

ANALYTICAL CHEMISTRY 256

ROLE-PLAYING LAB

1998-1999 Academic Year

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Introduction to Role-Playing and Laboratory Computing

Defining the Kinds of Role-Playing Responsibilities

Round-Robin Certification of Laboratory Glassware

PRODUCTION QUALITY CONTROL LEAD ANALYSIS

Statistical/Chemical Evaluation of Lead Data

Semi-Automated Weak Acid Titration

Graphical Analysis of Weak Acid Titration

Designing a Mock Robot Experiment

Executing the Mock Robot Experiment

The Incredible Edible Easter Egg Grass Advertising Dilemma

The Downsizing Dilemma

The Broken Pill Coating Machine Assembly Line Shutdown Dilemma

The Instrument Purchase Payment Release Dilemma

Closure

ROLES:

Manager:	Designing Round Robin Statistics and Scheduling the Experiment
Chemist:	Forming and Digesting the Lead Precipitates
Software:	Spreadsheet Organization for Round Robin Testing
Hardware:	Filtering, Drying Ppts, Making a Cable, and Connecting the Balance

OBJECTIVES:

Under the umbrella of designing an acceptable, humane method of production quality control for lead pastes in battery plates, a prototype chemical system is explored for flaws in its implementation. The method calls for a statistically valid comparison of homogeneous vs. heterogeneous precipitation techniques, an investigation of crystal sizes, a comparison of glassware drying techniques, and the actual generation of data to be used in round robin testing. The multitude of short attention span tests calls for a high degree of organizational planning to avoid technician demoralization due to "hurry and wait" lab situations, while also retaining quality. Constant weight gravimetric conditions are determined by computer plotted cooling curves.

MANAGEMENT INTERVIEW:

The interview has two parts. The first part concerns management of lab time and resources. The second concerns management of data in the round robin tests. Lab complications due to chemical waste disposal, spills, and other technique problems must be considered. Special attention has to be directed to time management and close communication between role players. Time required for glassware drying and the investigation of alternate techniques are key discovery issues.

The Possibility of Dual Roles

This is an experiment that can have dual roles. For example, **Manager** and **Chemist** can be combined into a single role called **Manager**. Alternately, **Chemist** and **Hardware** can be combined into a single **Chemist** role. **Software** should remain uncombined, largely due to the learning time creation of the spreadsheets may require. If the Company has 3 people in it, instead of 4, and the roles of **Hardware** and **Software** have already been combined, then **Manager** should consider the desirability of making the spreadsheet from scratch and using a pre-built cable, emphasizing the **Software** component of the dual role.

However, if the roles are combined, it probably will not be a good idea to attempt too much interfacing between the analytical balance and the lab microcomputer. After reading the experiment, **Manager** should determine if a dual role-play is desired based on the number of people in the Company. If it is, **Manager** should decide which roles are to be combined. There is risk here.

Introduction

This experiment mimics the classic daily lot of a Ph.D. analytical lab manager. **Quality Control (QC)** testing is, candidly put, not stimulating work! If the QC methods work, then their predictability is unquestionably boring. Things get interesting only when the method does not work.

Also, sample compositions are mostly the same, sample analysis times should be short, costs should be kept as low as possible, regulatory agencies should receive only the data they need, and the people doing the experiment should be reliable and sensibly content with their lot. If all this happens, and if the samples being routinely monitored stay well within specification, then the QC method quietly and successfully folds into the background of daily lab business. This is as it should be.

How do methods like this happen? That is the interesting part. They have to be **developed**. And such **methods development** must be done by people sufficiently skilled to cause the final product to produce all of the above "performance effects". The responsibility for making this happen is that of the Ph.D. lab manager (here played by **Manager**). So, this experiment is a mimic of a **methods development task** in an industrial quality control laboratory.

The single most important thing that **Manager** has to worry about when doing **methods development** is the **native sample**, and how to instruct his staff in obtaining a representative portion (or **aliquot**) of it. The next most important item is how to keep all personnel safe when handling the native sample, and, of course, in all further lab operations. Obviously, the priorities have to be this way since safe methods cannot be stipulated without knowing what the sample is and how it must be sampled. After this, **Manager** has to worry about **sample pretreatment**, which, for our lab, means dissolution and (usually) filtration.

Probably the most difficult responsibility that **Manager** has in any QC development effort is certification that the method works. If there were simple **primary standards** that truly reflected every natural sample **matrix** that came in, then there would be little challenge. But, those standards usually are just a "pure" sample.

The standard matrix usually is just water. So **Manager** has to judge the suitability of the method s/he chooses as the routine method based on **round robin testing**. This makes **timing** and **communication** critical.

While other members of the staff can do many tasks, and assume the responsibilities for doing them well, it is ultimately **Manager** who has to select the actual **method of choice**. A host of considerations then come up. In our mimic, we will only look into three methods, two of which are variations of a single chemical procedure. In the profession, sometimes as many as a dozen variations on five or six proven methods are at issue.

In a complex method like this one, where the tasks done in the company are diverse, outside consulting often is needed. For example, **Hardware** will need to build a serial cable and connector to connect between the electronic **analytical** balance and the Macintosh laboratory microcomputer. **Hardware** and **Software** will want to work together, using the instruction manual furnished for the electronic **analytical** balance, to get "cooling curve" data from the balance into the Macintosh lab microcomputer where it can be saved in a **disk file** and later used in any spreadsheets or exchanged between companies. This requires good timing and good communication.

Chemist and **Hardware** will have to explore the use of atomic absorption spectrophotometry (AA) as a possible competitive method to the gravimetric method that **Manager** and **Chemist** will prepare explore. In this case, **Software** will need to develop TI-86 calculator or spreadsheet programs for doing "standard additions".

Finally, when it is **necessary to interpret data**, either by round robin or local procedures, some kind of applied statistics have to be used. This is not a task for **Software** alone, since it calls for many interpreted judgments. While **Software** can implement statistical procedures (like running the Excel spreadsheet), it is up to **Manager** to work with **Software** to determine what tests to use, and, especially, how to interpret them.

That then forms the professional basis of what I have called **analytical methods development**. What remains for **Manager** to read, before specific resources can be used, is the **dilemma** that is posed, and the **specific context** of the problem.

The Dilemma

As **Manager**, you have been given the task of identifying the best procedure to use for the production quality control monitoring of the lead stock that is used to make the "paste" that fills the open spaces in the "grids" of the diesel batteries your company makes for farm tractor use. The paste is a fibrous mixture of lead, lead oxide, and binder. The grid is a proprietary structure, invented and patented by the engineering division of your company. The lead stock is a pure lead, which when dissolved to form a lead nitrate solution can be blended with the binder material and the lead oxide to form a paste that can be pressed into the open spaces in the battery grid.

Production quality control procedures you have used in the past call for random sampling of the lead stock, selecting about 1 gram material on a random basis from each 10 kilogram lot used. This sample can then be dissolved to make a lead nitrate solution containing (if the original stock is pure) about 3% lead. The monitoring is a policing action on the vendor of the primary stock to check for possible adulteration of the incoming stock, or the presence of impure stock.

It is tempting to look for "instrumental" methods of analysis for this lead stock. The idea of a fast answer is appealing. Yet, the sample surely will be >99.9% pure lead. The differences that you are looking for in the "assay" of the incoming lead are at the **principal constituent level** of concentration.

