The other products, CH$_4$ and CO$_2$, were not quantified as they were observed only in negligible amounts. Otherwise, their concentrations should be measured from calibration curves established based on blank experiments for each gas separately.

4.3 Discussion

DME can be obtained from methanol by dehydration over solid acid catalysts according to the following reaction:

$$2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}.$$
The fact that no other products formed made it easy to follow the reaction by FTIR spectroscopy since methanol and the product, DME, show strong distinguished FTIR peaks.

Figure 6. The % conversion of methanol as a function of the time on stream at 200 °C and a flow rate of 15 ml/min.

The spectra recorded in the blank experiment, Figure 2, show very similar absorbance for methanol over a period of 10 minutes. At a reaction temperature of 200 °C, DME was, almost, the only product, resulting from the dehydration of methanol, and only negligible amounts of CO\textsubscript{2} were observed, Figure 3. The catalyst showed a stable activity during the one hour on stream indicating a good durability of the catalyst. The % conversion was around 86% (with uncertainty of < 4%) during the whole reaction period as shown in Figure 6. The formation of DME as the only C-containing product indicates that at this temperature no other reactions other than the dehydration take place. Since methanol dehydration is known to take place on Lewis acid-base pair sites and its rate increases as the surface Lewis acidity increases [6], these results indicate the dominance of the role of Lewis acid sites (Al\textsuperscript{3+}) on the alumina surface and that they promote the dehydration reaction. On the other hand, raising the reaction temperature to 300 °C resulted in the decomposition of some methanol, or possibly DME forming a small amount of CH\textsubscript{4}, Figure 5. When the flow rate was raised to 30 ml/min at 300 °C, the overall conversion almost did not change but the selectivity to DME significantly improved as more DME and less CH\textsubscript{4} formed. Since lower flow rates are associated with longer contact time with the catalyst, the formation of CO\textsubscript{2} and CH\textsubscript{4} at low flow rates may indicate further decomposition of some DME product or the decomposition of adsorbed intermediates. This explains the higher selectivity to DME at the higher flow rate where the contact time is shorter and the chance for such decomposition is less.

5. Conclusions
The experiment utilizes FTIR spectroscopy to monitor a heterogeneous catalytic reaction. Employing FTIR spectroscopy to study the catalytic activity of γ-alumina in vapor phase methanol dehydration to DME was found very efficient where the products of the reaction were qualitatively and quantitatively monitored as a function of time. The experiment also allows students to easily vary some reaction conditions, including the reaction temperature and the flow rate of the carrier gas, which noticeably affect the reaction pathways and the products.

Acknowledgement
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References
In 2011, the Australian Learning and Teaching Council funded the establishment of the Chemistry Discipline Network, and by late 2011 it had over 80 members, representing all Australian universities. The aim of the Network is to strengthen the learning and teaching of chemistry by forming a community of practice to exchange experiences, share resources and implement best practice. The guiding principle of the Network is open communication and we have already observed benefits from this.

The Network aims to overcome barriers to the adoption of improved teaching methods by using strategies explored by others and through the open sharing of teaching techniques and resources. Everyone teaching tertiary chemistry is welcome to join (it is not limited to one member from each university).

We are currently working in three areas:

- a comparative mapping exercise of all current tertiary chemistry at several universities, including what is taught and how it is assessed;
- a website (chemnet.edu.au) for sharing learning objects and for discussion of any topic of interest to tertiary chemistry educators.

**Management Committee:** Madeleine Schultz, *Director*, QUT; Mark Buntine, Curtin and RACI; Glennys O’Brien, (UOW); Siggi Schmid, USyd; Daniel Southam, Curtin; Brian Yates, UTas. For more information, please contact the project officer, Dr James Mitchell Crow (chemnet@qut.edu.au).
2012 is the year of reflection on the great activities of IYC in 2011 and determining how those initiatives can be maintained and improved. ChemEd 2012 is the opportunity for chemistry educators, secondary and tertiary, and researchers from across Australia and the world to come together post-IYC and share ideas and strategies, and celebrate chemistry in its many guises. The 2012 conference will be held in Adelaide, South Australia with the 3 universities, the Australian Science & Maths School, RiAus and famous wineries and restaurants nearby. The venue is Immanuel College, a secondary co-educational school with excellent and modern conference, accommodation and recreational facilities. The venue is close to seaside Glenelg and also easily accessible to Adelaide CBD and the airport. Confirmed keynote speakers include Prof Renee Cole and Prof MaryKay Orgill (both US) and Prof Peter Mahaffy (Can.). All are involved in researching strategies to enhance the teaching and learning of chemistry across secondary and tertiary levels. Biographies are included in the link to conference website below. Themes include Experiencing Chemistry, Teaching and Learning Strategies, the National Chemistry Curriculum, Resources for Learning and Eat, Drink, Think Chemistry (including food and wine). You are cordially invited to possibly the final stand-alone chemistry education conference for the RACI, and we really look forward to welcoming you in Adelaide next July.

On behalf of the Italian Chemical Society and of its President prof. Vincenzo Barone, it is an honour, a privilege and a pleasure to invite you to Rome in July 2012 on the occasion of the ICCE and ECRICE conference. For the first time, the two major conferences on Chemical Education will join under the same roof, that of Rome, the eternal City: we are really proud of this and we will do our best to ensure full success of the event and a wonderful Italian trip of all. http://www.iccecrice2012.org/
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