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ANALYTICAL CHEMISTRY AND MEASUREMENT SCIENCE

(What Has DOE Done For Analytical Chemistry?)

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ABSTRACT

Over the past forty years, analytical scientists within the DOE complex have had a tremendous impact on the field of analytical chemistry. This paper suggests six "high impact" research/development areas that either originated within or were brought to maturity within the DOE laboratories. "High impact" means they lead to new subdisciplines or to new ways of doing business.

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INTRODUCTION

The purpose of this paper is to bridge the gap between earlier papers in this symposium--which dealt with the early accomplishments of analytical chemistry within the atomic energy program--and later papers that will deal with recent accomplishments and the challenges of tomorrow. The usual approach in a talk like this is to discuss what analytical chemistry has done for DOE (-ERDA, -AEC). This paper will take the opposite approach: it will consider what DOE has done for the field **of** analytical chemistry. The message is that we have had great impact on our **own** field. "Great impact" means we have done things that lead to whole new subdisciplines or caused our discipline to take a major detour in the way it **does** business.

The plan of this paper then is to present several DOE-derived contributions that have had a major impact on our discipline. Some old photographs will be used to illustrate the tremendous progress that we have made over the past forty years. Some related research opportunities will be suggested. Then, the almost incredible capabilities that we have today will be illustrated, using dollars as an analogy.

SOME MAJOR CONTRIBUTIONS TO ANALYTICAL CHEMISTRY BY DOE SCIENTISTS

~~Six~~ contributions are at the top of my list. (You may have other ideas about this.) Please note this disclaimer: we did not necessarily discover or invent these things, but we did bring them to analytical chemistry and made them viable within the field.

1. Nuclear and Radioanalytical Chemistry. We had to learn to deal with radioactivity, of course --it was forced upon **us**. But, we did much more than deal with it. We developed a whole branch of analytical chemistry based upon radiochemistry, we extended it to tracer chemistry, and we developed one

of the first ultratrace, multi-element techniques: neutron activation analysis. The necessity to work with radioactive materials prompted much work on specialty instrumentation, not just for radioanalysis but also for analysis of radioactive materials. I think the need for specialty instrumentation within **DOE** (and elsewhere) and the advances in instrumental electronics were synergistic. They built on each other. We owe much to men like Sam Reynolds, George Leddicotte, Vince Quinn, Bill Lyon.

One easy way to show what happened in radiochemistry is to look at the evolution of spectrometers. Figure 1 shows a 20-channel spectrometer, vintage 1953. Figure 2 shows a 400-channel spectrometer dating to 1964. A PDP-15 system of the 1970's, having 4096 channels, is shown in Figure 3. Figure 4 shows an **ND-9900** system, the big spectrometer of today; it has 16K channels. Finally, Figure 5 shows a personal computer based spectrometer, in use today and likely to be the technology of the future. Capacity has increased while the size has decreased.

One challenge that we have today is to develop software for spectrometry that matches the desktop computer hardware in sophistication and overall capability.

2. Analytical Separations. It was natural for new analytical separations to develop in parallel with developments in nuclear and radiochemistry. Radiochemistry was both a driver for the work and a tool for carrying it out. Thus, all sorts of solid ion exchange, solvent extraction, and liquid ion exchange studies were carried out. It became the foundation for much of what we do today. Of particular importance was work on the ion exchange of metals as their anionic complexes, a totally new concept at the time. The information was presented in terms of $\log D$ vs M Acid as shown in Figure 6. A whole repertory of separations -- today we would call it a database -- was developed in the fifties, sixties, and seventies by men like Kurt Kraus, Fletcher Moore, Jim White, Bill Maeck, Jim Rein, Fred Marsh, Jim Fritts, and many others. We still depend upon their science.

There is a real opportunity here today to apply expert systems to the vast amount of knowledge that

we have established in the area of inorganic separations. Expert systems offer a way to store our knowledge, use it efficiently, expedite methods development, trouble-shoot, and tutor non-experts.