For example, if a lot assayed at 99.0 % lead (and had 1.0% adulteration impurities), and you were paying \$35.00 per kilogram of stock, a 35 ton shipment would cost \$3,749.38 if it were pure, but yield only \$3,711.88 in lead at the 99.0% purity level. This is a difference of \$37.50 per shipment. Considering that your company accepts between 3,000 and 3,500 such shipments a year, the minimum loss due to accepting impure lead as pure lead would total \$74,997.50, and could get as high as \$112,500 in a "good year". Since the most you pay a technician is \$29,500 per year, it looks like the difference between accepting lead at the 99.0% purity level and the 100.0% purity level (only trace impurities) could easily be something like \$50,000 per year.

For this reason (checking your "old" quantitative analysis textbook!) you suspect that you will have

to use a "wet" method, and probably a gravimetric wet method, to get the necessary precision and accuracy. But, there is an overriding and general need to have a method that will provide accurate results with speed. Although gravimetric methods are slow in general, some are slower than others, especially in the "chemical steps" of precipitate formation.

Recently your division **Manager** returned from the Pittsburgh Conference trade show, where she had seen all of the advances in analytical instrumentation, including atomic absorption. While purchasing a new atomic absorption spectrophotometer is out of the budget, new AA's can run between \$50K- \$100K, she wondered if the older Buck 200A model on hand in the lab might be able to do the trick.

Using the AA with a Pb standard addition as an alternate method is a possibility. The samples used are much smaller, reducing the cost associated with disposal and is actually quite a bit faster. The AA, however, isn't without its problems. The large dilution factors necessary to bring the solutions into the range of the AA Pb Hollow Cathode Lamp, introduces quite a large possibility and likelihood for error, not to mention the cost of the elemental standard that must be purchased and certified by a commercial supplier. Performing a standard addition with the AA offers a great savings in terms of time. The question is whether or not this method sacrifices accuracy for speed and cost.

If the AA is found to be a superior method after all things have been considered, then not only would actual analytical time be shortened, with attendant savings in wages and charge-backs, but also the amount of lead waste that would have to be disposed of could be reduced. Such waste is a major headache. Working with less of it would be an immense savings to the Company.

There are two gravimetric methods that have been explored on a pilot scale previously. One is called "heterogeneous precipitation", and has proven to be fast. The other is called "homogeneous precipitation", and has the possibility of being more accurate due to larger precipitate crystals. These methods have to be competitively evaluated against each other, according to speed, accuracy, and waste disposal problems, as well as against the apparently faster AA method that has never been for this application in the Company before.

There is one very subtle point to these competitive methods. The two gravimetric methods are "stoichiometric". What this means is that no standards are needed to calculate the percentage of lead in the sample. All numbers are already known. The only measurement step is to use the analytical balance to weigh the precipitate. From then on, all calculations just use known stoichiometric compound ratios, and known molecular weights, to arrive at the concentration answer.

But, the AA method is "non-stoichiometric". A readout value is generated by the spectrophotometer. In order to relate the readout value to a concentration, a procedure called "standard addition" will have to be used. In this method the unknown is used as the matrix, and small additions of a lead standard are made to it. The lead concentration should change in a known manner, while the solution volume and the matrix composition should remain substantially constant. But, if there are errors in the standards, then there will be propagation of that error into the answer calculated from the potential measurement. However, using lead AA elemental standards which have been certified by the supplier alleviates this problem at a cost. New 500 mL commercial standards run from \$46 for lead to \$415 for a 500 mL Rhodium standard. Accuracy then is at issue, and a central question will be to determine if the accuracy of the two gravimetric methods is better than the AA method because the gravimetric methods are stoichiometric, and the AA method is non-stoichiometric.

The gravimetric methods do have one rather bothersome characteristic. Once the precipitates have been formed, they have to be dried, to remove any water, so that all that is weighed is a lead salt of known stoichiometric composition. The drying takes time. And, after the drying has been done, the crucibles containing the dried sample have to be brought back to room temperature before they can be reliably weighed. This, too, takes time. All of the gravimetric methods everyone has used over the

years have been plagued by the problems of bring crucibles and precipitates to **constant weight** after heating in any kind of oven to drive off water.

The problem lies in not overestimating the amount of time it takes the crucibles to cool, before they can be weighed. If they are weighed while still hot, the air around them will be rising while they are on the balance as they give off heat, disturbing the reading (usually they read "light" due to the air lifting up on the pan as it rises). Thus to get a correct reading, the crucibles have to be at the same temperature as the inside of the balance, which should then be at room temperature itself.

It does occur to you though that with your new **serially interfaced** electronic analytical balances, your **Hardware** person could cable the balance to the lab microcomputer, and your **Software** person could use the LabVIEW virtual instrument explored in the first experiment to query the balance for a weight every few seconds, and then a spreadsheet to present the weight in graphical form to see when it was actually constant. This might be worth exploring as a feature of the final production QC method!

Although it appears that the AA method would be far more desirable than a gravimetric method based on drying time alone, it is possible that, once the right chemical method has been chosen, automated oven drying could be used to speed up drying crucibles and precipitates when filtered. Also, some kind of robotic method could be used to filter the precipitate. It appears that the rate limiting step in any gravimetric method will always be the formation and digesting of the precipitate as such. For this reason, you have to look carefully at how much additional **accuracy** is achieved by procedures that call for slow formation of the precipitate, and long digestion times, both of which are claimed to produce larger crystals and minimize contamination of the resulting product.

Waste disposal and daily safety issues have to be taken very seriously. Lead salts can be nasty chemicals to handle in the lab. There are safety problems, including toxicity to the person doing the work, EPA and OSHA requirements on both handling and disposal of all the materials used, and the usual "mess" of hot acid digestions. Your **Chemist** is going to have to research this carefully, and all reagents in all intermediate dilution stages are going to have to be kept in capped, clearly labeled bottles.

OSHA inspection of reagent handling is possible at any time, and studied procedures for working with all reagents will be needed. MSDS sheets on all reagents and products will be needed, and all workers will have to be fully instructed in the nature of what is being handled, and how the intermediate storage methods are to be done. FPHA labeling is **an absolutely mandatory need!**

One thing is certain. In any QC method, you have learned from experience not to ask the technician who is doing the chemistry and weighing to do the calculations! Technicians who are happiest with this kind of work usually are not mathematically gifted. The usual situation is that the better they are with their hands, the worse they are doing calculations. This seems to be the classic "left/right brain" conflict. A technician with impeccable motor skills in the lab may be error prone and awkward with calculations, and the converse.

This time, you will have **Software** develop either a spreadsheet that will allow weights to be entered directly, or a TI-86 program, to allow all calculations to be done automatically. The results can then be transferred into a Microsoft Word text document that will go to the primary lead vendor telling them why or why not the shipment analyzed was accepted or rejected. In this case, the only dilemma you face is how much of this to do yourself, and how much to ask **Software** to handle.

Accepting final responsibility for the work suggests you handle the Microsoft Word report writing work yourself, while **Software** takes care of the spreadsheet or the calculator program and the "print file" output of the calculations.

The last, and most serious, dilemma you face is how to tell if the method is actually accurate!

Since there will be no absolute way of knowing what the “correct” answer is to the one single lead sample being analyzed by all of the Companies, the only practical approach to determining accuracy is by “round robin testing”. In simple terms, this means statistically comparing every Company’s results. If the means from each Company can be shown to statistically the same, then a grand average can be calculated, and used to compare the two gravimetric methods with the AA method.

This round robin testing is going to require **timely collaboration** with the other Companies in this class to get an average value for the test stock used in this set of tests. As soon as results are available, Managers from all Companies are going to have to exchange them. And, each Manager will have to use a similar form of expressing their Company’s data. Results are going to have to be worked up as soon as the precipitates have been weighed and the AA standard additions evaluated, so that data can be exchanged rapidly (well before the **Management Interviews** begin). The statistics that will have to be done are not hard. The last problems are to enable very good communication between staff in the company, and bring about smooth division of labor and collaboration when time lapses for a particular role.

