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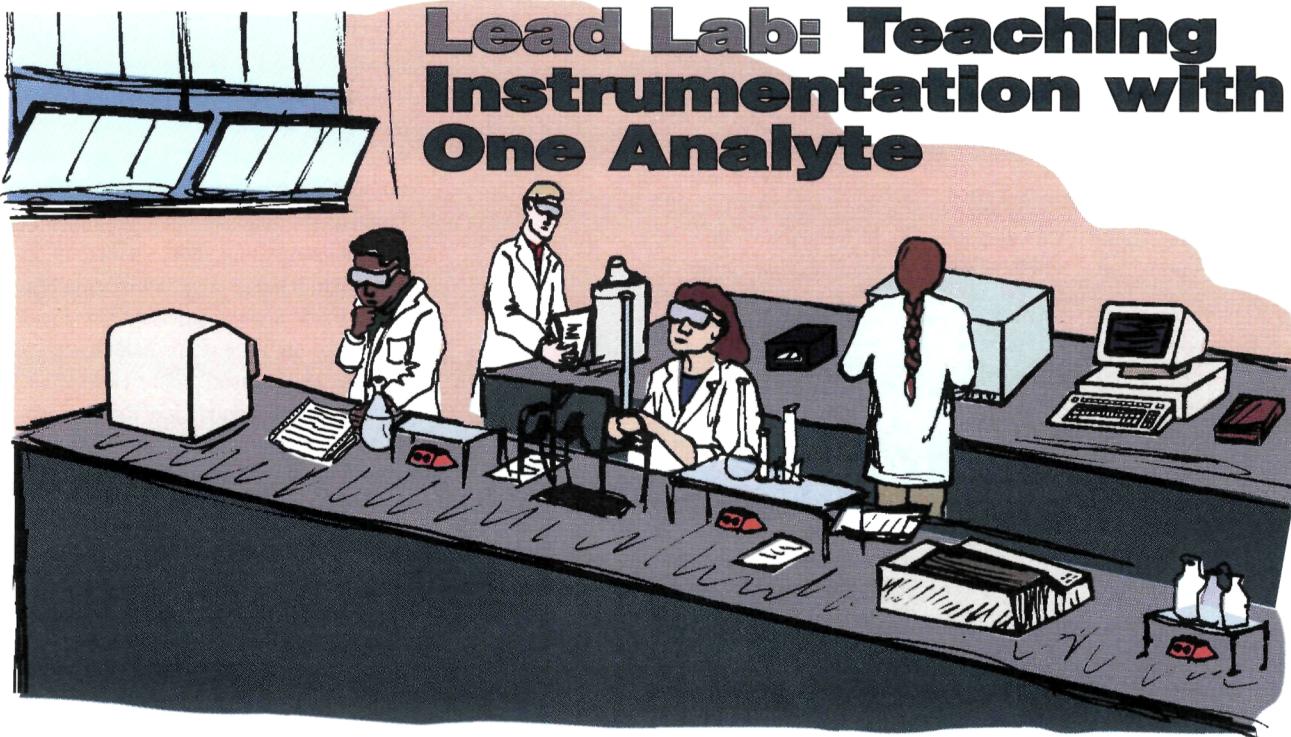
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## Lead Lab: Teaching Instrumentation with One Analyte



*Measuring lead in samples provided by the local community teaches students about chemistry, instrumentation, and life in the real analytical world*

Teaching instrumental methods of analysis has several inherent difficulties related to the quantity and variety of material to be taught. The course title implies that students will obtain skills in chemical analysis using instrumentation and a working knowledge of a wide variety of instrumentation. Teaching chemical analysis using instrumental methods is perhaps the most difficult objective to implement.

In response to the quantity of seemingly unrelated material, some textbooks prescribe the boundaries to be explored, allowing students to create a framework for organizing the material. For example, this ap-

proach may include a section on electronics as a means of integrating the material because all instruments have electronics. Although this provides a scaffold for learning, the end result still is exposure to only part of the process. In addition, students may experience difficulties because the figures of merit for an instrument are out of context. Comparing the detection limit for iodate obtained by permanganate titration with the detection limit for quinine obtained by fluorescence quenching is comparing the proverbial apple and orange.

