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Introduction

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Combatting professional amnesia - outcomes of twenty years of federally funded projects in tertiary chemistry education in Australia

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Abstract

All federally funded projects in chemistry education from 1995 - 2015 have been reviewed. Most of the projects generated outputs that are still in use. A gradual evolution from smaller, technology-based projects to larger, workshop based projects is observed. Common themes addressed by the projects are first year foundations, laboratory learning and interdisciplinarity. Reports, publications and websites resulting from the projects have been collected at http://chemnet.edu.au/?q=node/91.

Keywords:

chemistry education; topic specific professional knowledge; pedagogical content knowledge; dissemination

Introduction

It has been said with good reason that university teaching suffers from "professional amnesia" (Bucat, 2004, p. 225). This is because individual lecturers gradually improve their teaching over their careers, but their specific teaching strategies that make learning easy for students are lost upon their retirement. These strategies are topic and situation specific, and include useful representations, illustrations and demonstrations together with an understanding of common misconceptions and difficulties, along with a repertoire of analogies and examples that aid student learning. Shulman (1986) developed the notion of pedagogical content knowledge (PCK) to describe this set of information relevant to teaching specific topics. His concept was later expanded upon in the area of science education to be defined as the transformation of content knowledge into a teachable form (Magnusson, Krajcik, & Borko, 1999). Over the past thirty years, PCK has been adopted widely as a useful concept at the secondary level, particularly in teaching science. A sophisticated tool, the Content Representation (CoRe) has been developed to allow its capture (Loughran, Mulhall, & Berry, 2004), and methods for advancing high school teachers' PCK have been proposed (Loughran, Berry, & Mulhall, 2012; van Driel & Berry, 2012; van Driel, de Jong, & Verloop, 2002; van Driel, Verloop, & de Vos, 1998).

Shulman's original concept of PCK was thoroughly revisited in 2012 at a PCK Summit (Carlson, Stokes, Helms, Gess-Newsome, & Gardner, 2015). A new consensus model of PCK was developed to combat weaknesses of the model of PCK then in use (Gess-Newsome, 2015; van Driel et al., 1998). In this model, the new term "topic specific professional knowledge" (TSPK) is given to the set of knowledge "determining effective instructional strategies; selecting multiple representations; organizing content to use specific examples to highlight and build overarching ideas; understanding incoming student knowledge or misconceptions; and knowing how to integrate science and engineering practices, cross-cutting concepts, and the nature of science" (p. 32). Within this definition, TSPK is canonical, generated by research or best practice, codified by experts and available for study and use by teachers. In contrast, in the new model the terms "personal PCK" and "pedagogical content knowledge and skill" (PCK&S) are reserved for classroom practice, which is inherently personal and is gained through experience and reflection. This new definition recognizes that the actions of teachers in a classroom include responding dynamically to student feedback and cannot be completely planned in advance. In this manuscript the term TSPK is used to describe the public, transferrable knowledge resulting from studies into student learning, which was called PCK under the previous definition.

When looking to reduce professional amnesia in tertiary teaching by transferring TSPK it must first be recognised that there has been limited research into the concept at the tertiary level (Fraser, 2015). A few examples explicitly attempting to collect tertiary TSPK in chemistry have appeared (Davidowitz & Rollnick, 2011; Goes, Leal, Corio, & Fernandez, 2013; Padilla, Ponce-de-León, Rembrado, & Garrizt, 2008; Padilla & van Driel, 2011) but without discussion as to how the outputs would be used by less experienced academic staff. In addition to these projects, there is a growing body of tertiary chemistry TSPK resulting from projects in teaching and learning that develop teaching resources. The development of such resources involves careful reflection and feedback from students to ensure that the resources are effective. Such resources and their embodied TSPK should in principle be transferrable to novice academic staff. However, an effective mechanism for distributing them in a useful way is so far lacking.

The dissemination of the outcomes of tertiary education research projects is hampered by the diffuse nature of the research and the development of resources that are often specific to a particular institutional context. In addition, most academic staff are too busy to read through project reports and publications to obtain new teaching strategies and resources, so the results of such projects are rarely adopted by others. This leads to
significant duplication of effort and waste when research that has already been conducted is repeated, and project outputs and resources are not used by other teaching staff. It is important to note that the searchability of outcomes has become significantly easier in the past decade with the advent of Google Scholar and improvements in digitisation of historical data. The sharing of digital resources including images, video animations and simulations is very easy in the 21st century and there is certainly demand from academic staff for tested resources suitable for teaching particular content.

This situation in the learning and teaching domain can be contrasted with the research methodology in the physical sciences, where published reports form the basis of subsequent research projects that further progress the field. Such a methodology requires outcomes that are searchable together with the understanding that it is not generally acceptable nor worthwhile to repeat experiments that have already been published. Instead, new research adopts and builds upon published results.

This is not to claim that no dissemination of educational research ever occurs. Academic staff keen to improve their teaching frequently participate in formal courses on teaching at university, and such courses are now required for new academic staff at many institutions. In recent years in Australia this has most often been within the framework of a Graduate Certificate in Higher Education or similar program. In these courses, the current understanding of adult learning (pedagogy) and best practice in design and use of teaching environments (including virtual environments) is typically covered. However, such courses are inevitably generic and so TSPK, which is inherently discipline-specific and even sub-discipline-specific, is not included. In addition to such formal courses, disseminating outcomes and informing the community about projects through workshops is increasingly popular within educational projects.

This manuscript attempts to combat the threatened loss of TSPK within tertiary chemistry education by summarising all federally funded projects over the past two decades. Publications and other outputs resulting from the projects have been collated on a website to facilitate access. This will enable results of past projects to be used by others, and where possible will facilitate the transfer of TSPK that has been enunciated. It should be noted that there have been many other valuable projects over this period that have been conducted with internal institutional funding or without funding at all; those projects are beyond the scope of this manuscript.

Results and Discussion

Six different agencies have been responsible for distributing funding for tertiary education research in Australia over the last 20 years. These began with the Committee for the Advancement for University Teaching (CAUT) (1992 - 1995), the Committee for University Teaching and Staff Development (CUTSD) (1996 - 1999), and the Australian Universities Teaching Committee (AUTC) (2000 - 2004) (Parker, 2006). In 2004 the Carrick Institute for Learning and Teaching in Higher Education was established; the name was later changed to the Australian Learning and Teaching Council (ALTC) and this was closed in 2011 (McDonald, 2011). The most recent was the Office for Learning and Teaching (OLT), which was abolished in the May 2015 Budget and disbanded in mid-2016. All of these agencies were dedicated to improving tertiary teaching with minor administrative differences and gradual evolution of their priorities.

The 25 projects funded by the Australian federal government in chemistry education since 1995 are tabulated in Table 1. All available documentation and resources from these projects have been collated and included on the website http://chemnet.edu.au/?q=node/91. Unfortunately, for three of the earlier projects (projects 6, 7 and 14) no information could be found and attempts to contact the grant holders were unsuccessful. It should be noted that for some funding schemes, the signature of a Head of School or equivalent was required although this person may not have had any role in the project.

