

Quantitative Determination of Copper: Combining Project-Based Laboratories with Single-Analyte Detection

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Abstract: A multiweek experiment is presented for use in undergraduate instrumental analysis courses. The experiment combines project-based laboratories and single-analyte detection to provide students with experience in method development and validation, and to give them a more realistic experience in the analytical laboratory. Working together as a team, students develop methods for the detection of an analyte (i.e., copper) in water samples using at least two spectroscopic instruments (e.g., ICP-AES, AA, UV-vis, fluorescence). Student teams are given only topical information about their projects, and must research and plan the analyses, learn the instrumental methods to be used, obtain figures of merit (e.g., detection limits) from Beer's law plots, analyze commercial water samples, and produce a standard operating protocol for one of their methods, which will be validated by another team during a subsequent laboratory. Goals of this approach include promoting teamwork and building student confidence in approaching and operating unfamiliar instrumentation. Even more importantly, students are placed in the position of being scientists and having to make decisions and recommendations. Each step of the analytical process must be carefully considered, and its significance assessed as there are no recipes to follow as they develop their methods and make comparisons between different techniques for the determination of a single analyte.

Introduction

The teaching of analytical laboratory courses has undergone a transformation in recent years. Laboratories in junior/senior-level instrumental analysis have traditionally involved exposing students to a broad spectrum of techniques and instruments. The emphases in these laboratories are on data measurement and evaluation, while maximizing student exposure to chemical instrumentation. However, it has been argued that this approach does not expose students to the range and scope of topics dealt with by professionals in the real world of chemical analysis. [1–3]. It is also argued that these methods do not teach students the process of science or equip them with the problem-solving skills that are crucial to their success as chemical professionals [2, 4–5]. One approach to this problem has been the introduction of project-based laboratories [2]. Instead of weekly laboratories, students undertake multiweek [4] or semester-long [2] projects. In these labs students are given only topical information on their projects, and must proceed through all the steps of an analysis [6], for example, definition of the goal, sampling, separation of the sought-for constituent from other species present in the sample, measurement of the desired substance, and evaluation and interpretation of the data. Although exposure to instrumentation is limited (students in semester-long projects may only work with one instrument), it is felt that by understanding one instrument in greater detail instead of many instruments superficially, students will be better equipped to approach other instrumentation in the future. Also, involvement in a project in which they must apply course content toward solving problems, and in which there are no detailed road maps (i.e., cookbook recipes) for how to proceed, demonstrate to students how science really works.

Another approach is “Teaching Instrumentation with One Analyte” [7]. For example, weekly laboratories are performed using different instrumentation, but the focus is on a single analyte (e.g., lead). This approach maximizes student exposure to instrumentation, yet allows cross-comparisons to be made between instrumental figures of merit (e.g., sensitivity and detection limits).

This paper describes a multiweek experiment combining project-based laboratories with single-analyte detection. Students learn to successfully operate at least two instruments, quantitate the amount of copper in real-world samples using procedures developed by a group, make a recommendation based on analytical figures of merit of the preferred technique for analyte detection, and prepare a standard operating protocol (i.e., validation protocol) for their method of choice. During the laboratory period immediately following the completion of the project, student groups validate each other's procedures.

By combining project-based laboratories with single-analyte detection, we hope to provide students with a more realistic exposure to many aspects of analytical chemistry as it is practiced in the workplace. Other goals of this approach are to promote teamwork and teach students how to design analyses, and approach and operate unfamiliar analytical research instruments, while allowing comparisons to be made between different techniques for the determination of a single analyte (e.g., copper).

Experimental

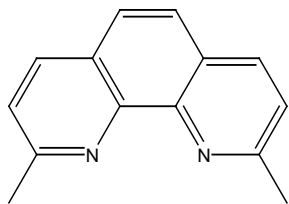
Reagents. A list of possible reagents follows. Depending on student creativity, group choices, and materials on hand, actual reagents may vary from those listed. Copper atomic absorption standards (EM Science), inductively coupled plasma standards (J.T.

Baker), hydroxylamine hydrochloride (Avocado Research Chemicals Ltd.), and 2,9-dimethyl-1,10-phenanthroline (dmp, neocuproine) (Aldrich) were used as received. Potassium phosphate monobasic and sodium hydroxide (ACS grade) were obtained from Fisher. (Caution: Sodium hydroxide is harmful if swallowed and should be handled with adequate protection.) Various bottled water samples, including Aquafina, Evian, and Ozarka were investigated. Unless otherwise indicated, deionized water passed through a Barnstead/Thermolyne triple filtration system was used in all experiments.