In this Report, we describe the development of a course focusing on a single analyte that maximizes students' exposure to instruments and allows for cross-comparison of instrumental figures of merit.

### Advantages of the single analyte

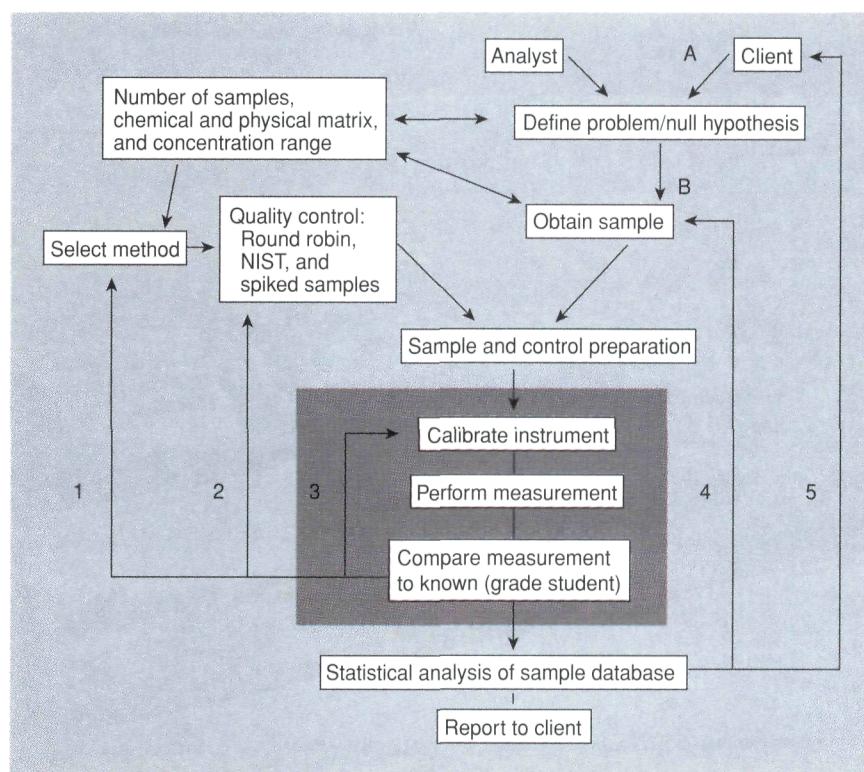
Most textbooks (1–3) describe the analytical process as in Figure 1. The client de-

fines the problem, and the analyst selects the appropriate method, performs the analysis, compares results with standards, applies statistical methods to the data, and, finally, presents the results to the client. Many of these steps are iterative and require judgment based on critical thinking at several points within the process.

Few upper-level undergraduate instrumental analysis courses attempt to teach students how to use every available analytical instrument, for obvious reasons. To practice methods development on each instrument would be prohibitively time-consuming and might hamper traditional methods of assessing the students' abilities. Consequently, a typical instrumental course focuses on a survey of instruments and a selected portion of the analytical process (the shaded area in Figure 1), allowing students to obtain hands-on experience for various instruments and discover the unique capabilities of each. However, the instrumental class can degenerate into a routine resembling a five-day tour of Europe: If this is Tuesday, it must be NMR. In addition, teaching the critical thinking and skills necessary in the workforce may receive short shrift (4).

If a single analyte is selected, however, some of the obvious problems can be mitigated. First, the amount of new material

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**Figure 1. The instrumental analytical process.**

The feedback pathways used by the students are numbered. A and B are starting points. The shaded area delineates the types of analytical processes used in the lab before the class was redesigned.

that must be added to the class is reduced because the aspects of a single analyte's chemistry that affect its measurement can be studied in increasing detail throughout the semester. Second, by using a single analyte, the students can learn to appreciate that the instrumental method is only as good as the chemistry that precedes it and that some types of instrumental methods, such as LC or polymer-based ion-selective electrodes, rely on a sound understanding of the chemistry.