It can be seen from Table 1 that while a number of projects were funded in the late 1990s, there was a gap of eight years from 1999 until 2007 during which the only funded project was ACELL (project 16) (Buntine et al., 2007), which was funded through the DEST Higher Education Innovation Programme in 2004. ACELL was the follow-on from the large CUTSD grant APCELL (project 13) (Barrie, Buntine, Jamie, & Kable, 2001), funded in 1999, that has continued to expand with ASELL (project 19) funded by the ALTC in 2009 (Yeung et al., 2011). From 2007 onwards there has been a small but consistent number of grants funded, most of which have attracted six figure sums. All projects since 2007 except for project 20 (which was interdisciplinary) have multiple institutions deeply involved, which is a significant change from the smaller, local projects funded earlier. This reflects the increased emphasis on collaboration and dissemination within more recent funding priorities, in part to ensure broader uptake of outcomes, after a review of the CAUT and CUTSD grant system in 2006 found weaknesses in that regard (Parker, 2006). Collaboration was expected in grant applications to the ALTC (McDonald, 2011) and OLT and it is expected that this will continue.

It is also apparent from the titles in Table 1 that prior to 2000, a significant focus of the projects was around the use of technology in teaching. This focus parallels the increased use of computers and information technology over those years. The decreased emphasis on projects focussing on technology since 2000 reflects the fact that computers, digital learning resources and on-line activities are now fully embedded in many aspects of university teaching. Most projects funded since 2000 include building a website as part of the output of the project. Although technological developments have made many of the specific outputs of the older grants redundant, the outcomes in terms of design principles for optimising student engagement with digital resources remain valid and important.
Table 1. Summary of federally funded chemistry education projects 1995 - 2015 (* = project outcomes still actively used)

<table>
<thead>
<tr>
<th>Year</th>
<th>Funding agency</th>
<th>Title of project</th>
<th>Authors</th>
<th>Amount of funding</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>1995 CAUT</td>
<td>Development and production of videos for microscale laboratory courses</td>
<td>Jacki O'Connor, Barry Shearer, T Smith</td>
<td></td>
</tr>
<tr>
<td>2*</td>
<td>1995 CAUT</td>
<td>Interactive multimedia materials which develop student understanding of chemical equations</td>
<td>Patrick Garnett, Mark Hackling, Ron Oliver</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1995 CAUT</td>
<td>Learning modules for computational chemistry over AARNET</td>
<td>Brian Salter-Duke, Margaret Wong, Brian Yates, Ted Lloyd</td>
<td></td>
</tr>
<tr>
<td>5*</td>
<td>1995 CAUT</td>
<td>Interactive teaching &amp; testing tutorials for first year chemistry (ChemCAL)</td>
<td>Peter McTigue, Peter Tregloan, Paul Fritze, Carmel Naughta, Quentin Porter</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1996 CAUT</td>
<td>Instruments on Computers: Teaching Chemical Instruments through Interactive Simulations</td>
<td>Mark Williams, Rodney Blanch</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1997 CAUT</td>
<td>Development of microcomputer software which employs anaglyphic graphics to aid the perception of three-dimensional chemical structures</td>
<td>Bob Vagg</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1997 CAUT</td>
<td>The role of video conferencing in enhancing teaching/learning via a virtual faculty</td>
<td>Greg Klease</td>
<td></td>
</tr>
<tr>
<td>9*</td>
<td>1997 CAUT</td>
<td>A model for the teaching of occupational health and safety and risk management within the science curriculum</td>
<td>Geoff Crisp</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1997 CAUT</td>
<td>Learning strategies and early intervention to enhance student learning in chemistry</td>
<td>Peter Zeegers</td>
<td></td>
</tr>
<tr>
<td>11*</td>
<td>1998 CUTSD</td>
<td>Demonstration experiments in the lecture room environment</td>
<td>Mark Riley</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1998 CUTSD</td>
<td>CoChem - An innovative approach to interdisciplinary advanced chemistry teaching</td>
<td>Joanne Jamie, Geoff Wickham, Joe Majej, Paul Keller, Robert Corderoy, John Brenner</td>
<td></td>
</tr>
<tr>
<td>13*</td>
<td>1999 CUTSD</td>
<td>Australian Physical Chemistry Enhanced Laboratory Learning (APCELL)</td>
<td>Scott Kable, Simon Barrie, Mark Buntine</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1999 CUTSD</td>
<td>Use of structure recognition software in computer assisted learning and assessment of organic chemistry</td>
<td>Julia James (as Director of First Year Studies)</td>
<td></td>
</tr>
<tr>
<td>16*</td>
<td>2004 DEST</td>
<td>The Australian Chemistry Enhanced Laboratory Learning project (APCELL)</td>
<td>Mark Buntine, Scott Kable, Simon Barrie, Bob Bucat, Geoff Crisp, Ian Jamie, Adrian George</td>
<td></td>
</tr>
<tr>
<td>17*</td>
<td>2004 Carrick</td>
<td>A cross-disciplinary approach to language support for first year students in the science disciplines</td>
<td>Felicia Zhang, Brett Lidbury, Jurgen Schulte, Adam Bridgeman, John Rodger, Gary Ellem, Brian Yates</td>
<td></td>
</tr>
<tr>
<td>18*</td>
<td>2008 ALTC</td>
<td>Developing leaders of change in the teaching of large university chemistry classes (ALIUS)</td>
<td>Dan Bedgood, Adam Bridgeman, Mark Buntine, Michael Gardiner, Kieran Lim, Mauro Mocerino, Gayle Morris, Simon Pyke, Daniel Southam, Brian Yates, Marjan Zadnik</td>
<td></td>
</tr>
<tr>
<td>19*</td>
<td>2009 ALTC</td>
<td>Advancing science by enhancing learning in the laboratory (ASELL)</td>
<td>Scott Kable, Mark Buntine, Alexandra Yeung, Manjula Sharma, Kieran Lim, Simon Pyke, Karen Burke Da Silva, Simon Barrie</td>
<td></td>
</tr>
<tr>
<td>20*</td>
<td>2009 ALTC</td>
<td>IS-IT Learning? Online interdisciplinary scenario-inquiry tasks for active learning in large, first year STEM Courses</td>
<td>Lawrence Gahan, Gwen Lawrie, Kelly Matthews, Peter Adams, Phil Long, Lydia Kavanagh, Gabriela Weaver</td>
<td></td>
</tr>
<tr>
<td>21*</td>
<td>2010 ALTC</td>
<td>Extending the science curriculum: teaching instrumental science at a distance in a global laboratory using a collaborative electronic laboratory notebook</td>
<td>Brynn Hibbert, Jeremy Frey, Mauro Mocerino, Matthew Todd, Piyapong Niamsup, Rosanne Quinnell</td>
<td></td>
</tr>
<tr>
<td>22*</td>
<td>2011 ALTC</td>
<td>The Chemistry Discipline Network</td>
<td>Madeleine Schultz, Daniel Southam, Siegbert Schmid, Gwen Lawrie, Mark Buntine, Glennys O'Brien, Brian Yates</td>
<td></td>
</tr>
<tr>
<td>23*</td>
<td>2012 OLT</td>
<td>Enhancing the secondary-tertiary transition in chemistry through formative assessment and self-regulated learning environments</td>
<td>Gwen Lawrie, Madeleine Schultz, Tony Wright, Roy Tasker, Glennys O'Brien, Simon Bedford</td>
<td></td>
</tr>
<tr>
<td>24*</td>
<td>2014 OLT</td>
<td>Supporting a new generation: development and transfer of pedagogical content knowledge in tertiary chemistry</td>
<td>Madeleine Schultz, Gwen Lawrie</td>
<td></td>
</tr>
<tr>
<td>25*</td>
<td>2014 OLT</td>
<td>Assessing the assessments: evidencing and benchmarking student learning outcomes in chemistry</td>
<td>Siegbert Schmid, Adam Bridgeman, Glennys O'Brien, Ian Jamie, Kieran Lim, Simon Pyke, Madeleine Schultz, Daniel Southam, Simon Bedford</td>
<td></td>
</tr>
</tbody>
</table>
In parallel with these developments, in 1994 the CAUT funded UniServe Science, which was designed to act as a clearinghouse for information about teaching software in the experimental sciences in Australian universities. UniServe also hosted the first national conferences on tertiary science and mathematics education in Australia, which originally were also focussed on the use of technology. The annual conference has expanded to include all research and practice in tertiary science teaching, and in 2011 was renamed the Australian Conference on Science and Mathematics Education (ACSM). This meeting forms the most important face to face forum for this community (Schultz & O'Brien, in press). The majority of grants listed in Table 1 have been disseminated at least in part at a UniServe or ACSME conference; details are included in the website http://chemnet.edu.au/?q=node/91.