3. Operational Amplifiers in Analytical 1 _____ (Figure 7). = Glenn Booman at Idaho Falls put operational amplifiers into an electrochemical instrument, he forever changed the nature of analytical instrumentation in general, and electroanalytical instrumentation in particular. Booman's device was a controlled-potential coulometric titrator, an instrument that had been impractical prior to the advent of operational amplifiers because manual potential control was tedious and the measurement of coulombs was difficult. Glenn's first application was the determination of uranium by reduction of U(VI) to U(IV) at a mercury pool electrode, and it was precise to a few tenths of a percent for samples of a few milligrams. Fred Scott almost immediately applied the new hardware to plutonium, using the Pu(III), Pu(IV) couple and a platinum electrode. Lots of work and lots of applications ensued, by Bob Stromatt, Jack Harrar, Bob Propst, myself, and others. CPC became a workhorse for us for a while and it is still used in many laboratories to determine milligram quantities of uranium and/or plutonium precisely. In fact, Wanda Mitchell, Dennis Troutman and Ken Lewis recently published a description of an automated CPC titrator that is in use today at the New Brunswick Laboratory.

Booman's concept of potential control by operational amplifier circuitry was extended by Myron Kelley and Dale Fisher to DME polarography and thence to voltammetry with solid electrodes. Thus, the whole idea of "three-electrode" electrochemistry was born. It is the conventional way to do electroanalytical chemistry today. Both Fisher and Kelley won the ACS Chemical Instrumentation award for their work in instrumentation. The Princeton Applied Research Corporation—now a part of EG&G—was built upon this technology.

Figure 8 shows a servo-controlled potentiometric titrator that was developed during the op-amp era to determine milligram amounts of uranium and/or plutonium. It could be used in or out of a glove box or hot cell, but it wasn't easy. Figure 9 is a view of a box--not gloved--with a potentiometric titrator on the

left and a coulometric titrator on the right. We could not work with milligram quantities of plutonium under these conditions today.

Figure 10 is included to illustrate the state of affairs in the operational amplifier era. It was a time of solder and wire and resistors and other electronic components. It was a time of hands-on instrumentation.

Future research and development in the general area of instrumentation is likely to emphasize sensors and methodology for in-line and at-line analysis.

4. Minicomputers in Analytical Instrumentation. Operational amplifiers were a great advance, a nice prelude to the minicomputer era. Jack Frazier at Livermore was first to **see** the enormous potential for minicomputers in analytical chemistry. We are all familiar with the PDP-8 series of computers that were **so** widely **used** in the seventies. Jack had an earlier version--a PDP-7--and interfaced it to first mass spectrometers, then to other things, "Interfacing" to him meant developing the hardware that could be operated by the computer, as well as the software to control the hardware. **His was** a "systems" approach, which is trite today but was visionary then. Jack Frazier also won the ACS Chemical Instrumentation for his leadership in analytical instrumentation.

Jack Frazer, Myron Kelley (shown in Figure 11 with Jim White and a PDP-8I minicomputer), Jack Harrar, Dale Fisher, Sam Perone, and many others made us think about our instrumentation in enlarged terms. We began to **see** that the computers expanded our horizons as well as our efficiency. They let us make measurements that we could not otherwise make. These men set the stage for the microcomputers that are **so** ubiquitous today.

Future research in this area is likely to be aimed at the development data management systems that are relational in nature, **so** that we or our clients can extract information from the database in virtually any

format they choose, and manipulate it to suit the occasion.

5. Optical Spectroscopy. This is another area of analytical chemistry in which great advances have been made since the fifties, and again it is one in which DOE-sponsored work has had tremendous impact. There are **two** techniques that warrant special mention here. One is fluorimetry and the other is inductively coupled plasma atomic emission spectrometry.

The fluorimetric determination of uranium illustrates just how far we have come. In the old days we put traces of uranium on NaF-LiF pellets, fused them by flaming (Figure 12), and then measured the uranium by fluorescence (Figure 13). We could measure 0.1 ppm at a time when parts per thousand measurements were considered good. Typically, we improved hardware to improve the method: better fusion systems (Figure 14) and better fluorimeter systems (Figure 15). **As** has often happened, it took a change of concept to provide a the quantum advance in methodology. Laser-based fluorescence plus carefully designed timing and measuring electronics have proved to be the “next step”, **as** indicated in Figure 16. **A** pulse from a nitrogen laser excites the uranium, which in this case is in solution. Measurements of fluorescence intensity are made as a function of time and extrapolated back to $t = 0$ to get the concentration dependent readout. This circumvents interference from impurities in the solvent. These measurements are quick, reliable, and sensitive to the 0.05 ppb level without pre-concentration.

