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Chemistry Newsletter

Frederick Duke
University of Iowa

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CHEMISTRY NEWSLETTER

Dr. Frederick Duke
Department of Chemistry
The University of Iowa

We promised a newsletter—here it is. We include a description of how we operate, what books we use, and how we arrange our laboratories and the like, along with some opinions we have. We also have a letters section, and since we didn't have permission to publish names and addresses of our correspondents, we have not included them. If you write to us, please state whether or not we can include your letter with name and address in the newsletter. In some cases it might lead to some useful correspondence from your colleagues.

INTEREST BUILD

If we can make any general criticism of what goes on in high schools relative to chemistry and science in general, it is that you spend so much time and effort getting students ready for college that you overlook the very great importance of keeping students interested. We find that those who come here for further science courses have been well founded in the principles, but too few of them look upon science as something interesting. Frankly, we'd like to have you teach a less rigorous course if it will "grab" the students; and rigor is really not easily defined.

Rousseau said that the best way to teach any course is to begin where the student is interested, and to develop things along interest lines; above all, he felt that courses should not be developed logically, since the manner of categorization of knowledge is a very individualistic thing.

So where are high school students in Iowa in regard to their interests in chemistry? I believe that a very large majority would be interested in fertilizers, pesticides, herbicides, growth enhancers in animals, in human food additives, in the chemical differences between males and females, in chemical energy production and many others. It is true that many of these topics involve somewhat complicated chemistry, but not too complicated for the students to get something out of these topics. It is *not* bad to leave the student's hunger for knowledge partly unsatisfied.

My experience in teaching this kind of thing at The University of Iowa leads me to believe that many if not most of you have neither

the knowledge nor the library facilities to teach this kind of thing. I believe that I know more chemistry than do most of you, and to teach this I had to learn a great deal. Ordinary chemistry courses at any level do *not* include this kind of interesting material. Thus, we propose to include in each newsletter a write-up about one such topic, along with good references for your library to buy and other references if you have access to a large library.

This time we are writing about fertilizers.

CHEMICAL FERTILIZERS

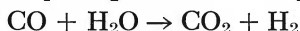
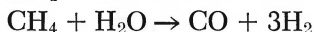
The three most used fertilizers are nitrogen compounds, phosphates and potassium compounds. Among these, nitrogen and phosphorus are taken up in quantity by the plants, and potassium plays a relatively complex catalytic role.

We shall first take a look at the chemistry and energetics of the production of fertilizers, then look at their use, and finally give some general material about the use of commercial fertilizers.

Production of Ammonia.

Ammonia is made by the direct combination of hydrogen and nitrogen, so first we shall see where these elements come from.

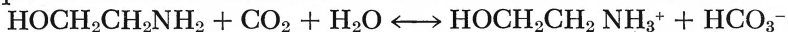
Hydrogen. Hydrogen is the most abundant element in terms of the number of atoms on earth. It is available as the element from a number of sources. Almost all of these processes involve water, because water is so abundant. The chief process involving water also uses natural gas, methane— CH_4 .



The methane from gas wells is passed over hot alumina which converts sulfur compounds to H_2S . The H_2S is removed with sodium hydroxide and water, or by absorption in activated carbon.

The sulfur-free gas is then passed through a furnace consisting of a group of nickel alloy tubes containing a nickel catalyst. Steam is injected and at a temperature of 1400° to 1800°F and up to 450 pounds per square inch pressure the first reaction above occurs. The gases are then cooled to 700°F and are passed over a catalyst of iron oxide containing a little chromium oxide, where the second reaction happens.

The mixture of hydrogen and carbon dioxide is scrubbed through an aqueous solution of monoethanol amine. This removes the CO_2 .



The latter is a soluble substituted ammonium bicarbonate. The gaseous hydrogen passes on. Then the monoethanol ammonium bicarb-

onate is heated and the reaction above reverses, yielding pure CO₂ which is made into dry ice, for example, and the ethanolamine solution is used over again. Ethanolamine is cheap and has low vapor pressure, so that it does not go along with the CO₂ gas. You now have pure hydrogen.