As shown by the asterisks in Table 1, a large proportion of the projects (18/22) for which information is available have generated outputs and outcomes that are still in use by at least one institution. (Note that for projects 6, 7 and 14, no information could be obtained and it is unclear whether these projects actually went ahead.) This includes projects from over a decade ago. Of those no longer in use, two (projects 3 and 8) were overtaken by rapid increases in information and communications technology, which made their outcomes no longer useful in comparison to faster and more advanced options that became available. For example, videos and interactive computer programs developed internally have been displaced by the World Wide Web, YouTube, Skype and in some cases software provided by textbook publishers. What has remained in use is content, such as the constructivist tasks from Bucat's team at UWA (project 4) still used in teaching first year chemistry, and the ChemCAL project at the University of Melbourne (project 5). ChemCAL received subsequent funding and has been upgraded to run on modern computers through the internet but the original content is still used. The videos made for project 1 are still used because they were transferred to DVD. Projects 2 and 11 are still in use but in both cases rely on very old computers; when these machines stop working, the project outputs will be lost because they are incompatible with more recent operating systems. In some cases such as projects 10 and 12, outcomes have fallen into disuse because the original proponent of the project has moved on from the institution. The electronic lab notebooks developed in project 21 remain in use at the University of Southampton in the UK although they are no longer used at the UNSW since the retirement of their champion.

Looking at the funded projects in more detail, of the 22 for which information is available, there are some common themes:

- First year foundations: 2, 4, 5, 6, 17, 18, 20, 23
- Laboratory learning: 1, 12, 13, 15, 16, 19, 21
- Interdisciplinarity: 12, 17, 20

It is interesting to observe that several older projects involve teaching and learning strategies that have become popular in recent years, including flipped learning (project 1) (Crouch & Mazur, 2001; Weaver & Sturtevant, 2015); inquiry learning (project 12) (Briggs, Long, & Owens, 2011); active learning (projects 2, 5, 10, 11, 18, 20) (Freeman et al., 2014). Project 15 began many years ago in recognition of the fact that demonstrators are critical to the student experience in laboratory. This project forms the basis for an OLT National Teaching Fellowship awarded to Mauro Mocerino in 2015 entitled "Enhancing learning in the laboratory: identifying and promoting best practice in the professional development of demonstrators". A series of workshops held in 2016 as part of the fellowship show that the impact of this funding is still being felt.

Project 18, the ALIUS project, has had lasting impact on the teaching strategies of the staff involved through the introduction of the Process Oriented Guided Inquiry Learning (POGIL) methodology to Australia (POGIL, 2016). That project involved multiple face to face meetings of those involved so that they were thoroughly trained in the teaching methods (Bedgood et al., 2010). Unfortunately the website developed through that project no longer exists and the resources are not available to those not directly involved, although in some cases other academic staff at the institutions in the grant have also adopted POGIL teaching methodologies. Since the funding period for that project ended, the intensive training in POGIL methods is not available to new academic staff, but those trained within the initial project are enthusiastic proponents and able to point interested people towards useful resources. Thus, a significant outcome that persists beyond the funding period is the adoption of the POGIL teaching methodology at several institutions.

Projects 13, 16 and 19, now known as ASELL, is an ongoing attempt to improve laboratory learning in Australian universities. The workshops organised within this project have been valuable for many academic teaching staff because they are exposed to some concepts of pedagogical theory as well as experiencing first hand laboratory exercises from other institutions. In many cases modifications to improve individual laboratory exercises have been made as a result of attending an ASELL workshop. The increased awareness among teaching staff of the importance of well-structured laboratory experiences represents an important outcome of these projects. However, as acknowledged in the final report of the ASELL project, its impact is largely confined to those who directly attend a workshop. The total was estimated at around 200 academic staff, which is around 5% of those teaching chemistry. In addition, due to staffing turnover, changes made to a laboratory practical as a result of attending a workshop are sometimes lost in subsequent years. No data have been reported for adoption of ASELL experiments that are published on the website.

Although as shown in Table 1 a very large number of the projects are still in use, most of these have only had an impact on the institution(s) holding the original grant, and often only direct participants are aware of the outcomes of particular projects. This is in spite of the
fact that many of the projects have led to publications in major international journals (Andrews & Kleese, 1998; Buntine et al., 2007; Zeegers & Martin, 2001; Zhang et al., 2010), in some cases many years after the original grant (Badiola et al., 2015; Barrie et al., 2015; Mocerino, Yeo, & Zadnik, 2015). Surprisingly few outcomes have appeared in this journal (Barrie et al., 2001; Jamie et al., 2007; Mitchell Crow, O'Brien, & Schultz, 2012; Schultz, 2012) although improvements to laboratory experiments based on the APECELL/ACELL methodology are published here. Several grants have lead to significant recognition for the project team including awards from the ALTC, OLT and the RACI, promotion and invitations to present in international fora. In some cases their impact has thus increased the seniority of the staff involved, giving them a broader platform for dissemination.

The lack of awareness of previous grant outputs results from the time pressures on typical chemistry academic staff; when seeking resources to strengthen their TSPK they are unlikely to search the educational literature, which is very diffuse and difficult to monitor. More recent projects (13, 15, 16, 18, 19, 22, 24 and 25) involved workshops of some form, often held in conjunction with ACSME, which increases awareness of the specific project and may lead to adoption at other institutions. However, participants may not retain much from those workshops that they can directly apply in their teaching, and those unable to participate are often unaware of the project. It is hoped that this article and the associated resources that have been collected and are available at http://chemnet.edu.au/?q=node/91 enable more of the outcomes to be used by others.