Inductively coupled plasma spectrometry (Figure 17), is by far the DOE-sponsored development of greatest impact on optical spectrometry. Velmer Fassel and his colleagues at the **Ames** Laboratory developed the inductively coupled plasma source, which now is in use in laboratories all over the world. The **ICP** was adopted promptly by the instrument companies and has become the standard method for trace element analysis in water. This technology caused the field of analytical chemistry to take a detour. The latest rage is to couple Fassel’s **ICP** source with a mass spectrometer, thereby obtaining improved sensitivity and selectivity, plus isotopic information. There are at least six ICP/MS systems within the DOE laboratories now and several others are on the way. **At** about the same time, Sam Hurst, Jack Young, and

Marvin Payne developed a laser-based spectrometric technique that was claimed to detect a single atom. In fact, there has been one claim in the literature of detecting half an atom. Half an atom! They must have done it with mirrors (or statistics).

Laser spectroscopy is certain to be a prominent **R** and **D** area in analytical optical spectroscopy in the future. Laser offers tremendous resolution, control, and speed.

6. Inorganic Mass Spectrometry. Inorganic mass spectrometry--isotopic analysis, gas analysis, major and minor component analysis--must be included in any list of very significant contributions to measurement science via **DOE**. **DOE** labs have been slow to get into organic mass spectrometry, but they have been prime movers in isotopic and inorganic mass spectrometry. We owe a great deal **to** people like **Al** Nier, **Gus** Cameron, Harry Svec, Leo Collins, and others who not only developed the instruments and techniques, but also set the foundations and expectations upon which the field is built.

Figure 18 shows a two-stage machine that **ORNL** built for the **IAEA** Safeguards Analytical Laboratory in Vienna in the **mid-1970s**, for high precision isotopic analysis of uranium. This machine has now been supplanted by commercial instrumentation that can do fantastic things. Isotopic ratios can be measured with precision and accuracy of 0.01%. With gas machines, the precision and accuracy approaches 0.003%. Mass spectrometry has become the premier analytical technique today, in sensitivity, accuracy, and applicability.

Research in analytical mass spectrometry in the future is likely to include trapped ion and laser-based techniques. Ion traps and ion cyclotron mass spectrometers are already attracting much attention in organic mass spectrometry, and resonance ionization mass spectrometry has already been shown to have great selectivity.

The above six areas of contribution were selected as having major impact on the field of analytical

chemistry. You may disagree with some of the choices, or perhaps with some of the future research opportunities that are mentioned. I hope you can agree with the premise that DOE scientists have changed the course of analytical chemistry.

WHAT HAS HAPPENED TO US IN FOUR DECADES

I want to conclude by illustrating what has transpired in measurement science since NBL was established. To do that I want to use the height of a stack of dollar bills as my reference. A stack of one hundred dollar bills measures **0.75** inch. We can relate accuracy and precision to stacks of bills. Thus, in 1950 we could determine major constituents with an accuracy of 99.8-99.9%, or about one part per thousand. This is analogous to measuring all but one or two bills in a stack of bills 7 1/2 inches tall. Today we can do almost 100 times better. The analogy **now** is measuring all except one or two bills in a stack 750 inches (**62.5** feet) tall. I believe we have made good, but not spectacular, improvement insofar as accuracy is concerned.

The real gains have been made in sensitivity. When NBL was born, detection limits for ionic analyses were generally in the tens to hundreds of parts per million. Using the above analogy, detecting ten ppm corresponds to detecting one blank paper in 100,000 bills. That is about **750** inches or **62.5** feet of dollar bills. Today, we operate routinely at the part per billion level. The analogy is detection of one blank piece of paper in a stack of bills about **6.25×10^5** feet tall. To put it in context: we detect constituents in our samples at levels that correspond to one blank paper in a stack of bills as tall as **424** Empire State Buildings. We have made unbelievable gains in practical sensitivity over the past forty years.

CONCLUSION

Forty years ago, analytical chemistry was perceived primarily as "wet chemistry" (Figure 19). Today it is perceived as fancy instrumentation and computers (Figure 20). To get here from there, we have had

to **be** technologically agile. We have had **to** learn new skills, develop and adopt new technology, and meet new challenges—and do **so** continually—over the years. It has been exciting and it has been fun. On the average, it has been fine (Figure 21).