These give a large view of **Manager's** dilemma in designing this method! Because the scope is large, and the lab is just getting started, **Upper Management** will give some "free consulting" in the form of suggestions as to how to start distributing the responsibilities for the first week of work. Recalling that only two weeks are allowed for all of the work, time management probably is going to be the biggest challenge **Manager** faces.

The Chemistry of the Gravimetric Methods

This part of the experiment calls for comparison of two gravimetric methods for the analysis of lead. To make the role-playing experiment practical in our lab, **Upper Management** has selected the two methods reported by Emeritus Professor Richard Ramette of Carleton College in his book, Chemical Equilibrium and Analysis, Addison-Wesley, 1981, pages **176 - 187** and **644 - 647**. Professor Ramette is a recognized authority in this kind of analysis, and we may assume that his text will communicate the chemistry of these two methods with rigor and accuracy. To help get oriented, recognize that the two methods being tested are **homogeneous** and **heterogeneous** precipitation of lead as the insoluble lead chromate salt (PbCrO_4).

It is **Chemist's** responsibility to review this chemistry, develop an understanding of Ramette's descriptions of what is happening, and then **Manager's** responsibility to see that this is explained (by whomever!) to the others in the group. This communication and teaching is important! **Upper Management** will be looking to see if **Hardware** knows what **Chemist** is doing, etc., and if holes appear in the communication, it is **Manager** who gets called on the carpet!

The homogeneous method generates the **precipitant** as a **product** of a slower chemical reaction. A redox reaction, involving bromate and chromium(III), slowly and uniformly (homogeneously) produces the **precipitant** throughout the entire solution. Think about what occurs in solution as only a few molecules of hydrogen chromate form and then when more is produced over time. As Ramette points out, we expect to see larger crystals produced, which should give a better product in terms of lower contamination by **coprecipitation** (look this up in our book), and a product that is easier to filter. At least that is what we expect.



In contrast to the above, **heterogeneous** precipitation occurs when the **precipitant** is suddenly dumped into the beaker, and precipitation occurs heavily and rapidly in the immediate region where the two solutions first mix. This we expect to produce a condition called **localized supersaturation** (look it up in our book), which could produce smaller crystals that are harder to handle, and lead to higher degrees of contamination by coprecipitation. The **precipitant** here is actually the same chemical species as in the homogeneous reaction; however, it is rapidly produced by a hydrolysis reaction that occurs in the preparation of the stock reagent. Thus, you are adding hydrogen chromate to the reaction vessel directly!



*Note that the **identical precipitate** is formed in both the homogeneous and heterogeneous case.

Chemist and **Manager** do need to work well together here in making sure that the chemistry is understood by all involved. **Manager** actually will want to determine if the expectations mentioned above do actually occur. In other words, are there larger crystals? Do the two methods actually produce different results in terms of accuracy when used on the same sample?

Manager should bring to the Management Interview all appropriate formulas, chemical equations (balanced, of course) and recipes used for the two methods.

Laboratory Recipes

There are some recipes and directions for making these two methods work in the lab described in Ramette. But, these have been generalized so that they can be used in any laboratory. The recipes offered for study here (not necessarily required!) come out of 6 or 7 years development work at the University of Wisconsin, and another 15 years here. They thus are a bit more specific to this course and environment. **Upper Management** offers them here as the contributions (from experience) of a **paid consultant**, and **Manager** is free to use whatever portion(s) of them s/he decides fit with his/her approach. Other sources are available in the library as well.

Cleaning the Crucibles

Six, sintered, glass bottom crucibles need to be used for this work. They are easy to handle, and filtration occurs rapidly through them. But, on the down side, they require **acid** cleaning before they are used. And if three determinations are done by the homogeneous method, and three by the heterogeneous method, then at least six crucibles have to be cleaned before any other work can be done.

Manager can decide that **Hardware** should finish cleaning the crucibles before **Chemist** starts forming the precipitate, or that **Chemist** can start forming the precipitates at the same time that **Hardware** is cleaning the crucibles and bringing them to constant weight. This is the first of many management decisions that will determine how much work gets done in the first period.



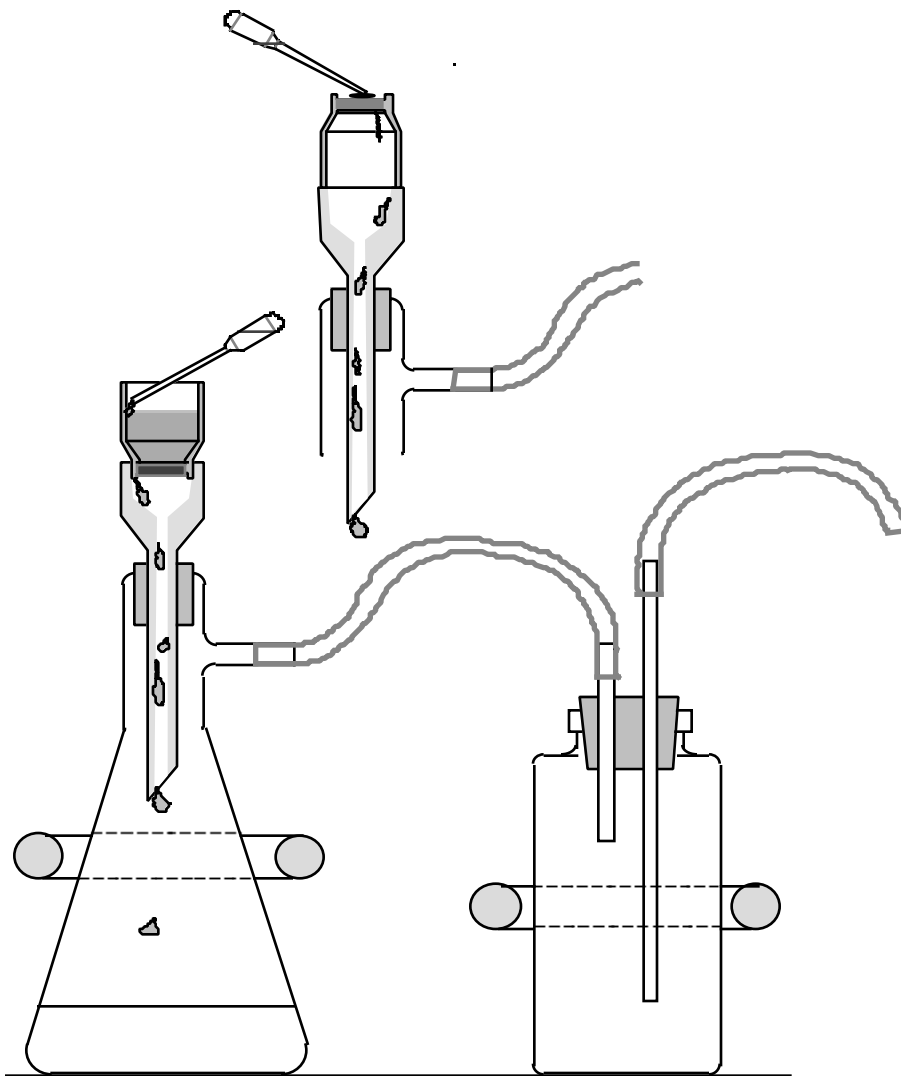
Cleaning sintered bottom crucibles is done by pulling an acid solution through them. First, **Hardware** has to assemble the proper **vacuum trap** to do this. The sketch on the next page shows the kind of trapping system that **Hardware** should set up. (Remember to plug in the vacuum.)