Specific outcomes from the projects listed that are suitable and readily available for adoption by current academic staff are:

- Project 4 - the constructivist thinking tasks developed within this project are available at http://chemnet.edu.au/?q=node/91
- Projects 13, 16 and 19 - APECELL/ACELL/ASELL - workshops are still held and all institutions are invited to send participants. This project is also suitable for secondary teachers. The educational template for ASELL experiments and the instruments available to survey staff and students are available on the website aSELL.org
- Project 22 - the Chemistry Discipline Network welcomes new members; anyone with an interest in improving the teaching of chemistry can join. Information is available at chemnet.edu.au
- Project 23 - the chemistry concept questionnaire and interactive remediation activities from the IAMMIC project are available at iammicproject.com. A description of the design of the website modules has been published (Lawrie et al., 2016)
- Project 24 - the searchable collected PCK and insightful quotes from a large number of experienced chemistry teachers are available at http://chemnet.edu.au/chem-pck
- Project 25 - the resource for evaluating assessment items has been published (Schmid et al., 2016)

Conclusions and Recommendations

In spite of the limitations of dissemination, it is clear that even small amounts of funding (less than $50 k) can lead to useful outcomes that impact student learning for many years at a single institution. It is to be hoped that any new funding body that will replace the OLT continues to see the importance of small projects in chemistry education, planned and executed by chemistry academics. One high impact use of small amounts of funding would be to migrate old software to function on current operating systems (for example for projects 2 and 11).

The TSPK that is embedded in project outputs should not be undervalued. Development of teaching resources necessarily involves investigating how these can be made most effective in supporting student understanding, which forms canonical TSPK. Thus, it is critical that when considering spending time and money in the development of new resources, novice academic staff engage with existing resources and if possible with the people involved in their development to further the educational outcomes. Attendance at ACSME should be strongly encouraged and incorporation of existing grant outcomes should be a condition of new funding.

Acknowledgements

I thank the many grant holders who were extremely generous with their time, digging through archives and sending me documents about historical projects. I am grateful to the Institute for Innovation in Science and Mathematics Education (IISME) at the University of Sydney that has maintained records of the UniServe and ACSME conferences as well as many documents relating to funded projects. I am particularly thankful to Bob Bucat who has inspired my interest in PCK.

References


Schmid et al., 2016)
Aspirin and Its Colored Complexes: How This Drug Reacts with Metal Ions

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Abstract
A laboratory experiment for extraction and purification of acetylsalicylic acid from commercial aspirins and its reaction with Fe(III) and Cu(II) solutions. The complexation reactions are easily observed thanks to the intense color variations, nevertheless the identity of the extracted and synthesized compound has been verified using thin-layer chromatography, UV-vis, fluorescence and infra-red spectroscopy, and mass spectrometry. This experiment demonstrates that varying the ligand and the transition metal can give rise to different structures, and hence different optic properties.

Keywords: First-Year Undergraduate, Second-Year Undergraduate, Demonstrations, Interdisciplinary / Multidisciplinary, Inorganic Chemistry, Hands-On Learning / Manipulatives, Crystal Field / Ligand Field Theory, Dyes / Pigments, Organometallics.

Introduction
General undergraduate laboratory experiments should to reflect modern research practice and it is essential that they include a range of elements, and that synthetic tasks are accompanied by qualitative analysis and complete characterization.

The first purpose of this experiment is to introduce undergraduate students in a chemistry laboratory to the extraction and purification of acetylsalicylic acid from commercial aspirins and its showy reaction with Fe(III) and Cu(II) solutions.

In this paper we report a sequence of experiments planned for the general chemistry laboratory based on a familiar substance: aspirin. Aspirin (acetylsalicylic acid, Asa) is a drug compound familiar to virtually all students. Even if labs involving aspirin are common, they are useful because these experiments aid general chemistry students relate chemistry to real-world problems.

Indeed, the second purpose of the experiment is to employ the extracted and synthesized complexes to verify the identity of the molecular structure using thin-layer chromatography, UV-vis, infra-red spectroscopy, and mass spectrometry.1,5

The use of aspirin makes the experiment close to everyday life experience. In the first experimental part, the strong color of the complex products is easily observable and has a strong emotional and cognitive impact on students.4,5

The laboratory experiment is designed for general chemistry laboratory course, with a prerequisite chemistry course, to reinforce how to use techniques together, which is a necessary skill in organic and inorganic chemistry. The objective is to provide students with an experience in two major areas common to organic chemistry: (1) extraction and purification of pharmaceutical compounds, and (2) synthesis of metal ions complexes and their photophysical and structural characterization, comparison between ligand and corresponding complex photophysical behavior.6-8

Herein, we investigate the extraction of the acetylsalicylic acid (Aspirin) from aspirin commercial tablet and the formation of several Fe(III) and Cu(II) complexes. One of the goals of this demonstration is to show the formation of complexes with aspirin as a ligand with Fe(III) and Cu(II) as the ions to be coordinated.9 The experiment uses two non-colored but fluorescent products to synthesize the corresponding deeply colorful and non-fluorescent complexes, this allows students to apply the concepts of the Crystal Field Theory and observe the modification of the spectral and optical properties after the complexes formation. Furthermore, metal coordination complexes of biological molecules have much potential for designing novel therapeutic and diagnostic agents, which target specific properties and show reduced side effects, avoidance of resistance and improved selectivity, as they can be used for treating a wide range of important human diseases.10

Additional challenges of this experience are the possibility to better understand the mechanism of action of small molecules (such as aspirin), in order to make a further evaluation and modulation of the chemical composition and reactivity. Of particular importance in the field of synthetic and biological chemistry are Fe(III) and Cu(II) complexes, because of the role these elements plays in biological systems.11-13 The interaction of transition metal ions with drugs is a subject of considerable interest, as aspirin has been previously reported to form molecular complexes with Ag(I), Zn(II), Cu(II) and Co(II) ions.14

Experimental Overview
The timespan of this experiment is two 4 h sessions, with a pre-lab quiz administered at the beginning of each session (See SI: Pre-work quizzes and Post lab questions). The experiment is ideally carried out in groups of 3–4 students.

Acetylsalicylic acid extraction from commercial aspirins.

In the first session, students extract and purify acetylsalicylic acid from commercial aspirins tablet.
Commercial aspirin contain a list of ingredients such as starch, lactose monohydrate, purified talc, silica dioxide, sodium carbonate, zinc stearate, carnauba wax, hypromellose or others depending upon the pharmaceutical recipes. The aspirin collected has been purified by recrystallization. In this purification method, the crude aspirin (2/3 commercial tablet) will be dissolved in a small amount of warm ethanol or acetone and filtered. Water will then be added at the filtrate and the solution will be cooled slowly and then chilled. The acetylsalicylic acid recrystallize, and the solid impurities (excipients) should remain dissolved in the solution (See SI: Instructor lab manual notes for experiment). The solid aspirin will again be recrystallized two times and tested for purity. The yield, appearance of the ligand, and melting point are recorded.