Part of the fun, of course, has been knowing and working with the people at laboratories like NBL. The New Brunswick Laboratory has been involved in every one of the **six** areas of analytical chemistry that I discussed. It has been a force within the field. I congratulate NBL and wish it continued success between now and 2028.

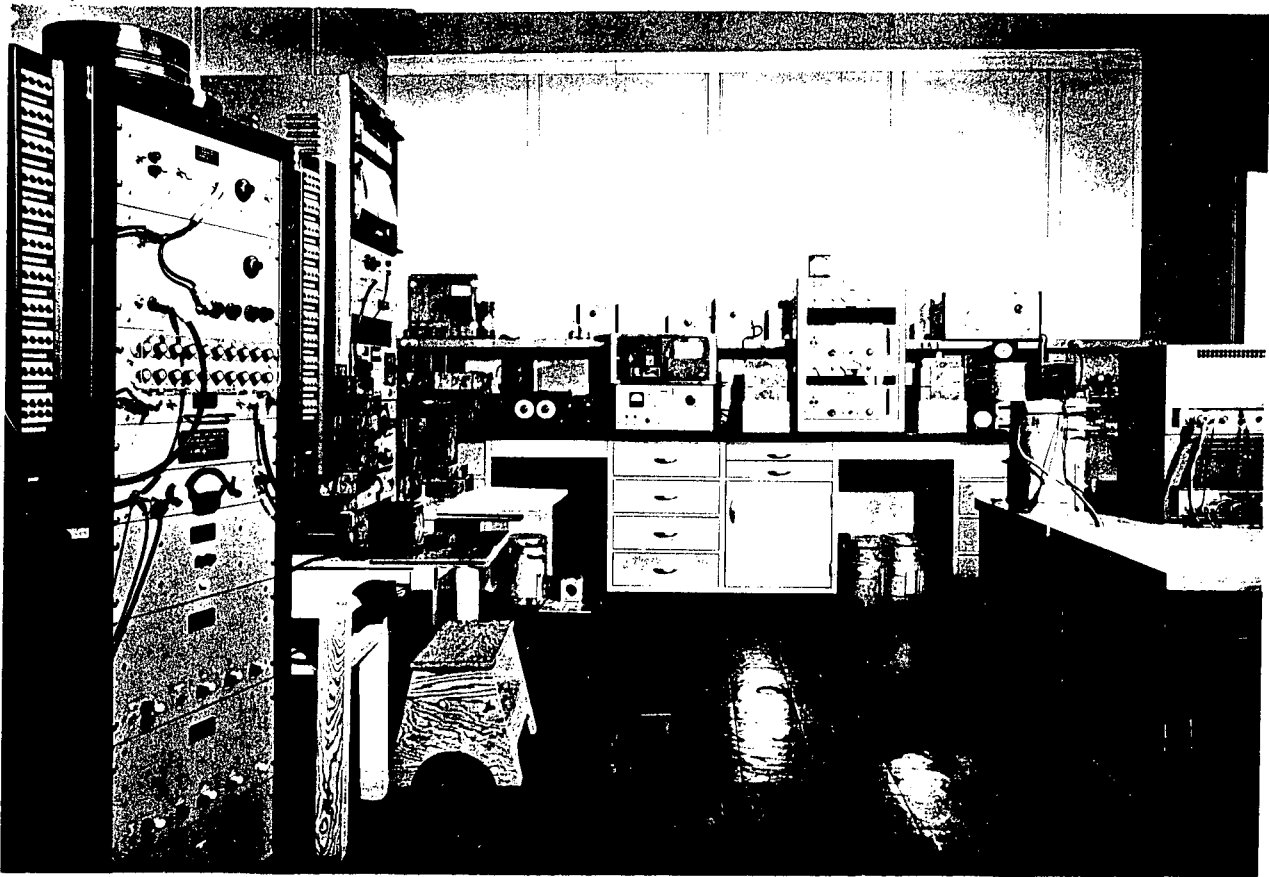


Figure 1. A 1950 vintage counting room. A 20-channel spectrometer is standing on the left.