It is particularly important when doing this that the work be done in the hood so that noxious vapors of the acid be exhausted outside the lab. **Hardware** should make the assembly of this apparatus a studied effort of quality, with special attention paid to **good clamping** of everything in place to avoid spills of crucibles filled with acid.

To begin cleaning the crucibles, it is best to run tap water through them in both directions. It is useful to lightly rub the bottom inside and outside of the frit with a rubber policeman to remove any debris while doing this. Then, using the firmly clamped filtration apparatus, run deionized water through them several times. This is important.

The next step in cleaning the crucibles is to pass 6 M HCl through them, right side up, on while one is on the filtration apparatus. Use a small, plastic dropper for adding the acid from a beaker. Do it slowly. Refer to the sketch on the next page. Filling the crucible with this acid to the brim is risky, and not really necessary. A few smaller portions pulled through the frit will work just as well and be just as effective. But remember, all of this **must be done in the hood**. When clean, the frit may still be a dull yellow color; a snowy white frit seldom occurs except when the crucible is new. Next, remove the crucible, turn it over, and pass the HCl through it in the reverse direction. See the sketch on the next page for guidance.

Removing the crucibles from the vacuum filtration apparatus has to be done with great care, slowly, and by gently lifting one edge of the crucible so that the vacuum is slightly "cracked" to open air. A light vacuum should be pulled, to avoid pulling water from the aspirator back into the filtration apparatus. When the vacuum is first cracked, there will be a hissing rush of air into the flask, so don't be startled by the noise. If the crucible seal is cracked to fast too fast, then the incoming air may cause the liquid in the flask to "bump" and splash out onto the hood floor. It takes practice and technique skills to do this well. Be careful! Finish the cleaning by running a few portions of deionized water through the crucible, and pull on it with the vacuum for a few minutes to partially dry it by evaporation.



Drying the Crucibles

Drying the crucibles is both important and tedious! **Manager** has to organize this part of the work well, mainly to avoid long periods of idle time. For example, **Manager** will realize that **Hardware** can be drying and bringing the crucibles to constant weight before (not after) **Chemist** begins forming and digesting the precipitate. But, it is up to **Manager** to make this as a studied decision.

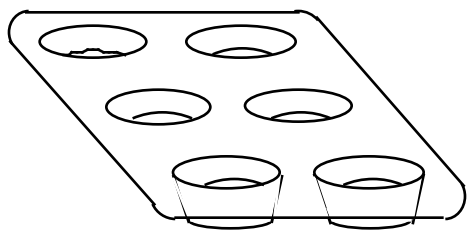
What makes this a tedious part of the experiment is that the crucibles must be at constant weight before they are used to filter the precipitate, and after they have received the precipitate. This means that if they are heated to drive out water, weighed, and then heated, and then weighed, again, the two weights will agree to within 0.000x tolerances! This is, indeed, constant weight!

The problem with this is not necessarily the time the crucibles spend in the drying ovens. Rather, when they come out of the oven, their weight is only correct when they have returned to room temperature. After removal from the oven, they should be allowed to cool for a few minutes, and then placed one at a time on the electronic analytical balance; **Hardware** records a "cooling curve" for them by recording their weights as a function of time. **Software** can quickly **import** the data collected into a Excel spreadsheet, graph the results, and tell when the last reading is the stable one.

With some coordination between **Software** and **Hardware**, the heating and cooling cycle can be reduced to a total time of 30 minutes per session, allowing at least four such cycles during an afternoon.

To help keep the heating cycle short, two ovens are set up in the lab. They are to be (and usually are) set between 110 and 120 °C, the temperature that is right to remove water from the lead chromate precipitate without decomposing it. If the ovens are at temperature, a crucible can be heated for 30 minutes, allowed to cool for 5, have a heating curve read on it for at least 5, and be ready for another heating 30 minutes after it was first taken from the oven. This will only work if the ovens are kept at 110 -115 °C, meaning the doors cannot be opened between 30 minute intervals. This is something **Hardware** must tend to.

To allow the 30 minute heating times on ovens that can only open every 30 minutes, the **door opening times** on the two ovens have to be staggered so that oven A opens on the hour and half hour, and oven B opens on the quarter and three quarter hour. This kind of organization can occur if the **Manager's** of each of the four Companies take **total control authority** over opening and loading and unloading the ovens. Else, there is chaos, and the ovens cool!



The crucibles are placed in a “muffin tin” that has each cup marked to identify the crucible it contains. The muffin tin is placed in the oven, heated, and then, when taken out, placed on a transite board on the Company bench while coming to room temperature. The tin is hot, and must be handled with a glove or hot-pad holder. Remember that all crucibles look alike when new; some identifying mark that will not melt or burn when heated is needed to distinguish them.

If **Manager** controls the ovens, and **Hardware** runs the cooling curves on the analytical balances, at least three cycles of heating, cooling, and weighing can be done in the first part of the lab. The same has to be followed with the filled crucibles.

Obtaining The Sample

The way in which **Chemist** handles the sample has a great deal to do with the success of the experiment. The sample used for the last two years is a liquid, stored in a bottle at the "wet bench" between the hoods for Laura and Bruce. It contains about 3% Pb made by dissolving about 4.8 grams of lead nitrate in 100 mL of water.

Since lead nitrate is not a primary standard, we really don't know what the exact amount of lead is in the sample. The only way to find that out is to do round robin testing between Companies. To make a comparison to other companies this semester, **Chemist** has to take an exactly measured amount of the stock solution to analyze.

How to take the sample? There are two ways. One is by volume, and the other is by weight (probably using the top loading electronic balance). The choice is not as obvious as it may seem. The volume method involves a pipette, which has just been certified and has thus known error limits in the hands of a skilled **Chemist**. The top loading balance has been calibrated, and also has known error limits. But, the degree of spillage is different when using the two devices. This must be considered.

Whatever method is used, the volume finally obtained should be near 10 mL and thus the absolute amount of lead near 0.3 g, so that the final weight of the precipitate will be between 0.4 and 0.5 g PbCrO_4 . **Manager** and **Chemist** are going to want to collaborate on this, but the final decision and the final responsibility for it lies with **Manager**.

The **Manager** of each Company **must** negotiate with the other **Manager's** on how the sample will be taken. Each Company must take it **exactly the same way** so that results later can be compared for round robin testing.

Chemist should transport portions of the stock solution to the place where the sampling is done only in **dry** beakers.

Contemplate this; if you dilute the master stock **before** you sample a portion, then the weight or volume will not have the proper units of absolute mass, and there will be error. Once the aliquot has been taken though, dilution from wet glassware no longer matters.

Manager has make sure that three samples are prepared for the homogeneous method and three for the heterogeneous method, for each Company. The samples must all be taken by the same method within a Company, and by the same method between Companies.

Forming the Precipitates

To start forming the precipitates, the solution first has to be brought up to a reasonable volume. It is recommended to add 25 mL of DI water to each "unknown" sample to do this. Then the precipitates can be formed according to one or another of the following methods:

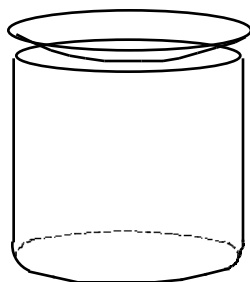
Heterogeneous Precipitation

To the above "unknown" solutions that are to be precipitated heterogeneously, **slowly** add about 10 mL of 0.1 M $K_2Cr_2O_7$ (potassium dichromate) solution. Avoid splashes, and watch carefully what happens as the solution is added.