**Qualitative Analysis**

TLC is performed on TLC sheets coated with 0.25 mm layers of silica gel 60 F254. After the application of the extract (about 10 µl), the sheets are developed in paper-lined all-glass chambers with solvent, previously left to equilibrate for at least 10 min. Spots are visualized with a UV lamp. The distance to the center of the spot (d_{solv}) and the solvent (dichloromethane-ethanol 94-6) front distance (d_{solv}) from the spot line are measured with a ruler, and the Rf (retention factor) for the spot is calculated from $R_f = \frac{d_{solv}}{d_{solv}}$. The TLC method uses commonly available supplies and laboratory glassware, facilitating its use in the general chemistry laboratory, such as 100 ml beakers, filter paper, and aluminum foil to cover the beaker (the “TLC chamber”). The TLC developing solvent efficiently separates acetylsalicylic acid (Rf = 0.53 in dichloromethane-ethanol 94-6).

Using a melting point apparatus, students determined the melting point of their crude and recrystallized aspirin samples, recording the value as a range from when melting commenced to when all the sample was liquid (In order to get a meaningful result for the melting point determination, the solids must be dry). The melting point of pure aspirin is 135°C, and the melting point of salicylic acid is 158°C. Four students (of 20) reported melting points were lower than literature values, indicating impurities. The students were asked to comment on the purity of their extracted aspirin based on its melting point.

**Synthesis Of complexes**

In the first session, each group uses the previously extracted acetylsalicylic acid to synthesize the corresponding Fe(III) and Cu(II) complexes (see fig. 1, 2).

The collected aspirin has been employed as a solution (2.5ml, 10⁻³ M) for reaction with acid metal ions solutions (Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) 2.5ml of 10⁻³ M. Only Fe(III) ion reacts to form a purple complex. Salicylic acid (Sal) contains a phenol group, but acetylsalicylic acid does not. Therefore, if you add FeCl₃ to an aspirin sample and you see a purple color, it means that there is some salicylic acid present. Co(II), Ni(II), Cu(II) and Zn(II) ions don’t show any change in color (see fig. 1).

Acetylsalicylic acid tends to hydrolyze in solution yielding salicylic acid, and we experimentally observe that the Fe complex did not originate from the Asa but from the salicylic acid present as an impurity, or as a hydrolysis product of the Asa.

Edwards first showed that the rate of hydrolysis of aspirin is independent of pH between pH 4 and 8. The hydrolysis reaction has been the subject of a number of studies, particularly by Garrett. Edwards considered that hydrolysis in the pH-independent region involves attack by a molecule of water on the aspirin anion. Typically esters are subject to hydrolysis by both aqueous acids and bases and Asa is an ester. Preparations having elevated amount of aspirin often smell like acetic acid because aspirin decompose through hydrolysis in wet conditions, yielding salicylic and acetic acids. Asa is stable in dry air, but gradually react in contact with moisture, otherwise the hydrolysis proceeds more speedily in solution with acid or alkalis.
any undissolved compound and is added to a solution of Cu(II) cations (Cu(II) nitrate, acetate or sulfate are suitable) (See SI). Bright blue crystals of copper aspirinate immediately form and precipitate (see fig. 2). The crystals can then be filtered from solution, washed, and dried.19

The reaction is very simple and can be carried out without special precautions related to oxygen or water presence. Even in the presence of impurities in the acetylsalicylic acid, the synthesis leads to the desired deep blue colored product because of the high selectivity of the reaction between metal and ligand. In any examined case we always observed an intense color changing due to the complex product.

In the second session, students record the full IR, ESI-MS, UV–visible absorption and emission spectra for solutions of the ligand, metal salt and metal complex. The wavelength of maximum absorbance/emission, intensity at this wavelength, and solution color are recorded for each solution.

Recrystallization and filtration, column chromatography and TLC are frequently taught as part of a second-year undergraduate organic chemistry laboratory curriculum in many institutions. However, these techniques are often taught in separate laboratory periods, and students sometimes have difficulty grasping the importance of when and how these techniques can be used in combination with IR, UV-vis, ESI-MS and NMR to enable structural determination of unknown compounds.

Result And Discussion

This experiment has been performed in an intermediate general chemistry laboratory course with 20 enrolled students. Students in this course had completed first-year general chemistry, comprising introductory organic, inorganic, physical and theoretical chemistries.

As previously stated, this experiment is split up into two separate sessions: the first being the extraction and purification of Aspirin and synthesis of corresponding metal complex; the second being a UV–visible, fluorescence, infra-red, mass spectroscopic characterization exercise, consisting of obtaining the complete spectra for comparison with literature data, as well as establishing the metal:aspirin stoichiometry.

All students reported the appearance of Aspirin as off-white crystals, with 14 (of the 20 students) collecting crystals following recrystallization, and the remaining 6 obtaining a white powder, even after purification, likely due to extremely rapid cooling during recrystallization. Yields ranged from 22 to 66%, with an average of 44%.

All students easily appreciate the strong color variations, facilitating the understanding of the Crystal field theory and discussion of the modification in the energy of the d-orbitals during the complex formation.

Spectroscopic Characterization

The acetylsalicylic acid is well known in literature for its photophysical properties.20,21 Two absorption shoulders fall in the wavelength range from 300 nm to 380 nm in water solution, while almost no absorption beyond 400 nm are observed/detected. The acetylsalicylic acid show large Stokes’ shifts (nm), high quantum yield (under UV excitation) and an intense fluorescent emission (λexc=335nm) at wavelengths in the 350-450 nm range in water (see fig. 3).22

Figure 2. a) (top) Left to right: copper sulfate solution (1M), copper aspirinate precipitate from synthesis. b) (bottom) The same copper aspirinate precipitate, observe the intense deep blue-green color.

Figure 3. UV-Visible absorption spectra (top) and emission spectra (bottom) of acetylsalicylic acid, recorded in water solution.
Absorption and emission spectra of dilute solutions (~10^{-4} M) of Fe(III) (water) and Cu(II) (water and DMSO, 50%) complexes are presented in Figure 4 and 5, and their absorption wavelengths are reported in Table 1. A strong color changing in the products solutions is easily observable because of the high molar absorption coefficient as previously reported. On the contrary, the complexes show no emission, it is evident that the optical characteristics of the complexes may be very different from those of the ligands (See Table 1).