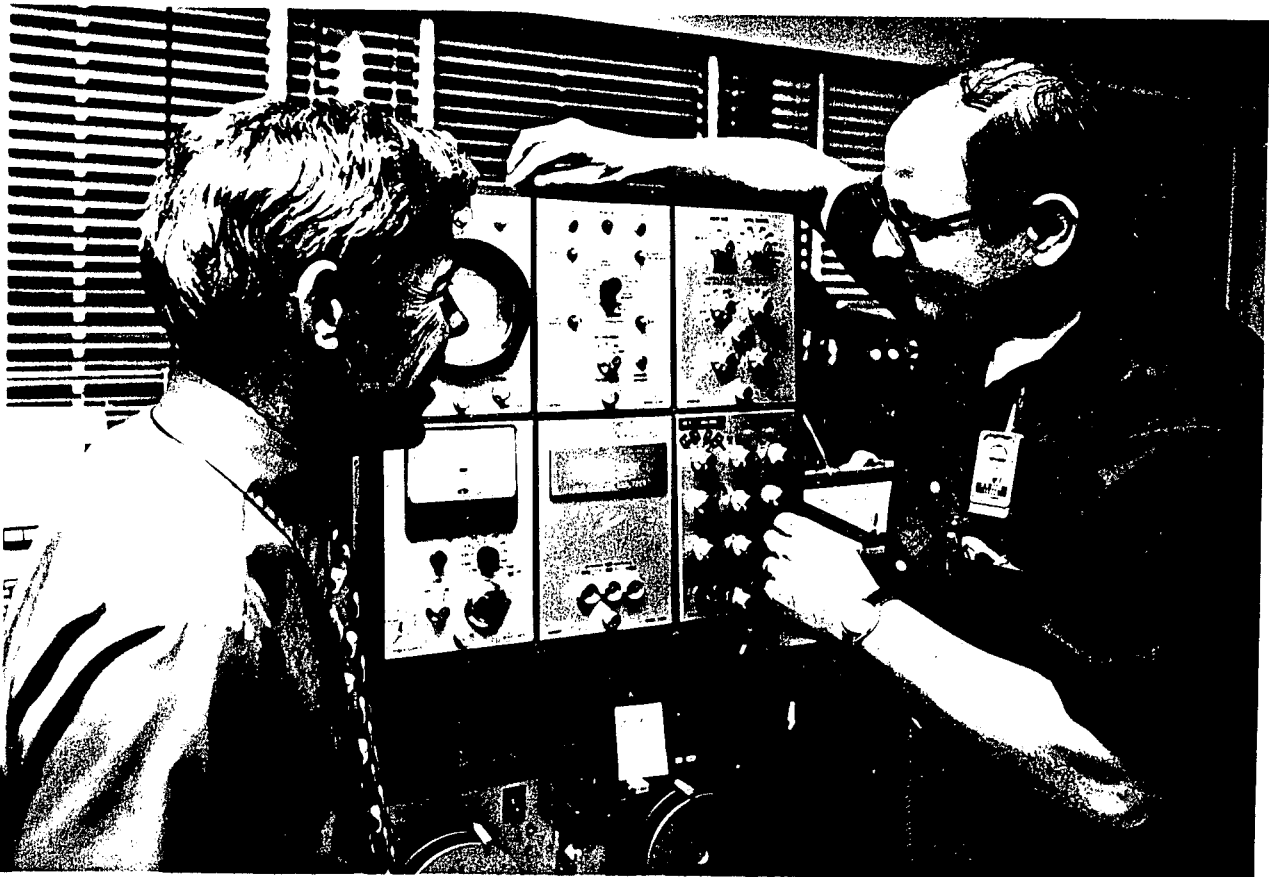


Figure 2. A 400-channel spectrometer, vintage 1964.