Third, opportunities for critical thinking are built into the process. Sampling statistics, S/N parameters, and detection limits acquire a true significance. By cross-comparing each instrument for S/N, detection limit, linear range, and background signals for the single analyte, students learn "instrument discriminatory skills" that will serve them in real-life situations when they must select a defensible method of analysis (path 1, Figure 1). Finally, using sampling statistics makes incorporating electronics sections easier: One can easily look at a summed sine wave as it passes through an RC circuit or

as it is digitized and summed for boxcar filtering.

### Selecting lead as the single analyte

The choice of lead as the analyte for the instrumental lab was endorsed by several community groups interested in tracking lead within an urban environment. Dealing with a group of clients (hereafter referred to as "the client") places the class squarely at the beginning of the analytical process (point A, Figure 1). The involvement of a real client highlights the role of quality control in the analytical process and places the entire analytical sequence within an easily grasped framework: The data obtained by the student, once released to the client, could be used by that client for various purposes, all of which depend on the assumption that the entire analytical process is defensible.

Other educational factors also had to be considered. Does lead analysis overly narrow the content of the course? That is, do sample collection and preparation require so much lab time that breadth of

instrumentation is sacrificed? Does the selection of lead as analyte result in additional sacrifices of instruments traditionally used in instrumental analysis classes so that the second course objective (exposure to a wide range of instrumentation) is not met? Instrumentation for organic functional group analysis leaps immediately to mind as something short-shrifted by this approach. If this is a particular concern, other single analyte lab sequences, such as one for benzene or formaldehyde, can be designed. (Based on our experience with the single analyte lab, the new biochemistry program at Loyola has adopted a single protein as the basis of the undergraduate lab sequence.)

We finally decided to use lead for several reasons. QC, at the heart of the analysis process, becomes a priority when working with a client. Ample data exist for comparison of results to the literature, as well as a large selection of standard materials. Lead is considered one of the main environmental health threats today and is a pervasive problem in Loyola's local community. In addition, lead occurs in a wide variety of matrices (blood, bones, biological tissues, water, soil, dust, air, brasses, bronzes, glasses, ceramics, gasolines, crayons, window blinds, and paints); this shows the students that although lead is commonly thought of in the context of a simple metal ion analysis, its chemistry is quite complex and interesting.

Although functional group analysis associated with the IR lab is not as educational as we had hoped, we decided that this was acceptable because students are routinely exposed to IR and NMR methods for functional group analysis within the organic chemistry labs. However, if the instructor wishes, several nontraditional methods of lead determination that emphasize IR analysis through functional group chemistry can be used. In addition, suboptimal performance of some instruments can serve as learning opportunities in the methods development process, while still giving students hands-on experience with the instrument.

### The lab sequence

To simultaneously pursue the themes of lead chemistry and sampling statistics, labs introducing these concepts are given early in the semester. At the first class meeting, students use a spreadsheet to do

a statistical analysis of a simple measurement such as the weight or circumference of red and white potatoes. They observe changes in the shapes and resolution of the sampled populations and explore the shape of the Gaussian curve as sample size increases.

In the next lab, the students take a field trip to sample soils. At each site, a 5-ft circular pattern of cuts is made, and soils are sampled to a depth of 1 in. The students explore sampling statistics of the soil and relate them to the sampling statistics in the first lab.

Digesting the samples begins in the third lab. Students randomly select a sequence of sampled soils, which are then combined, ground, and sieved. Four 1-g soil samples are weighed—two samples are considered unknowns, and the other two become internal standards (soil and added lead). A fifth sample is a soil-less spike. This fall, a sixth sample was introduced: a digestion of a NIST standard soil that has either a high or low lead content. (The high and low lead soil standards were distributed randomly among the students.)

While the soil is digesting, students sample a simple electronic signal with an A/D converter and resolve it (on a spreadsheet) from the noise using whole-wave averaging, boxcar filtering, and RC filtering. The final introductory lab is a classical precipitation experiment in which students confront QC issues, problems of matrix effects within the soil, and how pH affects lead chemistry.