Instrumentation. To date, fluorescence, UV-vis, atomic absorption (AA), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) have been used in this project. A Shimadzu RF-5301 spectrofluorophotometer was used for fluorescence measurements. Excitation, as determined by UV-vis spectroscopy, was generally at 450 nm, the lowest energy absorption maximum for the Cu(dmp)_2^+ luminophore, with detection between 550 and 650 nm ($\lambda_{\text{em}} \cong 610$ nm). UV-vis absorption spectra were recorded with a Hitachi U-2001 spectrophotometer. Atomic absorption analyses were accomplished using a Shimadzu AA6804 atomic absorption flame emission spectrophotometer with an air/acetylene flame. A Liberty Varian ICP AX Turbo inductively coupled plasma system was used for all ICP-AES measurements.

Results and Discussion

One method for the determination of copper using absorption and emission spectroscopy involves the complexation of Cu(I) and 2,9-dimethyl-1,10-phenanthroline to produce a stable and intensely colored complex, Cu(dmp)_2^+ [8].



2,9-dimethyl-1,10-phenanthroline (dmp)

The intensity of the orange color of Cu(dmp)_2^+ is due to a metal-to-ligand charge transfer transition between the copper and the π orbitals of the dmp ligands. Further details concerning the absorption and emission properties of Cu(dmp)_2^+ are provided in the laboratory handouts (supplemental material). Complexation is not necessary for AA and ICP methods because metal atoms are detected. Iron can easily be substituted for copper in these experiments because Fe complexed with 1,10-phenanthroline (to form Fe(phen)_3^{2+}) has absorption properties similar to Cu(dmp)_2^+ .

The "Quantitative Determination of Copper Project" takes place over a period of six to eight weeks. Laboratories meet once each week, typically for three hours. Students are encouraged to work off hours with the understanding that they tell the instructor prior to beginning any experiments.

Week one comprises the planning phase of the project. Before the first laboratory session, students are assigned to teams, laboratory expectations are discussed (in terms of both individual and team efforts), and the teams are given time during lecture to discuss the project and outline their plans of

attack. The instructor serves as a facilitator by giving suggestions to the myriad of questions students ask, and guiding them along the many possible routes that a project might take, without giving them a specific plan for accomplishing their goals. For example, during the first week students typically realize that a literature search might prove useful. Students who wish to reinvent the wheel without consulting the literature are more than welcome to do so. For those wishing to consult the literature, an online search (e.g., Chemical Abstracts Service) produces very few useful references for the detection of copper using 2,9-dimethyl-1,10-phenanthroline (dmp). Although there is active interest in the photochemical and photophysical properties of Cu(I) diimine complexes, few of these are useful for the development of an analytical method [9]. At this point the facilitator may suggest that looking up the properties of Cu(I) and dmp might be useful. Some of the most useful references for this are commercial catalogs (e.g., Aldrich, Sigma). Students quickly realize that 2,9-dimethyl-1,10-phenanthroline is also called "neocuproine," and many rush to do another literature search. Again, few useful references are found. However, a quick perusal of the properties in these catalogs may also lead students to the *Merck Index*, which does, in fact, list several pertinent references dealing with the detection of copper in industrial samples [8]. The reason for the lack of success using on-line search engines is that these typically only search the post-1967 literature, while the most pertinent papers dealing with spectrophotometric copper detection are from the period 1952–1964. This is also a subtle way of showing students that technology can't solve every problem, and that a vast chemical literature existed before 1967.

The references do not give step-by-step experimental methods for the determination of copper using neocuproine, since determining copper is often only a small component in these papers [8]. They do, however, give teams a starting point, and allow them to discuss how they might approach their analyses. By week two, these teams are usually preparing standard solutions, and learning at least one of the instrumental techniques they will use. Students who chose not to do a literature search usually realize by week two that they should have done so, and quickly remedy the situation.

Unlike traditional laboratories, students are not given much background on the instruments they will use. Often, the instrumental techniques have yet to be covered in lecture. Students are pointed to the appropriate sections in their textbook [10], and handed the manufacturer's instruction manual. Before students are allowed to run samples on a particular instrument, they are checked out on the instrument by the instructor, and appropriate safety precautions are discussed. Once students have displayed a certain competency with an instrument, they are left to their own devices. Some approach each instrument as a team, while others separate to have one student learn the appropriate technique and then instruct the rest of the team in the fundamentals of the particular instrument. Again, the division of work within the team is left for that team to decide, and appropriate means are used to ensure that all team members take an active role (see Assessing Student Performance).

The remaining laboratory periods are typically devoted to planning, learning the instruments, experimentation, and the testing of commercial water samples. Beer's law plots are obtained using standards and detection limits (both theoretical

and practical) and the lower limit of quantitation obtained for each method. Based on the analytical figures of merit, teams then make a recommendation to the instructor for their method of choice in detecting copper. Students are then given two commercial water samples, one that is unopened and a second that has been spiked with copper. The spiked sample allows the instructor another avenue in testing the quality of the students' method. During the final laboratory period, students are required to hand in an experimental protocol; another group will later use this to validate the chosen method.