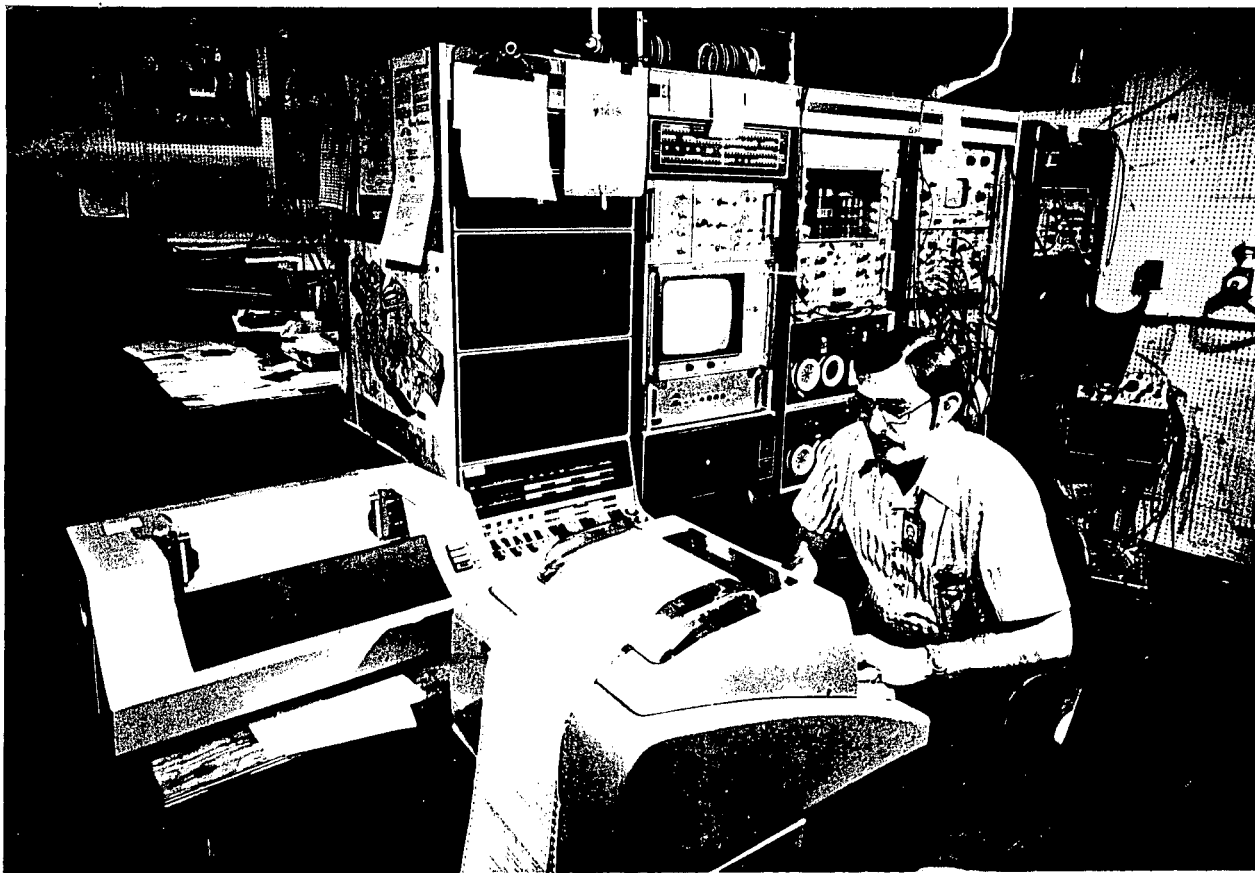


Figure 3. A minicomputer-based spectrometer system, vintage 1975.



Figure 4. A microcomputer-based spectrometer system, vintage 1980.