The first instrumental method, the UV-vis measurement of lead by extraction with dithizone (5, 6), bridges the worlds of classic wet chemistry and instrumentation. The themes emphasized in this lab are the chemistry of extraction (chelation of lead via sulfur functionalities and the extraction of organolead from an aqueous phase), the need for reagents to mask zinc and other metals (equilibrium chemistry), and pH control.

A full-spectral measurement of free dithizone and lead dithizone is used to reiterate the concepts of resolution. Deliberately adding zinc to the lead standards emphasizes the resolution of lead dithizone and zinc dithizone from background and sample matrix effects. The result is a nice instrumental calibration, but the stu-

dents are unable to take measurements on a contaminated soil because of interferences from the sample matrix. They find that things don't always work out as they had planned.

Next is fluorescence quenching of Calcein Blue by lead, a lab developed specifically for this course (7). Again, the chemistry of the analysis depends strongly on the pH behavior of lead and Calcein Blue, repeating the emphasis on chemistry. The fiber-optic bread-board instrumentation used in this lab is "transparent" and demonstrates spectroscopic components; the use of a chopper reiterates the theme of signal processing. Alternatively, erythrocyte protoporphyrin fluorescence, a fairly common indirect method of measuring blood lead before 1980 (8–11), can be used. This method has the advantage of

increased co-added spectra and the increase in resolution of the main peaks  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ , and  $^{208}\text{Pb}$  from the satellite  $^{207}\text{Pb}$  peak with the increased S/N.

An optional FT-IR lab based on the dithizone–lead chelation, in which students are asked to identify the lead–sulfur vibrational peak, can be incorporated here. The chelate stability is low, and the signal dependence on pH is quite high, so this lab is fraught with potential for catastrophic failure.

The final third of the semester is devoted to electroanalytical and chromatographic methods. Cyclic voltammetry (CV) is used to explore the rate of electrolysis of the dithizone reagent by  $\text{Fe}(\text{CN})_6^{3-}$ . In the classic dithizone UV-vis determination of lead, cyanide is added to mask metals competing for binding to dithizone, and citrate is added to prevent the formation of  $\text{Fe}(\text{CN})_6^{3-}$ . The presence of  $\text{Fe}(\text{CN})_6^{3-}$  within the sample will accelerate the decomposition of the dithizone reagent via an oxidative dimerization through the sulfur moieties (19, 20). Although the voltammograms obtained will not be perfect, they demonstrate the instability of the dithizone reagent in the presence of an electron-transfer reagent and, consequently, the use of CV as a kinetic tool.

Anodic stripping voltammetry (ASV) nicely demonstrates the resolution of lead from background contaminants. This is a good place to teach the method of standard additions, particularly for the soil samples that have a large background current caused by organics from the soil (21–25). Organolead in leaded gasolines can be measured by GC, and appropriate LC methods include the extraction of lead as a hydrophobic chelate onto an organic solid phase and lead–EDTA ion pairing.

Lead ion-selective electrodes (ISEs) do not work well for directly determining lead because of pH and competitive ion effects in the sample. Titrating lead can work if other metals are masked. We are developing an experiment based on a polymer-based lead ISE with chemistry that depends on a sulfur-based ligand immobilized in the polymer, a process that mirrors the extraction process used in the dithizone UV-vis labs.

The final lab is a summary session on statistics, QC, and ethics. At this point in the semester, students should be able to

## *Labs introducing lead chemistry and sampling statistics are given early in the semester.*

being historically validated, yet it does deviate from measuring lead in soils.

The graphite furnace atomic absorption spectroscopy (GFAAS) lab (12–17) that follows is particularly nice because the chemistry of the soil digestion becomes important—HCl digestions result in highly volatile lead chlorides. The gas-phase chemistry within the furnace exactly mirrors the chemistry involved in the municipal incineration of trash. Lead is also one of the classic examples of spectral line interference, because the most intense atomic transition occurs at 405.7 nm and can be masked by potassium and manganese.