Set up a hot plate in your Company hood. Set the above solutions on the hot plate (it may take 2 hot plates depending on the beaker sizes), and cover each beaker with a watch glass. Then, raise the heat control setting so that you slowly bring the solutions to a ****gentle**** boil. Pay close attention here. If the solutions begin to boil vigorously, you may lose portions of the precipitate by spattering; this is a direct error.

This can all be controlled by adjusting the hot plate setting. Turning it on and leaving to do something else is **inviting disaster**.

Let the solutions boil until the color of the liquid above the precipitate is a transparent brownish yellow. This is a judgment call. There should be no suspended colloids making the solution look cloudy. The precipitate should be clearly coagulated and settling to the bottom of the beaker. Then, turn off the hot plate and let the solutions cool enough that you can comfortably handle them before you attempt to filter the precipitate.



Small amounts of deionized water may have to be added while digesting the precipitates to keep the total solution volume roughly constant. Do this very gently with a wash bottle. If there appear small salt particles on the side of the beaker due to spattering and drying, wash them very carefully back into the bulk of the solution with a fine spray from the wash bottle. Be gentle!

Homogeneous Precipitation

To each of the "unknown" samples that are to be precipitated homogeneously add 20 mL of 0.1 M $\text{Cr}(\text{NO}_3)_3$ solution and 20 mL of 0.2 M KBrO_3 solution.

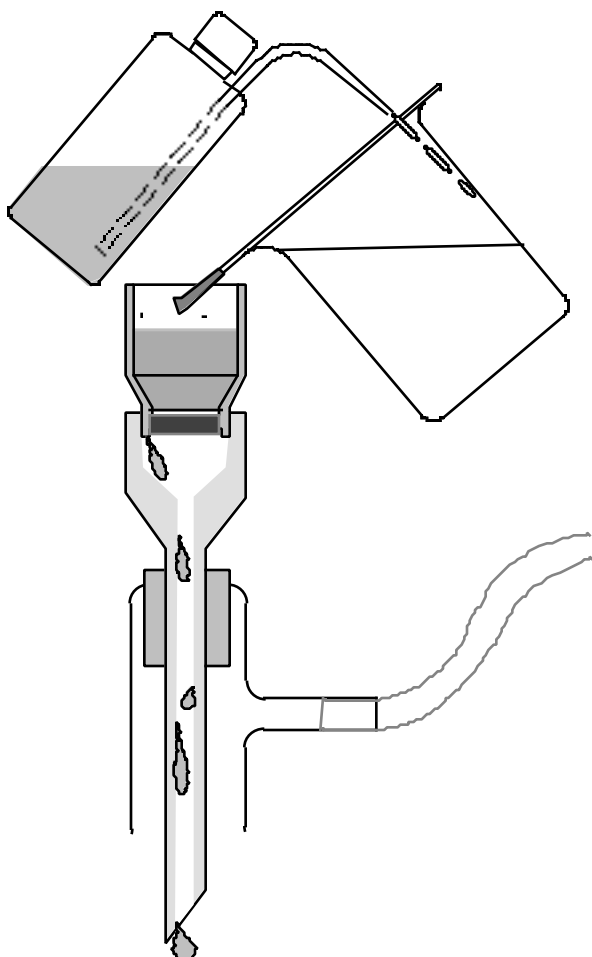
Set up a hot plate in your Company hood. Set the solutions on the hot plate (2 may be needed depending on the size of the beakers), and adjust the heat control to **bring the solutions to a gentle boil**. Pay close attention here. If the solutions begin to boil vigorously, you may lose precipitate by spattering. Lower the hot plate temperature if it appears that the solutions are starting to boil vigorously.

Let the solutions boil gently until the color of the solution above the precipitate is a transparent brownish yellow. Then add 10 mL of 1.0 M NaAC (sodium acetate) solution. Then continue the heating for another 15 minutes **but this time without boiling** the solution. Add small amounts of deionized water with your wash bottle during all of this to keep the solution volume roughly constant but, be gentle and avoid splattering.

Filtering the Precipitates

Turn off the hot plates and let all of the solutions cool to the point that you can comfortably handle the beakers before you start the filtration. At the same time, be assured that the crucibles you are going to use are at constant weight, and that a safe, secure vacuum filtration apparatus has been set up in the Company hood.

Using a rubber policeman and a wash bottle filled with deionized water to help you, quantitatively transfer all of the precipitate from the beaker to the crucible.



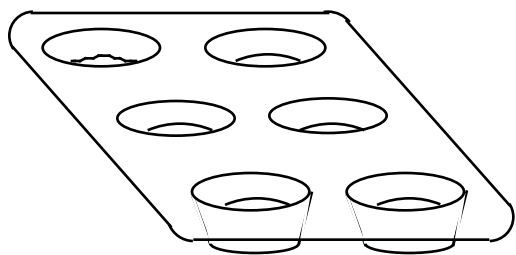
Chemist can look at the figure here at the left to see how the wash bottle and glass stirring rod are used to make sure that all of the liquid in the beaker containing the precipitate is poured into the filter. When the liquid is all passed through the filter, the last bits of precipitate are chased out of the beaker with small, directed shots from the wash bottle. The rubber policeman on the end of the stirring rod is used to scrub those sticky bits of precipitate off the walls of the beaker so that they can be washed into the filter with the wash bottle.

All of the precipitate must be in the filter. If any is left in the beaker, or if any spills out of the filter, the results will be in error. This is what is meant by "quantitative" transfer.

Drying the Crucibles/Precipitates

After all the precipitate has been transferred to a crucible, fill it about 2/3 full with deionized water (too much will cause the small buoyant particles of precipitate to "creep" over the edge!), and pull this through the "pack" at

least three times. Then, for a few minutes, pull lab air through the pack to help air dry the pack before you put it in the drying ovens.



Hardware can then prepare the aluminum "muffin tins" to hold the crucibles in the oven. Each cup in the muffin tin should be dry, and have a mark scratched near it to use for identification. But, the mark should be scratched into the aluminum; if you paste a paper label on it, the label may char in the hot oven and fall off.

If you use a grease pencil, the grease will melt and run down the cup! Hardware can put the crucibles in the beaker, and put the whole business in the oven when the schedule calls for the ovens to be opened!

One set of crucibles can be drying while the others are being filtered. If the crucibles are left in the oven for longer than the first half hour (perhaps until the next week?) then the muffin tin should be covered with another duplicate tin placed upside down on top of it. If the crucibles are removed from the oven but not weighed, they can be stored in the Company desiccator.