Most d-transition metal ions act as Lewis acids (accept electron pairs) by forming complex with covalent bonds with ligands (Lewis bases). Complex include cationic, anionic, and neutral species ([CoCl_{2}(NH_3)_{3}]^+, [Mo(CN)]_6^{3-}, [Cr(H_2O)_6]Cl_3) and they are colored. The color of complex depends from the metals and the ligands type. Most transition-metal compounds are colored, a characteristic that distinguishes them from most compounds of the representative elements. In transition-metal complexes, d-orbitals are frequently split into two sets energy levels separated by definite energies. The absorption of visible light causes electronic transitions between orbitals in these energy levels. The wavelength and color of the light absorbed are related to structure end nature of the complex because are connected to the energy of the d-orbitals. Crystal field theory proposes that the presence of any ligand bound to a metal ion modify the energy of the 5 d-orbitals so that there are energy modifications between them. So transition-metal ions with partially filled d-orbitals can absorb photon energy if the energy of the photon approximately matches the difference in the d-orbitals. In this phenomena, an electron absorbs the light energy, going from an energy level to a higher energy half-filled or empty d-orbital energy orbital. The colors of the complexes strongly depend on the ligands and the metal nature.

The IR spectra show that acetylsalicylic acid behaves in a bidentate manner, coordinating via the two oxygen atoms of the acidic group with the displacement of a hydrogen atom (see fig. 6). This mode of chelation is supported by the disappearance of the peak at 1680 cm^{-1} and 2900-2920 cm^{-1} (g carboxylic acid) and other peaks resulted shifted to lower frequency, indicating participation in coordination (see Table 2).

The positive mass spectrum reported in Figure 7 is relative to the Fe solution with acetylsalicylic acid extracted. In this case is the salicylic acid that forms a Fe^{3+} complex (salicylic acid (Sal), C_7H_6O_3, MW=138,12, salicylate, C_7H_5O_3, MW=137,02 ). Figure

**Table 1.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{abs} ) (nm)</th>
<th>( \lambda_{em} ) (nm)</th>
<th>Stokes’ shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylsalicylic acid</td>
<td>285, 300*</td>
<td>408</td>
<td>108</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>237</td>
<td>450</td>
<td>147</td>
</tr>
<tr>
<td>Fe complex</td>
<td>530</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Cu complex</td>
<td>760</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

**Table 2.**

<table>
<thead>
<tr>
<th>Compound/signal (cm^{-1})</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspirin sample</td>
<td>( \gamma ) (O-H) carboxylic acid</td>
</tr>
<tr>
<td>2500-2920</td>
<td>1751</td>
</tr>
<tr>
<td>1680</td>
<td>1607</td>
</tr>
<tr>
<td>1455</td>
<td>1178</td>
</tr>
<tr>
<td>Cu-Aspirinate</td>
<td>( \gamma ) (C=O) free acetyl group</td>
</tr>
<tr>
<td>1760</td>
<td>1730</td>
</tr>
<tr>
<td>1607</td>
<td>1455</td>
</tr>
<tr>
<td></td>
<td>( \gamma ) (C=O) binded acetyl</td>
</tr>
<tr>
<td></td>
<td>( \gamma ) (C=C) ring</td>
</tr>
<tr>
<td></td>
<td>( \gamma ) (C=O)</td>
</tr>
<tr>
<td></td>
<td>( \gamma ) (C=C) ring</td>
</tr>
</tbody>
</table>

**Mass-Spectrometry Characterization**

The positive mass spectrum reported in Figure 7 is relative to the Fe solution with acetylsalicylic acid extracted. In this case is the salicylic acid that forms a Fe^{3+} complex (salicylic acid (Sal), C_7H_6O_3, MW=138,12, salicylate, C_7H_5O_3, MW=137,02 ). Figure
7 shows two major peaks at m/z= 330.06, attributable to the corresponding complexes [Fe(Sal)_2]^+ m/z= 330.09 (see fig. 7). The isotopic patterns confirm peaks assignment (free mass spectra simulators are available online to simulate FeC_{14}H_{16}O_{6} peak MW=330.09, see fig. 8).

The negative mass spectrum reported in Figure 9 is available online to simulate FeC_{14}H_{16}O_{6} peak MW=330.09, see figure 7. The isotopic patterns confirm peaks assignment (free mass spectra simulators are available online to simulate FeC_{14}H_{16}O_{6} peak MW=330.09, see fig. 8).²⁴

Figure 7. ESI-MS spectrum of Fe ([Fe(Sal)_2]^+ m/z= 330.09).

Figure 8 Top) ESI+/MS spectrum of Fe-acetylsalicilic acid complex; Bottom) simulate ESI-MS spectra of peak FeC_{14}H_{16}O_{6} peak MW=330.09.

The negative mass spectrum reported in Figure 9 is relative to the Cu(II) solution with acetylsalicylic acid extracted. In this case, the acetylsalicylic acid forms a copper complex (acetylsalicilic acid (Asa), C_{9}H_{8}O_{4} MW=180.16). Figure 9 shows a major peak at m/z= 600.03, attributable to the corresponding complexes [Cu(Asa)]^+ m/z= 600.04 (Asa as acetylsalicylate, C_{9}H_{8}O_{4}, MW=179.16), (see fig. 10 top).

The isotopic patterns confirm peaks assignment (free mass spectra simulators are available online to simulate CuC_{22}H_{22}O_{12} MW=600.99), (see fig. 10 bottom).

Figure 9. ESI+/MS spectrum of Cu complex product.

Figure 10. Top) ESI-/MS spectrum of Cu-acetylsalicilic acid solution; Bottom) simulate ESI-MS spectra of peak CuC_{22}H_{22}O_{12} peak MW=600.99.

The clear fragmentation obtained in MS/MS spectrum revealed that the complex can lose a ligand (600.43-180.16=420.27; see peak m/z=420.76), see figure 11. The stoichiometry of the two complexes are confirmed by isotopic pattern (see free mass spectra simulator online).

Solid copper aspirinate is a neutral dimer C_{36}H_{24}Cu_{2}O_{10} (dicycopper 2-acetyloxybenzoate) but in DMSO/water solution the [Cu(Asa)]^+ m/z= 600.04 is present as demonstrate from the ESI-MS spectra.

Hazards

Students must wear safety glasses and laboratory coats at all times. Extraction and recrystallization, synthesis and TLC analysis should be performed in a fume hood. The Cu(II) and Fe(III) salts are harmful if swallowed and by inhalation.

Ethanol is highly flammable. Students are provided with access to the material safety data sheets for all chemicals, and are asked questions on safety aspects of...
the experiment as part of their prelab work. Remember to wear safety glasses when preparing or presenting the experiment. All starting materials waste can be disposed in non-hazardous waste (See SI: Work instructions for service room).

Figure 11. ESI-MS-MS spectrum of Cu complex product, peak m/z=600.

Conclusions
This laboratory experiment is appropriate for an intermediate and general course. It involves simple, inexpensive starting materials, and demonstrates a number of important principles related to modern chemistry research.

The experiment has the following key learning outcomes:

- Improve the synthetic skills (extraction-recrystallization of acetylsalicylic acid), assessed by yield and appearance of the extracts.
- Exposure to a range of analytical techniques (TLC, Mass spectrometry, absorption and emission spectroscopy, Infra-Red spectroscopy), assessed by reported spectra.
- Improve data analysis (comparison between experimental and reported spectra).
- Improve understanding (for example, of the relationship between absorption spectra and structure of ligand and complexes), assessed through planning of the experimental report.