Nitrogen. The nitrogen is taken from the air. To remove the oxygen, two processes are used: liquefaction and fractionation of the air (oxygen boils more easily than does nitrogen), or by converting the oxygen to CO₂ and scrubbing it out with ethanolamine.

Ammonia. The Haber process is used for ammonia manufacture: $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$. The gases are passed under high pressure (300 to 600 atmospheres) over a catalyst of iron oxide containing small amounts of Al₂O₃ (3%) and potassium oxide (1%). The temperature is 475°C. Both H₂S and CO poison the catalyst, so the incoming H₂ and N₂ must be pure. The gases are passed over the catalyst several times, resulting in 20 percent conversion per pass, the NH₃ being removed by cooling and liquefaction between passes. Eventually 85-90 percent of the N₂ - H₂ mixture produces NH₃. At room temperature a pressure of 175 pounds per square inch will liquefy ammonia. It is shipped and stored as a liquid and applied to the soil as NH₃.

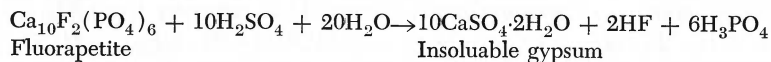
The lack of nitrogen compounds in the soil is the chief limiter of plant growth in this country. The on-farm requirements are about 19 million tons of nitrogen, and in the form of ammonia, about 8 million tons need to be added each year as fertilizer. About 11 million tons come from native soil supplies and nitrogen-fixing legumes such as alfalfa. Around 5 million tons of NH₃ are exported for foreign use.

About 90 percent of the nitrogen in crops raised is used to feed animals to produce meat. In this process, some 80 percent of the protein is wasted.

Well applied fertilizer nitrogen is recovered in crops to the extent of about 50 percent. The rest is washed away or decomposed biologically to N₂ gas.

Phosphorus Compounds

The phosphorus compounds are all made from commercial grade phosphoric acid. This in turn is made from phosphate rock, which is mined, and sulfuric acid.



The yield is about 95 percent.

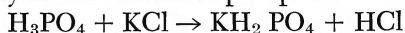
The phosphoric acid is treated with base (ammonia, caustic soda or potash) to make one of the phosphate salts. Often the impurities present are able to contribute trace minerals which crops need.

The chief use of energy is in the making of the sulfuric acid, in grinding the phosphate rock, and in the filtration. The gypsum is used for gypsum board and the HF is used to make freons, etc. Also, energy is used in mining the phosphate rock.

The phosphate used as fertilizers in this country amounted to 5 million tons of P_2O_5 equivalent. About 20 percent of applied phosphate ends up in the plant. The rest usually becomes immobilized and unavailable to plants in insoluble form.

Potassium Compounds

Potassium fertilizers are made from underground deposits of various potassium salts, which are mined and used with no processing in some cases (KCl) or they are converted to phosphates:



About 68 percent of potassium is applied in mixtures with phosphorus and nitrogen fertilizers. The rest is applied as KCl. About 4.4 million tons of K_2O equivalent are used in the U.S. each year.

Energy Requirements for Fertilizer

Some 40 thousand cubic feet of natural gas are required to make a ton of NH_3 . The total production of NH_3 takes about 2 percent of the natural gas produced. About 60 percent of the natural gas used is for the production of hydrogen, and the rest is used to provide the heat for the various processes. There is presently no satisfactory alternate source of pure hydrogen. All other known methods of preparation provide hydrogen which is either too expensive or too impure.

The production of phosphate fertilizer takes about 10.4 million BTUs per ton. (Methane has about 1000 BTUs per cubic foot.) About 85 percent of this energy goes to produce the sulfuric acid used in the process, the other 15 percent for mining, grinding and other processing.

The energy used in producing potassium fertilizers is very small.

Some Facts About Commercial Fertilizers

The use of inorganic fertilizers *does not* cause soils to become hard and unproductive. Soils which have been fertilized with inorganic substances continuously for 130 years are still very productive.

Fertilizer generally increases protein, mineral and vitamin contents of foods. So called "organic farming" does not produce better foods

than does "inorganic" farming, because most of the nitrogen and phosphorus, to be used, has to end up in exactly the same form whether applied as "organic" or "inorganic" substances.