Preparing the Spreadsheets

	A	B	C	D	E	F
1	TIME: 13:23					
2	DATE: 2/23/93					
3	Manager: Youngun Pae					
4	Software: Mons Mitchell					
5	Hardware: Becky Moxness					
6	Chemist: Pete Leland					
7						
8	FINAL REPORT ON ANALYSIS OF LEAD DATA					
9						
10			Cruc. wt.	Cruc. wt.	Wt. of ppt.	
11			w/ppt. (g)	empty (g)	in grams	
12	HOMOGENEOUS	1	12.5489	12.5125	0.0364	
13		2	12.8719	12.8352	0.0367	
14		3	12.5105	12.4737	0.0368	
15	HETEROGENEOUS	4	12.3651	12.3291	0.0360	
16		5	13.1619	13.1267	0.0352	
17		6	14.3678	14.3316	0.0362	
18						
19			Wt. as Pb	% Pb in		
20			in grams	solution		
21	HOMOGENEOUS	1	0.0233	0.2334		
22		2	0.0235	0.2353		
23		3	0.0236	0.2359		
24	HETEROGENEOUS	4	0.0231	0.2308		
25		5	0.0226	0.2257		
26		6	0.0232	0.2321		
27						
28			Avg. %	Std. Dev.	%RSD	
29	HOMOGENEOUS		0.2349	0.00133	0.568	
30						
31	HETEROGENEOUS		0.2295	0.00339	1.478	
32						

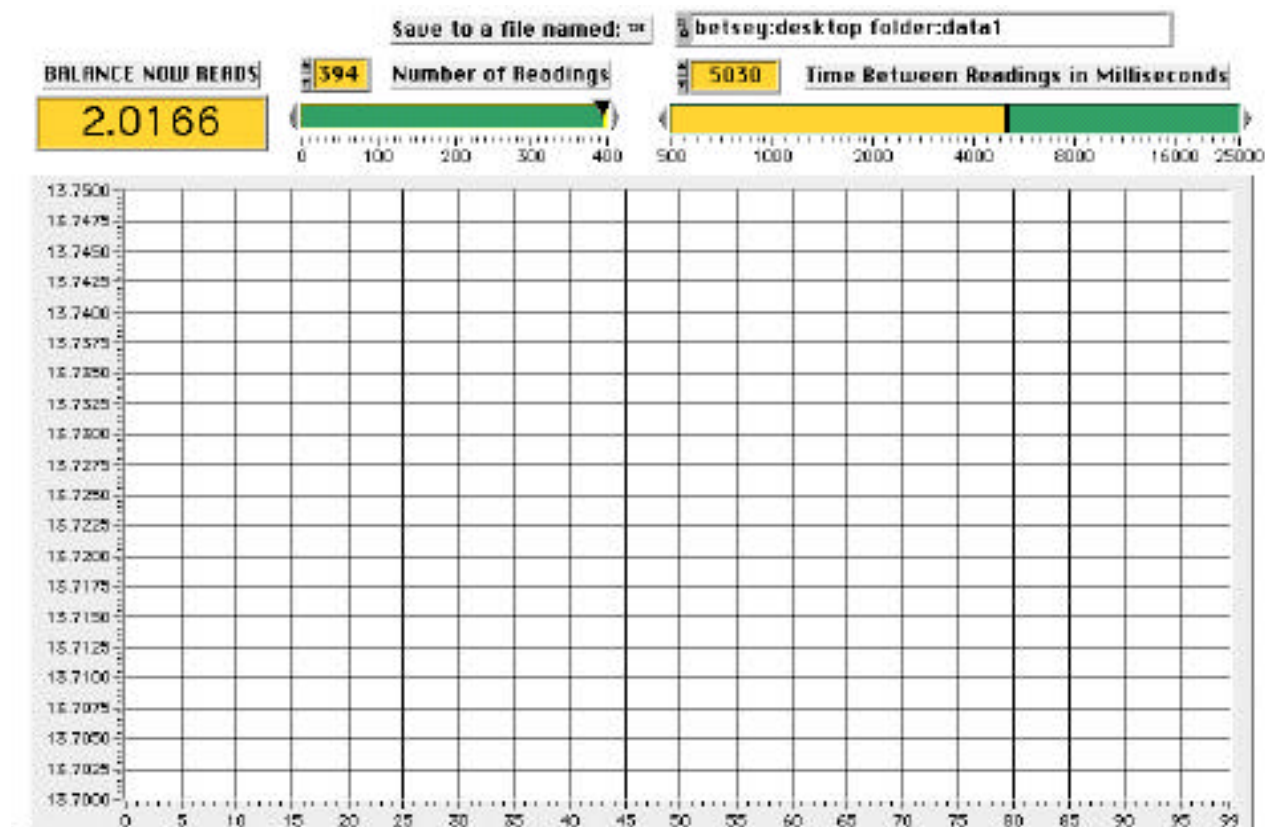
The Mac company computer holds the Excel spreadsheet. Excel will be used with **Hardware's** help to record and graphically display the crucible cooling curves to determine when they have cooled enough that their weights can be taken as stable. **Hardware** will connect the electronic analytical balance to the Macintosh.

To do this, **Hardware** will have to solder connectors to a wire to make a cable to connect between the balance and the serial port of the computer. **Upper Management** will tutor this, but **Manager** will have to schedule when **Hardware** should do the tutorial and make the cable. If there are mix-ups, **Upper Management** will sell a commercial cable to each company (fee is at least

one apple!). An example of a spreadsheet is shown here.

Software will enter and run the LabVIEW virtual instrument that will query the balance and cause data to be stored in a file in the Macintosh computer. This program (an example of which is shown below) establishes a communications port connection to the balance to allow it to be run (i.e., printed readings taken) from the computer.

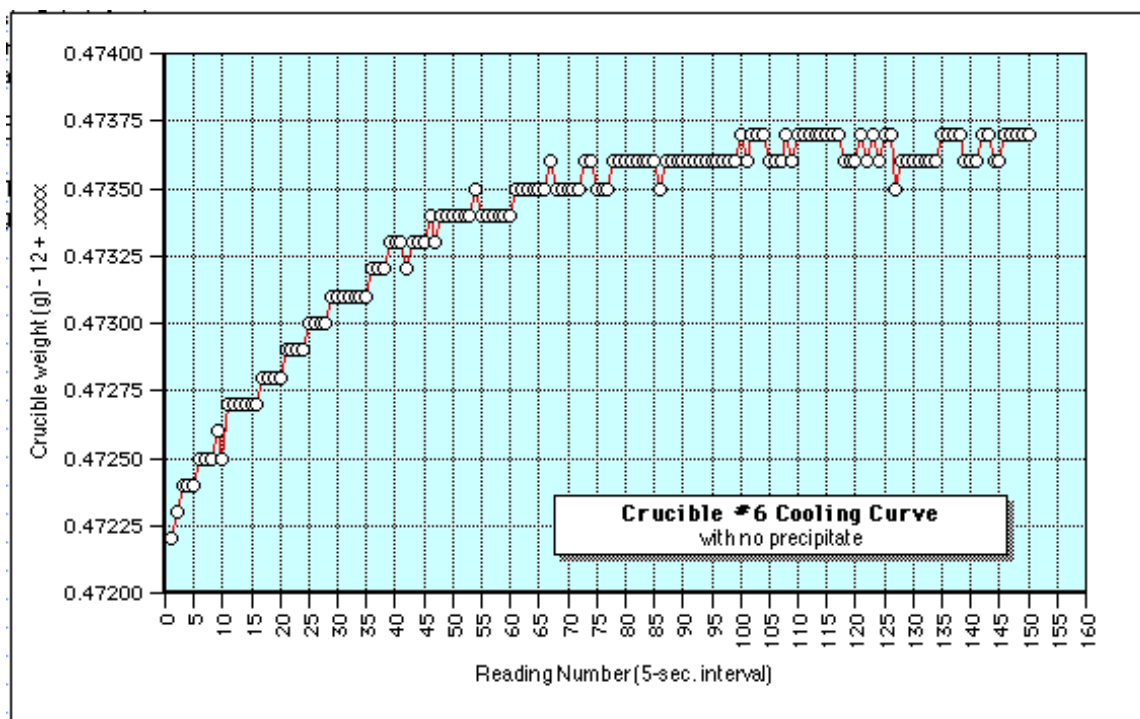
Software will run the program; it will open a "spreadsheet file" on the Macintosh disk to record the balance readings. Manager and Software will have to decide how many readings to take, and how often to take them, in order to capture a full cooling curve and determine when the crucible has reached a stable weight.