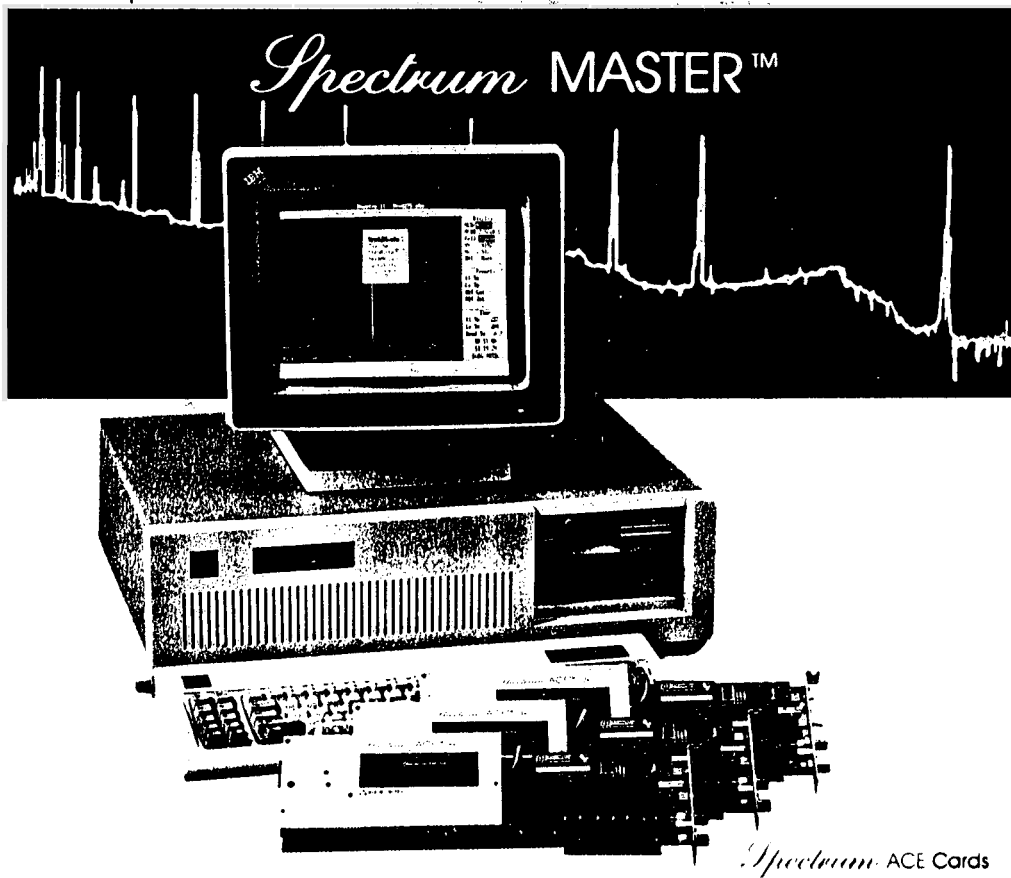
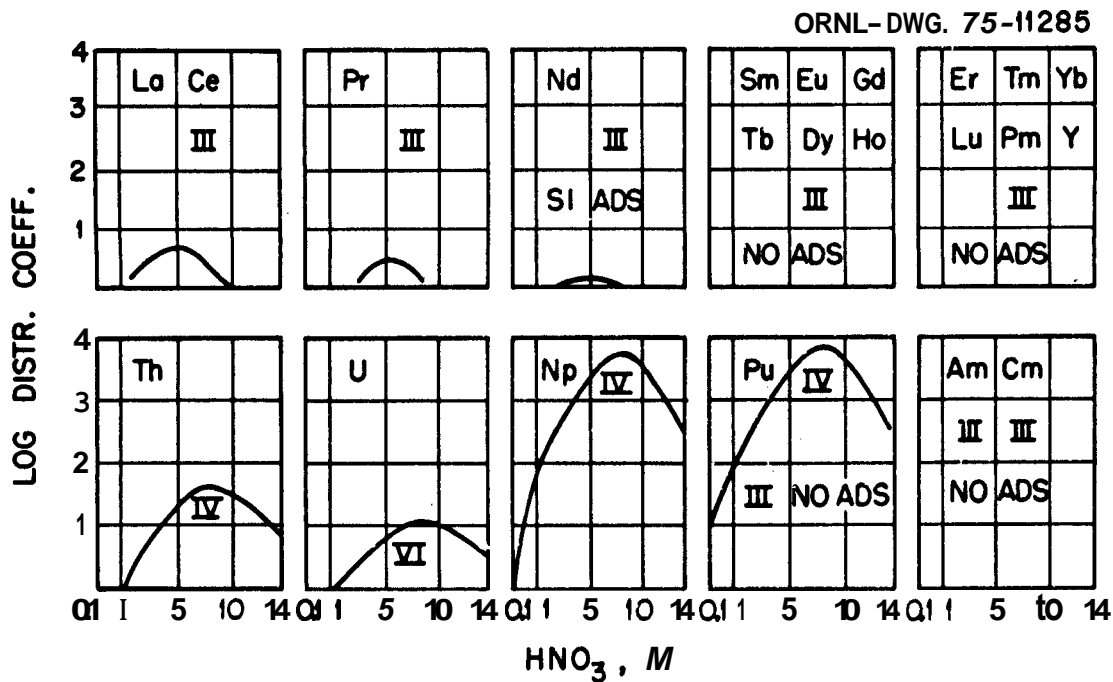


Figure 5. A desktop computer based spectrometer, vintage 1990.