The FT-NMR lab (18) builds on the chelation chemistry encountered in the UV-vis dithizone lab. Lead is chelated with EDTA, and its spectrum is obtained. Chemical shifts and functional groups are identified, and the natural abundance of  $^{207}\text{Pb}$  is determined. The subtext to this lab is the S/N enhancement obtained with

choose a method, quantitatively defend their choice, and apply it to their soil samples. Students uniformly indicate that ASV and GFAAS are their methods of choice. They pool data obtained from the methods from which calibration curves were obtained and subject it to statistical analysis.

In addition, the group uses its knowledge of population statistics to dissect the early results of Needleman's seminal paper, which set the tone for the public health debate on the effect of lead on the IQs of elementary schoolchildren (26). This discussion leads into the ethics charges brought against Needleman (27–29) and inspection of biases introduced by the students because of preconceived expectations of soil lead distribution.

### QC and assessing student performance

Students are assessed in individual labs by their ability to obtain figures of merit for the methods that are in the published literature and/or within the population of values obtained by previous generations of undergraduates, graduates, and faculty. Quantitative lab skills are assessed by the students' ability to obtain a 50-ppm lead measurement via acid digestion of a soil-less 50-ppm lead blank.

For a particular group of students, the average soil-less blank is  $63 \pm 55$  ppm. Student data obtained for sample soils with unknown lead content are assessed by the ability to measure the 50-ppm lead added to the soils. When all student data are taken as a composite, the total variability of the data is used to discriminate student outlier data points, bringing the internal control value to  $58 \pm 21$  ppm.

In addition to these quantitative assessments of performance, students are assessed by the traditional lab report write-up, which incorporates questions to be considered in the essay portion of the report. Because of the number of reports written, this is the first science class ever designated as "writing-intensive" at Loyola.

### Implementation

Each lab has been designed to fit within the traditional four-hour time slot for the instrumental analysis lab. To ensure QC, the number of students is restricted to six per lab, making two subgroups of three per lab period. Typical enrollment is

14–24 students, and three or four lab periods are offered. Each subgroup operates a different instrument, so two instruments are run concurrently for two weeks.

Graduate student teaching assistants (TAs) are assigned an instrument and must be present at all labs in which that instrument is used, resulting in an allotment of 8–16 lab periods concentrated within a two-to four-week period. Although this requirement represents an increase in teaching resources, TAs are not solely responsible for grading labs. (Because this class is designated writing-intensive, faculty feedback is required.) Because much of the lab work is group-structured, students are encouraged to write the materials and methods, instrumental calibration, and discussion portions of the lab together as a group. Raw data and conclusions are to be appended individually to the group report. A final report to the client is required.

### The client

The client's presence in the process adds some logistical problems to the lab. The

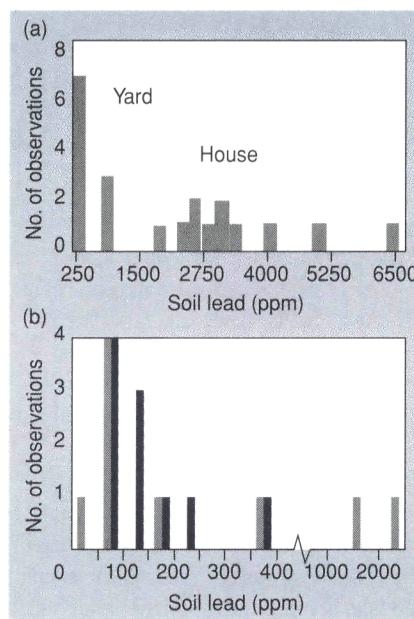
client may be under the mistaken impression that the process is similar to that of a commercial laboratory, and samples are sometimes submitted at times that do not mesh well with the time frame of the lab. Sample turnaround time is longer in a teaching lab than in a commercial lab, and the number of samples may not be appropriate for the size of the class. Other problems include the communication required between the client and the class and the changing nature of the student class.

Depending on the type of questions posed by the client, the class may simply provide a measure of soil lead to which some quality assurance is attached. For example, when the sample is delivered to the class, students start at point B in Figure 1. Alternatively, the question posed by the client may require some definition of a null hypothesis and incorporation of methods to determine the validity of the null hypothesis, which means the students start at point A in Figure 1. This introduces another iterative step into the sequence, which may involve several semesters of students.