Improper fertilization can, however, be harmful. Too much fertilizer will damage a crop, and the amount of fertilizer one can use is closely tied to the amount of moisture a crop gets. Too much rapid growth in an early wet season with lots of fertilizer can result in a complete crop failure if drought sets in at the wrong time. However, more lightly fertilized and less thickly planted fields may survive a drought.

Excess fertilizer may wash off into rivers and ponds and cause eutrophication.

PACE

Many of you know about the PACE program, and your letters indicate that many of you would like to know more about it, what experiences others who use it have had and the like. PACE stands for Personalized Adventures in Chemical Education, and is a self-paced program started by Professor Harold W. Wengert of the Malcolm Price Laboratory School, University of Northern Iowa, Cedar Falls.

Self-paced programs have been gaining favor. Many colleges and universities use them: Botany at Purdue, Zoology at Ohio State, Geology and Geography at Carroll College and many more. The general idea behind these programs is to get something better than a typical lecture-textbook operation, with the student gaining a feeling of more involvement and therefore more interest. The self-pacing program gives the student much less of a feeling that he is being "processed" instead of educated.

In general, self-pacing programs divide a subject into "units," "modules" or "packets." The laboratory work is often the backbone of the course, and the student will work through a group of "packets" or "units" in the course. Although the packets are generally self-explanatory, they carefully avoid tipping off what the expected results are, allowing the students a chance for discovery. A student normally finishes a set number of packets in the process of the course, and the teacher will examine the student orally or in writing to assess whether a project or packet is finished.

Both the student and the teacher have some adjustments to make in going to the PACE program. The student has to exert some self-discipline and it is harder for a student to hide a lack of progress than is the case in conventional courses. For the teacher, he is somewhat less

capable of dominating the classroom or laboratory situation in an impersonal way, but he should have an opportunity for much more one-on-one interaction with the students. The teacher is certainly no less important in the PACE program, but his role is changed from that of lecturer more to that of helper and adviser when the students need help or advice.

We have asked some of the local people to write briefly about PACE. Professor Lunetta of U of I Science Education Department, and two local high school teachers, Malcolm Gore and David McLaughlin have all had experience with PACE and believe in its virtues. Their comments follow:

Some Thoughts on Pace

Dr. Lunetta

The individualization of instruction is a national concern at this moment in time. Many educational researchers and psychologists have called attention to the substantial differences in human learners; if these differences do exist, they should be reflected in instructional systems, in curricula, and in specific courses. Benjamin Bloom has written:

Each teacher begins a new term with the expectation that about a third of his students will adequately learn what he has to teach. He expects a third of his students to fail or to just 'get by' . . . The system creates a self-fulfilling prophecy such that the final sorting of students through the grading process becomes approximately equivalent to the original expectations. . . . The cost of this system in reducing opportunities for further learning and in alienating youth from both school and society is so great that no society can tolerate it for long.

Most students (perhaps over 90%) can master what we have to teach them, and it is the task of instruction to find the means which will enable our students to master the subject under consideration. . . .

We are very fortunate here in Iowa to have a number of teachers who have spent several years developing individualized science courses that are now a reality. Interestingly enough, much of the leadership here has come from chemistry teachers with resources and printed materials provided by PACE (created by Harold Wengert). The individualized teaching skills that have been developed in Iowa are without parallel elsewhere in the United States, in my opinion. Science

teachers in Iowa who want to learn more about the potential and strategies for individualizing instruction should not have to travel far to get first-hand information. Needless to say, PACE, like any other curriculum, does have its problems as well as its many positive features. [Some of these problems and assets are discussed in the notes from Malcolm and Dave which follow.]

I personally would quarrel with Dr. Duke's remark above wherein he says: "The self-pacing program gives the student much less of a feeling that he is being 'processed' instead of educated." The feeling of being processed, of being a little cog in a massive wheel, can easily be stimulated in PACE classrooms, as well as in more conventional classrooms. The feeling of being "educated" can be enhanced, however, when PACE materials are in the hands of concerned, skillful teachers. I would say that the current form of the PACE materials does not provide sufficient options for students with diverse interests, but those options can be created with time and effort. PACE does provide an excellent starting point for teachers who want to develop a more individualized chemistry program.