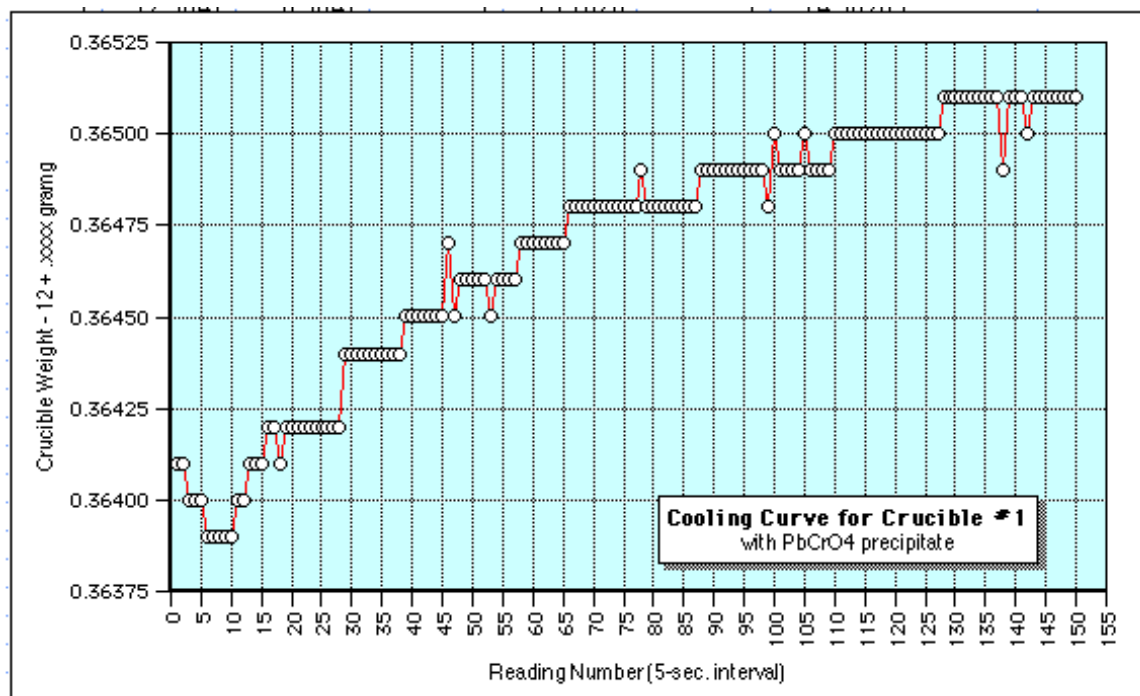
After the data have been collected in a .prn file, then they can be imported into the Excel spreadsheet and graphed. The best way to learn is this is by tutorial. Staff will gather a group together to do this when **Manager** says it is OK to do so. Each **Software** will then pass this skill on to others in the group by a similar tutorial.

An example of a cooling curve prepared this way is shown on the next page. From these data, Software can determine how to set up the LabVIEW VI so that it takes the right number of samples and at the right time interval.

Example of a Cooling Curve for an Empty Crucible



Example of a Cooling Curve for a Crucible Containing Dried Precipitate



Software also has the responsibility of setting up the Excel spreadsheet so that **Chemist** or **Manager** can make the calculations needed to get the lead concentration in the "unknown" solution from the weights of the dried precipitates. Coordination with **Chemist** is quite important here, since this spreadsheet has to contain the **gravimetric factor** for converting lead chromate to lead in the percentage calculations.

Software can become aware at this time that **Upper Management** has made a corporate wide management decision that all folders on the Analytical Chemistry Server will be **read allowed**. In simpler terms, this means that anyone with a login name can read anyone else's files who is in the same "group". This has an interesting practical consequence. It means that if **Software** for Wendy has prepared a spreadsheet for this experiment, and **Software** for Laura wants to look at it, or make a copy of it, that is fully allowed.

The **Manager's** for Wendy and Laura would be accountable for squabbles that arose if "stealing" were assumed, but for the most part, with the proper professional mail etiquette (and remembering that we **do not play the zero sum game**) this is an excellent way of learning.

The Electronic Analytical Balance

Hardware will operate the Ohaus interfaced electronic analytical balances, and be responsible for their calibration and connection to the Macintosh lab microcomputer. The manual for these balances is available in the Company library. To test the cable that **Hardware** has made, and to learn how the balance responds, **Software** can connect to the balance from the Macintosh using the LabVIEW VI and see if it runs. The analytical balances, in contrast to the top loading balances, want parameter sets of 9600 baud with even parity.

The Data Analysis

The statistical analysis of the data, and the material **Manager** needs to wrap up the work for the **Management Interview**, are discussed in the second write-up for this experiment. The report should be prepared with **Microsoft Word**, and have the printout from the spreadsheets imbedded in it as printed forms (not binary code!).

Some Closing Comments for Manager

Chemist has some tough work in this experiment getting the MSDS sheets around to all concerned and assuring proper waste disposal. This will become more evident as the second part of the experiment is done and you begin to prepare for your **Management Interview** with **Upper Management**. But, by far the biggest challenge is to make sure that all Companies have their data on the analytical server in time to do the round robin testing needed to determine what the correct concentration of lead is in the common sample. To help you see what some other folks did while you are managing this part of the experiment, the following material is appended

This table was prepared by the **Software** and **Manager** of WenFri and placed on the analytical chemistry server. Each Company then entered their data into it. The problems that resulted though were that the companies did not report how many determinations were made to arrive at an average and a standard determination - some companies had dropped samples, and others had discarded what they felt were bad data. This made the t-test impossible when comparing the homogeneous and heterogeneous methods within a company, as well as between companies.

Heterogeneous method							
	Wentue	Lautue	Brutue	Wenfri	Laufri	Brufri	Deafri
#	?	?	?	?	?	?	?
Aver. %	0.2230	0.2300	0.2192	0.2368	0.2370	0.2070	0.2404
Std Dev.	0.0016	0.003	0.0071	0.0013	0.017	0.008	0.017
% RSD	0.0072	1.48	3.23	0.56	0.72	4.01	0.071
Homogeneous method							
	?	?	?	?	?	?	?
Aver. %	0.2134	0.235	0.2311	0.1996	0.222	0.206	0.2271
Std. Dev.	0.006	0.00133	0.0081	0.0055	0.0589	0.0089	0.01667
% RSD	0.0281	0.568	3.48	2.78	2.65	4.36	0.0734

In this case we can use an additional statistical test to compare methods within or between companies. The F-test provides a simple method for comparing the precision of two sets of measurements. The quantity F, defined as the ratio of the variances of the two measurements, is computed and compared with the maximum values of F expected if there were no difference in the precision between the two sets of measurements. Just like the t-test, we must specify a probability level we wish to test at. If the calculated F-value is less than the tabulated F-value, then there is no statistical difference in the precision of the data sets at the given confidence level.

Table of Statistical F Values at the 95% Confidence Level

		1									
2	2	3	4	5	6	7	8	9	10	12	
2	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.50
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.74	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.54
11	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.40
12	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.30
	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.00

$$F = \frac{S_A^2}{S_B^2}$$

Recall that the variance is simply the square of the standard deviation. For the purpose of comparing whether there is a difference between the precision of the methods (or Companies), the convention is to place the larger variance in the numerator. We assume that there are three data points for the method tested by each company; thus, there are two degrees of freedom for each variance. From the table on the preceding page, we see that the critical F-statistic is 19.00

For example, if Wenfri wishes to compare the precision of their heterogeneous and homogeneous methods, they would perform the following calculation:

$$F = \frac{s_A^2}{s_B^2} = \frac{(0.0055)^2}{(0.0013)^2} = \frac{3.025 \times 10^{-5}}{1.69 \times 10^{-6}} = 17.90$$

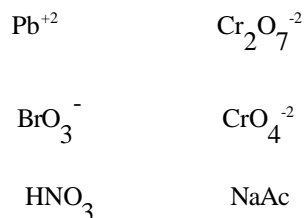
Since F calculated is less than the critical F-statistic, there is not statistical difference in the precision of the two methods at the 95% confidence level.