Students are able to observe that the identity structure of the acetylsalicylic acid and the employed metal ion affected the photophysical behavior of the product itself. Furthermore, students are required to compare measured spectra to literature values, which let them experience literature search.

In conclusion, in this experience it is possible to observe an example of purification of organic compounds from common drug and the formation of two interesting metal complex with strong color changing.

At a somewhat more advanced level, other things which can be included in the discussion are the structures of pharmaceutical products as well as the corresponding metal complex derivatives, and their optical and structural behavior, as students can properly understand the results.

The paper is focused on Fe(III) and Cu(II), owing to their strong color changes of the products, anyway the experiment could readily be expanded to include other metal ions as previously reported.

These compounds represent an interesting class of colored complexes with potential interest for pharmaceutical applications. Moreover, high reaction yields, absence of catalysts, high accessibility and stability, ease of handling and preparation make this procedure useful for student laboratory.

Furthermore, students were required to compare measured ESI-MS/MS, UV-vis, IR spectra to literature values, which gave them the experience of searching the literature for such information.

Crystal Field Theory can be used to justify the diverse colors of the Fe(III) and Cu(II) solutions and of the different complexes or, conversely, the colors can be used to give a visual demonstration of the theory.

Summary
This laboratory experiment was appropriate for an intermediate, general or inorganic chemistry course. The experiment used not toxic, simple, inexpensive starting materials, and demonstrated a number of important principles related to modern chemistry research such as Crystal Field Theory, the interaction of transition metal ions with drugs, and improve the synthetic skills of the students, and also exposes them to a wide range analytical techniques.

Supporting Information
CAS numbers, Instructor lab manual notes for experiment, Pre-work quizzes, Post lab questions, Student lab manual notes for experiment, Work instructions for service room.

Acknowledgments
Author thanks Roberto Buscaino for the scientific support.

References


10. Swarts J. C.; Cook M. J.; Baker E. N.; Metal-Containing Proteins, Macrocycles, and Coordination Complexes in Therapeutic Applications and Disease. Metal-Based Drugs. 2008 Article ID 286363.


Supplementary Information: Aspirin and Its Colored Complexes: How This Drug Reacts with Metal Ions

Giorgio Volpi*, Francesca Turco, Giuseppina Cerrato

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NOTES FOR THE INSTRUCTOR

Here we present some of our procedures and results to facilitate the work of the instructor.

1. Reagents, standard solutions and materials
Copper nitrate Cu(NO$_3$)$_2$$\cdot$3H$_2$O (or Copper Sulfate CuSO$_4$$\cdot$5H$_2$O), ethanol, dichloromethane, HCl, FeCl$_3$, NaHCO$_3$ all of technical grade, were used as received from commercial suppliers without further purification; in addition, deionized water from a Milli-Q system (Millipore) was used. TLC has been performed on 10 × 20 cm TLC sheets, coated with 0.25 mm layers of silica gel 60 F$_{254}$ (E. Merck). It is possible to use different aspirin commercial tablet.

2. Disposal of wastes and unused solutions
All starting materials (aspirin) waste can be disposed in non-hazardous waste. All solutions (metal solution, solvent, complexes) in waste container in hood. Waste must be disposed of in accordance with federal, state and local environmental control regulations. The organic solvents used in this experiment are harmful for human beings and the environment and all experiments with them should be done under fume hood. After usage, the wastes should be disposed in the proper containers, taking special attention to chlorinated hydrocarbons.

3. Spectroscopic characterization
UV-Vis spectra were recorded on a CARY-60 spectrometer, fluorescence measurements were recorded using Cary Eclipse Varian V. The range for fluorescence emission recording was between 300 nm and 700 nm, $\lambda_{exc}$=335 nm, water solutions.

The FT-IR spectrum of solid Cu-Aspirinate product was recorded in the region 400–4000 cm$^{-1}$ on Spectrum Two (Perkin Elmer) spectrophotometer in ATR mode (number of scan=16).

ESI (Electro Spray Ionization) experiments were conducted with a Thermo Finnigan Advantage Max Ion trap spectrometer in positive ion acquiring mode; sheath gas flow rate was set at 25 (arbitrary unit), auxiliary gas flow rate at 5 (arbitrary unit), spray voltage at 3.25 (KV), capillary temperature at 270 C, capillary voltage at 7 (V), and tube lens offset at 60.00 (V). Nitrogen was used as sheath and auxiliary gases.

4. Direct experience facilitating discussion with students
The students in the Faculty of Chemistry were surprised seeing the intense color variation of the metal ion solutions reagent. Previously, they were advised that gives a red coloration with iron and blue precipitation with Copper. Therefore, this experience leads to some considerations concerning the stability and the kinetics of complexes, which are linked to the crystal field theory, spectrochemical series and the energy separation between the $d$-orbitals in the metal ion complexes.
PRE-WORK QUIZZES

1). According to the MSDS, what risk phrase applies to ethanol?
   a. R5 – Heating may cause an explosion
   b. R11 – Highly flammable
   c. R36 – Irritating to eyes
   d. All of the above

2). At the end of the first step of this experiment (extraction of aspirin), you collect your product by filtration. Where will you dispose of the waste filtrate?
   a. In the organic waste
   b. In the halogenated organic waste
   c. Down the sink
   d. In the rubbish bin

3). According to the MSDS, what route of exposure of copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$$\cdot$3H$_2$O) has the most severe (toxic) effects?
   a. Eye exposure
   b. Skin exposure
   c. Ingestion
   d. Inhalation

POST LAB QUESTIONS

1) How to verify the aspirin presence in the extract?
   Using thin-layer chromatography and the corresponding product purity by melting point apparatus.

2) How do you explain the color change from yellow to purple in the Fe(III) solution after aspirin addition?
   In neutral or acid solution, Fe$^{3+}$ ion is present as the [Fe(H$_2$O)$_6$]$^{3+}$ ion. This ion can bind to salicylic acid because water is replaceable in iron complexes. One water can be replaced by the negative oxygen ion in salicylic acid as salicylate. In the extracted aspirin the acetylsalicylic acid tends to hydrolyze in solution yielding salicylic acid, and we experimentally observe that the Fe complex did not originate from the aspirin but from the salicylic acid present as an impurity, or as a hydrolysis product of the acetylsalicylic acid.

3) How do you explain the precipitation after the addition of Cu(II) solution to the aspirin solution?
   In neutral or acid solution, Cu$^{2+}$ ion is present as the [Cu(H$_2$O)$_6$]$^{3+}$ ion. This ion can bind to acetylsalicylic acid because water is replaceable in copper complexes. One water can be replaced by the carboxylic group in acetylsalicylic acid to form final copper aspirinate complex.

4) In this experiment, you wash your products with solvent: ethanol. Why do you need this washing step, and what temperature solvent should you use?
   The washing step will help remove any impurities. The solvent must be kept ice-cold to ensure that only a minimal amount of product is dissolved into the filtrate.