One parting shot! Why must teaching be *either* self-paced or group-paced? Must we be at either wild extreme? Students as well as teachers like a little variety in their lives. Should PACE teachers *never* give an exciting lecture on some relevant issue? Now that I teach an "individualized course," shall I never again get my class together for a large group discussion or unit?

Some Thoughts on PACE

Malcolm Gore

City High School

Iowa City

Five years ago, I finally decided that the chemistry program, at least in the way I was utilizing it, had shortcomings that I could no longer tolerate. Some of my major concerns in teaching have been how to reach students, help them to improve themselves, and have them leave with a better understanding of science and a favorable attitude toward science using the discipline of chemistry. Experience has given me some basic premises about students to consider in achieving these goals. I feel that all students are not interested in the same things from the same course, that all students do not learn at the same rate, and that all students are not able or willing to take responsibility for their own learning. I feel that chemistry has something to offer for a wider

range of students than it was attracting, not just the college-bound; thus, a chemistry course should be primarily designed for general education. I was unhappy with the uncommunicative students and the ones who were satisfied to do the minimum amount of acceptable work. I felt that they were being cheated, although they seemed content at the time. I could not adequately evaluate the silent students, and I was dissatisfied with the usual problems of the under-achiever.

To meet these assumptions and concerns, the PACE program was adopted. It is structured, but with a flexibility great enough to provide in-depth experiences for the science-prone as well as the development of basic ideas that can be conceptualized by the less able student. The program is individualized, self-pacing, and lab-oriented in approach, with the expectations for the students of continuous progress and understanding of the material. Tests as a means of determining a grade are de-emphasized. Evaluation is based on the following criteria: general understanding, presentation of ideas, lab activities and techniques, self-discipline, responsibility and use of time, and performance test evaluation.

I feel that the PACE program is the best vehicle for me to use in meeting these concerns. It offers success in chemistry to students with a wider spectrum of abilities. It provides different modes of learning, gives the students options, allows them to proceed at their own rate, and demands student-teacher interactions through use of teacher checkpoints or initials throughout the program. I feel that I can better evaluate the student because I know more about his understanding of the material and have a current record of his progress. The author intended that the program could be modified, realizing that teachers with a variety of strengths and interests would be using it. You can delete with caution as the program does have storyline threads of continuity, and you can most definitely supplement the program which stresses basic fundamentals. Organization in this program, as with any individualized program, is a must. The paper work seems to multiply as it is normally done outside of class. This consists of grading performance tests, checking packets, and recording student progress. Initial outlay for audiovisual equipment is expensive, but necessary, if you wish to offer different modes of learning. The problems of the under-achiever are not necessarily solved by the program, but I can identify this individual much sooner with an accurate record of his progress; the rest is up to me.

Some Thoughts on PACE

David McLaughlin

West High School

Iowa City

Good points:

Students do have the opportunity to work at their own pace, thus allowing bright students to work ahead and other students to take their time.

Students have the chance to help each other. Students generally work in small groups; often they help each other and discuss certain questions, etc.

When questions arise, students can get answers immediately from their teacher. In group-paced programs, teachers often answer questions for the entire group and only a handful of students are curious. There are many options open to the students to do a large variety of things ranging from written reports to experiments.

It is easy for a student to earn a grade of A or B if he applies himself.

The course is well organized and definitely written with the student in mind.

Bad points:

Many young people are not self-motivated, which results in their wasting a lot of time.

The teacher has limited control over what the student learns. (This is true in any course, but I believe, more true in self-pacing courses.)

There is a great temptation for students to copy answers on their packets or on tests.

Classes are generally too large, and students may find themselves waiting a lot to talk to their teacher.

It is very difficult from the teacher's perspective to be completely objective in grading. At this point I don't have data to compare PACE chemistry students to non-PACE chemistry students regarding what they have learned.

I thoroughly believe some students would function more efficiently in a more structured atmosphere; the only difficulty is that you never know this until it is too late. (This can work both ways.)

OUR UNDERGRADUATE CHEMISTRY MAJOR

We are outlining for you below the essence of what we do in our undergraduate program. We have not been very explicit about things,

but rather we hope to give you the general flavor of our program. If you will write us relative to any specific questions you have about our program and how it meshes with yours, we will answer them in later newsletters.