F-test comparing all the other companies with Wenfri company							
Heterogeneous Method							
	Wentue	Lautue	Brutue	Wenfri	Laufri	Brufri	Deafri
Std. Dev.	0.0016	0.003	0.0071	0.0013	0.017	0.008	0.017
F value	19						
F-test	1.51	5.33	29.83	1.00	1.71	37.87	1.71
Homogeneous Method							
	Wentue	Lautue	Brutue	Wenfri	Laufri	Brufri	Deafri
Std. Dev.	0.006	0.00133	0.0081	0.0055	0.0589	0.0089	0.01667
F value	19						
F-test	1.19	17.10	2.17	1.00	114.6	2.62	9.19
The F-test measures the precision of a set of measurements. By comparing our standard deviation to the standard deviation of each other group, we determined that there was a difference in precision between our heterogeneous data and those of Brutue and Brufri. The same holds true for the homogeneous method when comparing our value with Laufri. This is true because the calculated F-value was greater than the given F-value .							

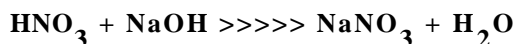
Exemplary work by a past Ole on how the lead waste would be handled were we to dispose of it ourselves, here, as part of the lab experiment.

Lab -- Gravimetric Determination of Lead
Waste Disposal Plan
Company ---- Laura
Prepared by **Chemist** ----- Doug Beussman
3/8/90 -- 3/10/90
Chem. 56 -- Prof. J. P. Walters

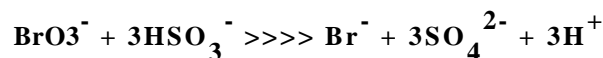
This is a report on how to get rid of the excess chemicals and the waste materials from the lead analysis lab. Items to get rid of include:



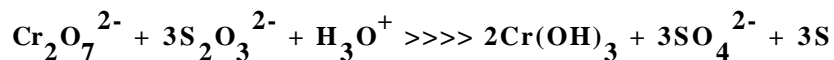
In all cases, excess reactants should be saved for future use if at all possible. If the excess nitric acid can't be saved for future use, then it can be diluted with water until it is not more than 1 M in strength. A base such as potassium hydroxide or sodium hydroxide can then be added so that the final pH is about 7. This neutralized solution can then be washed into the drain with large amounts of water¹.



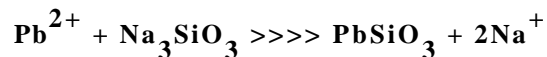
The same procedure can be used for the HCl and also for the sodium acetate. The BrO_3^- should be diluted to under 10% solution. In a hood, 10% aqueous sodium bisulfite should then be added until the yellow color of the bromate is gone. This will require about 20 ml of sodium bisulfite for every 10 ml of bromate. The resulting solution can then be neutralized with sodium carbonate, and the result can be washed down the drain with copious amounts of water¹.



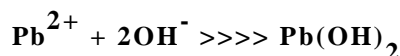
The excess $\text{K}_2\text{Cr}_2\text{O}_7$ should be reacted with $\text{Na}_2\text{S}_2\text{O}_3$ and H_2O which will yield insoluble $\text{Cr}(\text{OH})_3$ which should then be packaged up and disposed at an EPA approved waste site, making sure that EPA standards are followed¹⁻².



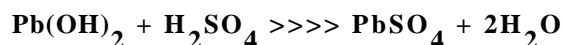
Since the PbCrO_4 precipitate cake is soluble in acid, the solid cake product should be dissolved in acid³. The CrO_4^{-2} can be treated in the same way that the excess $\text{K}_2\text{Cr}_2\text{O}_7$ was treated above. The Pb^{+2} can be treated in a couple of different ways. The first method involves reacting the Pb^{+2} with Na_2SiO_3 which then will yield the insoluble solid PbSiO_3 , which can be disposed of in an EPA approved facility^{1,4}.



Another option is to treat the Pb^{+2} with NaOH, which will produce a precipitate of $\text{Pb}(\text{OH})_2$, which can be sold to a company that produces nickel-cadmium batteries, where $\text{Pb}(\text{OH})_2$ is used⁵.



The $\text{Pb}(\text{OH})_2$ could also be reacted with H_2SO_4 , yielding PbSO_4 , which is used in the car battery field.



Depending on the costs of the waste disposal facility, the costs of the chemicals and the time to purify the products, the best method for disposing of our product can be found.

A break down of the costs for 200 samples follows (all prices taken from the 1988-89 issue of Aldrich). It is assumed that the average sample weight is 0.50 g. This would give a total of about 100 g that would have to be disposed of 100 g of PbCrO_4 is equivalent to 0.31 moles. If the waste facility method is to be used, 0.31 moles of Na_2SiO_3 will be needed to react with the Pb^{+2} ions. This corresponds to 37.84 g of Na_2SiO_3 . The CrO_4^{-2} can be precipitated by adding 0.93 moles of $\text{Na}_2\text{S}_2\text{O}_3$ and 0.62 moles of H_2SO_4 to the solution. This equals 230.81 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 60.81 g of H_2SO_4 .

37.84 g Na_2SiO_3 @ \$11.70/1000 g	\$0.44
230.81 g $\text{Na}_2\text{S}_2\text{O}_3$ @ \$23.10/1000 g	\$5.33
60.81 g H_2SO_4 @ \$16.70/1000 g	\$1.02

Chemical total	\$6.79
2.5 hours @ \$12.50/hr labor	\$31.25

total	\$38.04

If the method of converting the solid into $\text{Pb}(\text{OH})_2$ is used, 0.62 moles of NaOH will be needed. This is equal to 24.80 g NaOH.

24.80 g NaOH @ \$29.40/2500 g	\$0.29
2.5 hours @ \$12.50/ hr	\$31.25

total	\$31.54

If the $\text{Pb}(\text{OH})_2$ is to be converted to PbSO_4 , an additional 0.31 moles of H_2SO_4 needs to be used, which is equivalent to 30.40 g of H_2SO_4 .

Cost to convert to $\text{Pb}(\text{OH})_2$	\$31.54
30.40 g H_2SO_4 @ \$16.70/1000 g	\$0.51

total	\$32.05

Therefore, depending on how much extra effort it would take to purify the precipitates so that they could be used in the battery field, the most economical method of getting rid of the lead waste can be devised.

Aldrich sells sodium bisulfite for \$45.00 for 2500 g, and sodium carbonate for \$40.00 for 2500 g. Depending on how much excess reactants need to be gotten rid of, these figures can be incorporated into the total cost.

Sources of information

1. Armour, M.A. *J. Chem. Educ.* **1988**, 65, A64-A68.
2. Armour, M.A., Browne, L.M., Weir, G.L., *Hazardous Chemicals Information and Disposal Guide*, 2nd ed.; University of Alberta, 1984, pp 111-112, 382-383.
3. *Lange's Handbook of Chemistry*, 13th ed.; Dean, J.A., Ed.; McGraw-Hill: New York, 1985.
4. Armour, M.A., Browne, L.M., Weir, G.L., *Hazardous Chemicals Information and Disposal Guide*, 2nd ed.; University of Alberta, 1984, pp 200-202.
5. *Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley and Sons: New York, 1981; Vol.14, pp 165-175.