Assessing Student Performance

Students are assessed based on both team and individual performance. Team evaluations include weekly oral and written progress reports. Oral progress reports take the form of a discussion between the instructor and one (or more) of the students in a group during class time. These generally last 1–2 minutes, and a different student is asked to report each time. Written progress reports are generally collected on a biweekly basis, and are limited to half a page. Students are encouraged to be *brief*; reports longer than half a page (single-spaced; 10-point font minimum) are handed back to be rewritten. These reports outline what the students have accomplished since the last report, and what they intend to accomplish in the next week. Extensive experimental detail is discouraged; the instructor can easily look in their notebooks for these data. Having industrial experience, the author places a heavy emphasis on short reports such as these since, in his experience, industry requires such reports on a *frequent* basis. Finally, teams are required to hand in an operating protocol for their technique of choice. The formats are as individualized as the teams, but the reports are expected to have enough experimental detail to allow another group to duplicate their results. The validation of their protocols is done during a subsequent 3-hour laboratory period. Grades for the validation protocol laboratory are given to both the team performing the analysis, and the team that generated the protocol. Therefore, cooperation among the teams is important, and groups realize this very quickly.

Individual evaluations include an oral quiz (supplementary material) midway through the project to assess whether students are active members of the group, and understand the chemistry, methods, and instrumentation they are using and developing in the laboratory. The quiz normally lasts no more than 10 minutes, and each student meets with the instructor individually to answer questions. "Pulling teeth" is a very good description of the process of getting answers from some students, but with patience it becomes clear whether a student is merely nervous or does not have a clear understanding of the material. Each student also writes a final paper summarizing the findings, and making comparisons among the different techniques using analytical figures of merit, simplicity of sample preparation, and other factors in order to recommend the best technique for the determination of copper in aqueous samples. The final paper format is included in the supplementary material.

Conclusions

The advantages of project-based laboratories [2] and single-analyte detection [7] over traditional laboratories have been

discussed elsewhere. Combining the two methods allows problem-solving, method development and validation, cross-comparisons of analytical methods, and student interests to be combined. Many students realize the inherent usefulness of problem-solving to their long-term survival in whatever careers they eventually choose. Scientists are trained as problem-solvers, one of the traits that make them so valued in industry and business. However, many students have also expressed an interest in gaining hands-on experience with many different instruments. This interest stems partially from the real and perceived benefits in marketing themselves for a job (i.e., experience with many different techniques), but perhaps more importantly from student enjoyment of learning and using the variety of chemical instruments available for analyses. Disadvantages of combining the two methods include not gaining full expertise on one instrument (as can occur if only one instrument is used in a semester-long project [2]), and comparing analytical figures of merit for fewer instruments (e.g., 2–3 as described here) than if weekly or biweekly experiments were done using a different technique each laboratory period [7]. In our experience, the advantages far outweigh the disadvantages. Also, it seeks to accomplish the same goals, namely, providing students with a more realistic experience in the analytical laboratory while equipping them with the problem-solving skills to ensure their success in today's ever-changing workplace.

As reported by others [2], many students display a level of independent thought and creativity not normally observed in traditional laboratories. For example, $\text{Cu}(\text{dmp})_2^+$ often forms a precipitate at concentrations higher than 15 mg/L (ppm). Student solutions to this problem have varied. Some decide to work at concentrations below 15 ppm, while others have extracted the aqueous solution with an organic solvent (e.g., methylene chloride). After proving the extraction was quantitative, one rather clever group decided the extra steps were too tedious and time-consuming. After a phone conversation with a chemist at a local water company, they determined that in practical samples, concentrations above 10 ppm would rarely be found, so they opted to work in aqueous media only. This group also received much better performance evaluations than groups who did not justify their reasons for working at concentrations below 10 ppm (mg/L), because this instructor does not consider "because a precipitate forms" a valid reason for abandoning a concentration range for analysis.

Opportunities to expand on this laboratory project are also possible. This experiment has been designed so that four or even five instruments can be incorporated into the laboratory exercise if more time is allotted for experimental work. One could also perform a comparison of the quantitation of different metals using two or more instruments (e.g., analyze for copper and iron using UV-vis and atomic absorption spectroscopy), and have students compare the strengths and weaknesses of each method.

Supporting Materials. Supporting files are available in the single compressed file 610021mrs1.zip (<http://dx.doi.org/10.1007/s00897000453b>). The supporting files are created with Microsoft Word 2000: (1) Lab3-1.doc; student laboratory handout; (2) Lab3-2.doc; student laboratory handout; (3) Lab3-3.doc; student laboratory handout; (4) projrep.doc; student handout for the formats of oral and written progress reports; (5) labreport3.doc; student handout on final paper format; and

(6) oralquiz.doc; questions asked of students during an oral quiz on the laboratory.

References and Notes

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