We try to give good treatment to our undergraduates as human beings as well as potential chemists. Not only do we encourage their participation in and attendance at campus-wide happenings, but we also do some internal things. For example, we provide an undergraduate room where the students can meet and become acquainted, can talk over things chemical or otherwise, and can study. We also have a weekly combined social and professional get-together, where students visit with faculty and hear talks on the latest advances.

Campus-wide happenings include University symphony concerts (we have probably the best university symphony in the country) and other music programs, in which students are encouraged to participate, lectures by prominent Americans, art exhibits at the University's fine art museum, and the like.

Now for a brief description of our major's program.

The B. S. chemistry major program includes each of the four major areas in chemistry in a series of lecture courses. An integrating laboratory experience is provided in a separate parallel sequence of courses which progress from closely guided work in the freshman year, to individual research projects in the senior year. Each laboratory course begins with the second semester of the companion lecture course(s).

The first year's lectures are on principles of chemistry with most examples coming from inorganic chemistry. (A placement examination provides for the acceleration of well prepared students.) Organic chemistry is the second-year course. In the junior year, physical chemistry provides a sounder mathematical basis for the principles of chemistry and also provides basic background for the companion course in analytical chemistry. The analytical chemistry course covers separation, identification and determination by gravimetric, volumetric or instrumental methods with emphasis on the selection of the appropriate method. Inorganic chemistry is covered at an advanced level in a half-year lecture course in the senior year.

The beginning one-semester laboratory course, companion to principles of chemistry, is operated on an elementary quantitative basis, teaching basic laboratory techniques, and is highly organized. Intermediate laboratory, companion to organic chemistry, covers synthetic methods, the identification of compounds by nmr and infrared and by

physical properties of the compound and its derivatives, and some quantitative methods. The second half of this course is less guided than the first and provides the traditional qualitative organic analysis experience. Advanced laboratory, an integration of analytical and physical chemistry laboratories, has the minimum amount of direction. Detailed laboratory procedures and analytical schemes are devised by the students, complete analysis of the effect of measurement and operational errors on the experimental results are made, computations are made by student-written computer programs, and the results are presented in a statistically significant form. All common instrumental methods of analysis and physical measurements are covered, in many cases using the specialized research equipment of the Department. Finally, in senior research, each student carries out an individual research project with some member of the faculty, culminating in an oral report to the students and faculty in the spring of each year. A senior seminar provides instructions on how to carry out a research project, use of the chemical literature, presentation of scientific talks, and usually a trip to some outstanding scientific laboratory.

In the non-major area, we have courses for people going into health sciences (premeds, medical techs, nurses, pharmacists), engineering, and general liberal arts. In these service courses, we attempt to choose examples and laboratory techniques which will be interesting and useful to these people when they become professionals. In the courses for general liberal arts students, we emphasize current issues in chemistry, and the general philosophy of science.

We have attempted, in all cases, to reach conclusions about what these non-chemists need to know about chemistry by observing professionals in these other areas, by talking with experienced people and the like. I believe that we now have a group of excellent courses for people not aiming to be professional chemists. These courses are under constant review and evaluation to keep them good.

QUESTION CORNER

Questions from high school teachers.

If glass is so stable (unreactive with acids, etc.), why does it break so easily?

Glass is made largely of one of the chemically most stable substances known, namely SiO_2 . Other substances such as metal oxides, alumina and others, also very stable, are added to lower the melting point so

that the glass can be blown and shaped. The physical stability of a substance on the other hand has to do with the strength of bonding, often physical, between the various parts of the material, with its ability to deform and assume new shapes, and, to some extent, with its elasticity. Glass is really quite strong (it is hard to break glass fiber threads) but it has exceptionally poor ability in respect to deformation, as one might expect if bonds are very strong. If you drop a plastic bottle, it will deform and the energy of the fall will dissipate in internal friction, which heats up the bottle. If, on the other hand, you drop a glass bottle, much of the energy goes into rupturing bonds between areas of the glass, since internal movement of the molecules which allow the glass to deform is not possible to any great extent. Thus, even though glass is much stronger than most plastic materials, kinetic energy is dissipated in different manners in the two cases, due to the inability of glass to deform.