For example, the client for the Loyola classes of '94 and '95 asked, "How does the lead deposited by the incinerator within the surrounding soils compare to average Chicago soils?" The first iteration of this question involved sampling soils of homeowners within a 1.5-mile radius of the incinerator. The students' GFAAS results shown in Figure 2a are consistent with the published literature values of 1500–2500 ppm near the housing structure and 200–400 ppm away from the housing structure (30). Background values for Chicago obtained from the published literature are 250–400 ppm (31). The students' report to the homeowners indicated that soil lead was highest near the house and less farther away but that the soils were not noticeably higher in lead than the literature value for urban Chicago.

A second iteration (path 4, Figure 1) involved increased sampling to include housing units 17 miles away matched for age and housing type. Data from these homes were added to those of the original pool, and no statistical differences were detected.

A third iteration (path 5, Figure 1), initiated by the original lab group, changed the null hypothesis to "Are there higher values of soil lead downwind compared



**Figure 2. Student-derived lead data from soil.**

(a) Combined GFAAS and ASV data for soil samples with large amounts of lead near the house walls and lower amounts of lead away from the house. (b) Resolution of soil samples taken within a block of the incinerator (gray) and farther than a block away (blue). Students' statistical analysis suggested poor resolution. Several high-lead samples near the incinerator led students to suggest an increase in the sample population.

with upwind from the incinerator?" Resampling was initiated in fall 1995, and soils were sampled between the road and the sidewalk and in parks and empty lots, away from all housing. This sampling pattern was based on data acquired during the preceding year.

Statistical analysis of the data showed no difference between up- and downwind samples, but it did show some data that fell outside of the urban background pool. Those few data points lay within a one-block distance of the incinerator. Using atmospheric models, we found that the sampling grid lines were too far apart. Data were re-analyzed on the basis of total distance from the incinerator (Figure 2b). The students' report to the client suggested that no soil lead deposition was detected but that the hot spots should be further investigated, both historically and by using a finer sampling grid.

### Conclusion

One of the difficulties with this program is maintaining a high-quality, sophisticated level of instrumentation, particularly if that instrumentation is not routinely used for other functions within the department. The program works best when the more elaborate instrumentation, such as an ICP mass spectrometer, is part of a thriving research program.

Although administering the community-driven research, which is the heart of this program's success, is the most difficult aspect of the program, it has attracted both external and internal attention, as well as financial support. On the basis of a student-made videotape highlighting the goals and results of the program, Anheuser-Busch chose this program as one of three awardees in the collegiate division for environmentally related projects at educational institutions. This recognition provided the leverage for increased internal support to bring the ICPMS instrumentation on line, incorporate microwave digestions, and develop a CE lab. The workload for the students has not lessened, but because some of the changes that we have implemented relate their work in the laboratory to what goes on in the real world, some of the complaints about the work itself have diminished.

The biggest plus is that each semester 15–25% of the students are volunteering for

related activities. These volunteer activities include researching airflow patterns; sampling at alternative locations; video presentations; verifying dust sampling protocols; and assisting at campus field trips when elementary school children, who have taken dust samples at their own schools, come to observe what happens to the sample in the lab. Graduate TAs have also been similarly motivated.

Other measures of success are unrelated to volunteer activities but testify to the impact of the research and QC skills learned in this program. Letters from former students indicate that participation in this lab was one of the most important

### *The client's presence in the process adds some logistical problems to the lab.*

factors in receiving job offers. One student will be an intern in a United Nations-supported air pollution project in Croatia because of the skills and experience he gained in this lab.

This project was initiated with a subcontract from Loyola's Policy Research and Action Group's MacArthur Foundation Grant. The ICPMS instrumentation donated by Chemical Waste Management is supported with Loyola capital budget funds. The Anheuser-Busch Corp. "Pledge and a Promise Environmental Awards" program supports an ongoing collaboration with surrounding elementary schools for measuring lead in house dust. The 300-MHz NMR instrumentation was supported with an NSF ILI grant to Keith Jameson.

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