5) Why is IR spectroscopy used to identify molecules?
   IR spectroscopy is used to identify molecules because many times, each functional group possesses a characteristic stretching frequency that can be quickly identified. After complexation the characteristic peaks show a typical shift because change the stretching frequency.

6) What band stretching frequency would you expect to see for each of the three molecules isolated in this lab? Which functional group do these correspond to?
   For the aspirin molecule and relative complexes: Peaks corresponding to the CH bonds should be found between 2800 and 3200 cm$^{-1}$ (both sp$^2$ and sp$^3$ hybridized C-H stretching frequencies). Finally, peaks corresponding to the C=C bonds should be present between 1500 and 1650 cm$^{-1}$. In addition, a peak should be observed between 1700 and 1800 cm$^{-1}$ indicating a C=O bond.

7) Why is ESI-MS spectrometry used to identify molecules?
   Mass spectrometry is an analytical technique that can provide both qualitative (structure) and quantitative (molecular mass or concentration) information on analyte molecules after their conversion to ions. The ions then travel through the mass analyser and arrive at different parts of the detector according to their mass/charge (m/z) ratio. ESI-MS spectrometry gives important information about the charge, the mass, fragmentation and therefore the stoichiometry of the complex and the isotopic distribution also confirms the type and stoichiometry of metal ions.

8) Why both salicylic acid and acetylsalicylic acid show no color and the corresponding Fe and Cu complexes appear deeply colored?
In transition-metal complexes, $d$-orbitals are frequently split into two sets energy levels separated by definite energies. The absorption of visible light causes electronic transitions between orbitals in these energy levels. The wavelength and color of the light absorbed are related to structure end nature of the complex because are connected to the energy of the $d$-orbitals. Crystal field theory proposes that the presence of any ligand bound to a metal ion modify the energy of the $d$-orbitals so that there are energy modifications between them. So transition-metal ions with partially filled $d$-orbitals can absorb photon energy if the energy of the photon approximately matches the difference in the $d$-orbitals.

STUDENT LAB MANUAL NOTES FOR EXPERIMENT
This experiment will take place over two days, and will involve:
First day: the extraction of acetylsalicylic acid from commercial aspirin and complexation reaction of the extracted aspirin in mild conditions;
Second day: photophysical studies and characterization of the obtained compound in solution. All sections of this experiment are to be completed in group of 3-4 students.

1. LEARNING OUTCOMES
After undertaking this experiment, you will achieve the following laboratory skills:
• Solvent extraction;
• Recrystallization;
• Vacuum filtration;
• Thin layer chromatography;
• Metal complexation equilibria;
• Mass spectrometry (ESI and ESI-MS/MS) and Mass spectra simulation;
• IR, UV-vis, Fluorescence spectroscopy.
Crystal field theory demonstration and visualization and discussion about the modification of the energy in the $d$-orbitals during the complex formation.

Other improvements in understanding crystal/ligand field theory, acid - base equilibrium and hydrolysis, reaction with an organic compound (aspirin or salicylic acid) and different transition metal ion, as well as the colors of some complexes of iron, copper ion and verify the presence of different compound in a commercial drug.

2. PROCEDURE
SAMPLING AND EXTRACTION
The extraction and purification of acetylsalicylic acid from commercial aspirins
• Weigh 2 tablets (about 1-1.50 g) of aspirin in beaker.
• Add 10 ml warm ethanol or acetone and stir for 30 min.
• Filter in Buchner using glass wool.
• Collect the filtrate together. (If there is any impurities re-filter).
• Add water (1ml) at the filtrate and the solution will be cooled slowly and then chilled.
• Repeat crystallization.

Fe(III) COMPLEX
• Fill test tubes with 2.5ml of $10^{-2}$ M metal ion water solutions (Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) and add 1 drop of HCl 1M.
• Employ the collected acetylsalicylic acid as a solution (2.5ml, $10^{-2}$ M) for reaction with acid metal ions solutions (Fe(III), Co(II), Ni(II), Cu(II), Zn(II)).
• Observe any color variations.

Cu(II) COMPLEX
• Dissolve the previously purified acetylsalicylic acid (about 1g) in aqueous solution of NaHCO$_3$ (10%) 12ml.
• Filter the resulting solution to remove any undissolved compound.
• Add a solution of Cu(II) (Cu(II) nitrate, acetate or sulfate are suitable) (about 350mg in 10 ml of water).
• Bright blue crystals of copper aspirinate immediately form and precipitate.
• Collect the filtrate together for the analysis.

3. REPORT
In the results section of your report, you should include the following:
• A description of the appearance of your solutions;
• The yield of your extraction of aspirin, and the percentage yield, showing your working;
• The IR, UV-vis, fluorescence, ESI and ESI-MS/MS spectra of your ligand and complexes, with comparison to a reported literature;
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A narrative tying together the various results reported here.

In the discussion section of your report, you should include answers to the following:

Discuss the binding stoichiometries of the Fe and Cu complexes, suggesting reasons for the difference or similarity between the two complexes;

Using ChemDraw, or a similar structure-drawing software, propose the structure of the complex that you synthetized.

Using a free mass spectra simulator (as: http://www.chemcalc.org), simulate every compound that you have synthetized and compare the simulated spectrum to the experimental one.

WORK INSTRUCTIONS FOR SERVICE ROOM

Based on a group of 15 students each lab session

Chemicals
150 g aspirin tablet
1L ethanol
50 g copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O or copper(II) sulfate pentahydrate (Cu(SO₄)₂·5H₂O)
50 g iron(III) chloride (of FeCl₃·6H₂O)
500g sodium bicarbonate (NaHCO₃)
1L dichloromethane
10 TLC sheets
100ml of HCl 1M
Fume hoods
Each fumehood (x9) should have 2 setups. Each setup should contain:
2x 100 mL beaker
1x 100 mL conical flask
1x 50 mL measuring cylinder
1x 250 mL filter flask
1x Buchner or Hirsch funnel
Steam bath

Communal lab space
2 tray reagents containing aspirin tablet, ethanol, Cu(NO₃)₂·3H₂O, FeCl₃, NaHCO₃ (Beside each balance)
9x ethanol squirt bottles (Place one per fumehood)
2x preparative balance (One at the end of Bench A & Bench C)
Small tray of plastic weigh boats (beside each balance)
Tray of spatulas (one beside each balance)
Tray of heat gloves (End of bench A or C)
2x boxes of filter paper (beside each balance)
8x acetone wash bottles (2 per sink)
4x “non-halogenated organic waste” 5L bottles with ECOfunnels (1 per sink)
2x “iron(III) waste” 5L bottles (1 every 2nd sink)
2x “copper(II) waste” 5L bottles (1 every alternate 2nd sink)

Instrument and Equipment Preparation
Cleaning/Preparation of Workstations/Instrument Rooms
(The amount of daily cleaning is dependent on staff and time constraints; not all of the following may be possible every day. The order is in decreasing priority.)
- Check for missing/broken/obviously dirty glassware; replace/clean
- Refill ethanol and dichloromethane squirt bottles
- Restock chemicals beside balance
- Wipe any obvious spills on benches/fumehoods