What seems to be the students' major problems in terms of background you feel they lack in coming to your university and taking a freshman chemistry course?

See the paragraph on "Interest."

What text would you recommend?

See the material herein on PACE. We'd like to hear from other high school teachers on this one. We are pretty ignorant in this area.

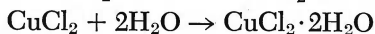
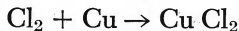
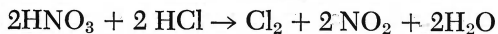
Would it be possible to include a check-item for teachers from which a temporary summer campus mailing list might be compiled?

I interpret this to mean, "Can you find out how many teachers are coming to U of I for summer school?" and "How many might be interested?" If this is the wrong interpretation, forgive me. We do not now teach a course of interest to high school teachers in the summertime, with the exception possibly of organic chemistry. The Science Education Center does much better at present. But how many of you would be interested in a course on contemporary issues in chemistry, as written about under Interest Build?

I have a question that needs research and information beyond what I've been able to do. The question suggests that the student "prepare a plan for the preparation of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from about 0.5 grams of pure copper. Record all equations for all reactions you expect to take place and give your step-by-step procedure."

Dissolve the copper in a mixture of HNO_3 and HCl (concentrated) add enough water to keep the reaction from being too violent. After

dissolution, add more HCl and water and evaporate over boiling water (like a double boiler). Do not heat over 100° C. Crystals will form. Use a hood.



Excess HNO_3 will disappear since $\text{Cl}_2 + \text{NO}_2$ are gases.

I would like my chemistry students to have the experience of working on a research project preferably a laboratory project of some kind during the last nine weeks of school. My problem is that I cannot find enough projects for all my students. If you have a list of simple projects that would be suitable for high school students, I would appreciate receiving it.

1. Protein from leaves and grasses for human consumption. Take a bushel or so of, for example, dandelion greens (the lusher the better) and run them through an ordinary old fashioned food grinder, being careful to catch all of the juice. Put the ground up greens in a stout piece of cloth and twist down to wring the juice out of the plant material. Then pour the juice slowly into a half-inch or so of boiling water in a vessel of appropriate size, keeping the whole thing close to boiling as the juice is added. The protein precipitates as green curds not unlike cottage cheese. After salting, it can be eaten by humans and is quite tasty. It is better than cereal protein because it contains lysine, methionine and other animal-like proteins scarce in cereal. Some kinds of leaves, like poplar trees for example, allow a bitter taste to come through, but most leaves which aren't bitter will work. Grass works but is so fibrous it is hard to grind up. Keep the leaves moist by spraying with a little water before grinding and grind them as soon as possible after picking. Don't get them hot while grinding or the protein will precipitate.

2. Heat storage with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. If a sample of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ containing about 0.1% by weight of borax is heated to about 31° C a change occurs giving water and anhydrous Na_2SO_4 . This "melting" process takes up about 10,000 BTUs per cubic foot. If done in a test tube and then cooled with shaking, the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ reforms at around 30° C or so with the evolution of noticeable (by feeling of it) heat. This is a possible way of storing solar energy for later use in heating. The borax acts as seed crystals for reformation after heating of the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals. The temperature of the transition

can be lowered by adding a little NaCl, the more NaCl, the lower the "melting" temperature.

3. Methane production from manure. Take a can (5 gal. or so) and pour in a slurry of chicken manure up to about half full. Fit the opening with a water barometer. If this is kept in a warm place (room temperature to 140° F) soon bubbles will be seen to be coming out through the water barometer. If the stopper is fitted with another hole containing a glass tube drawn down to a fine tip, the methane may be lit with a match. It may take a few days to get the thing going and one variation is to hook it up through another opening to a large inner tube with the valve removed, to act as storage for the methane. The tube should start out as completely folded and collapsed as possible. It will gradually fill with gas, the pressure depending on the depth of the water in the monometer.

4. Have the students get some brown clay or similar soil from a river bank or elsewhere. Treat for a few hours with concentrated HCl or concentrated HNO₃, dilute about 10 times, filter, and evaporate the filtrate. Try to identify the stuff in the crystals that form.