IONIC METAL ADSORPTION BY STRONGLY BASIC ANION
EXCHANGE RESIN (Dowex 1-X2)

Figure 6. Typical separation data; ion exchange in nitrate medium.

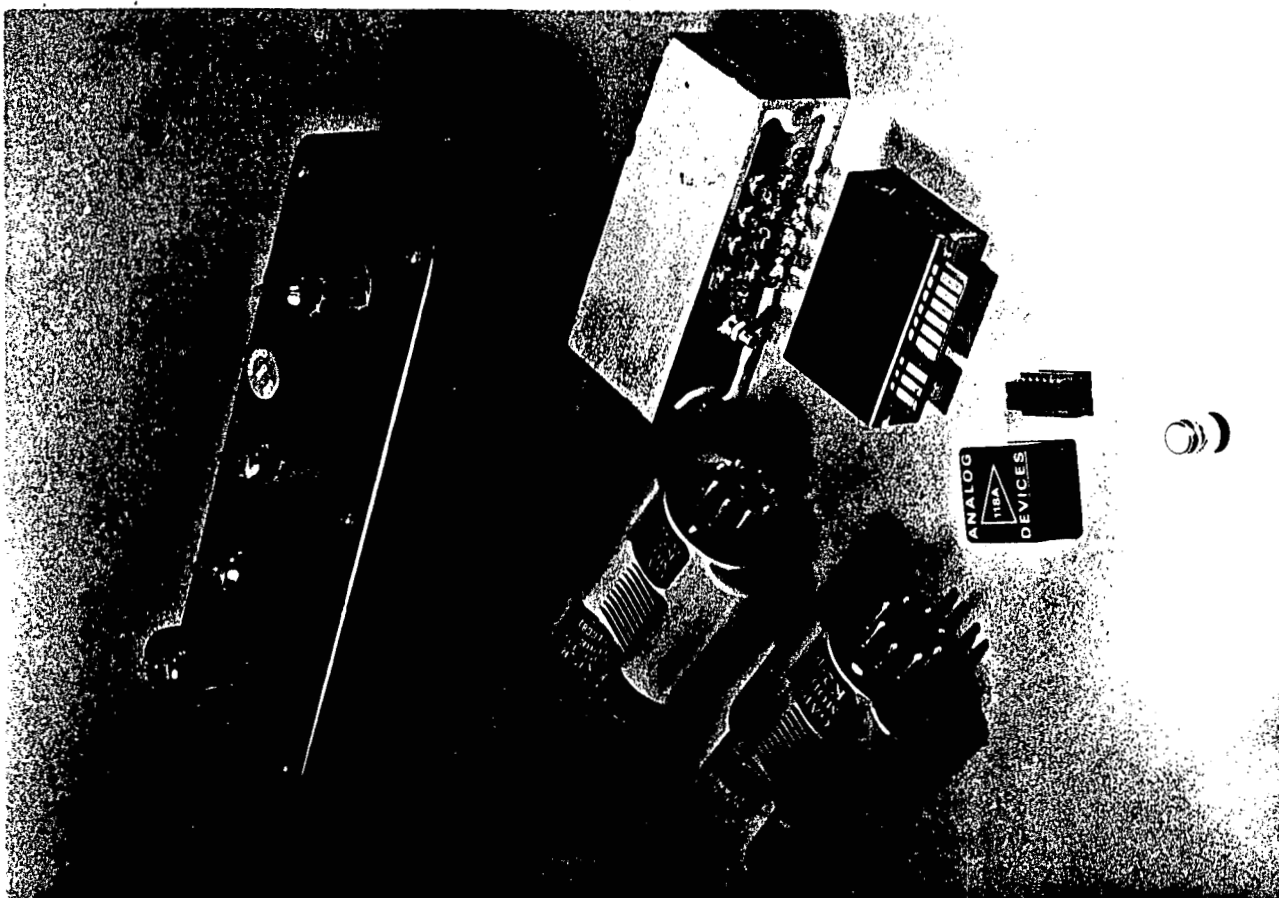


Figure 7. Operational amplifiers, vintage 1960.

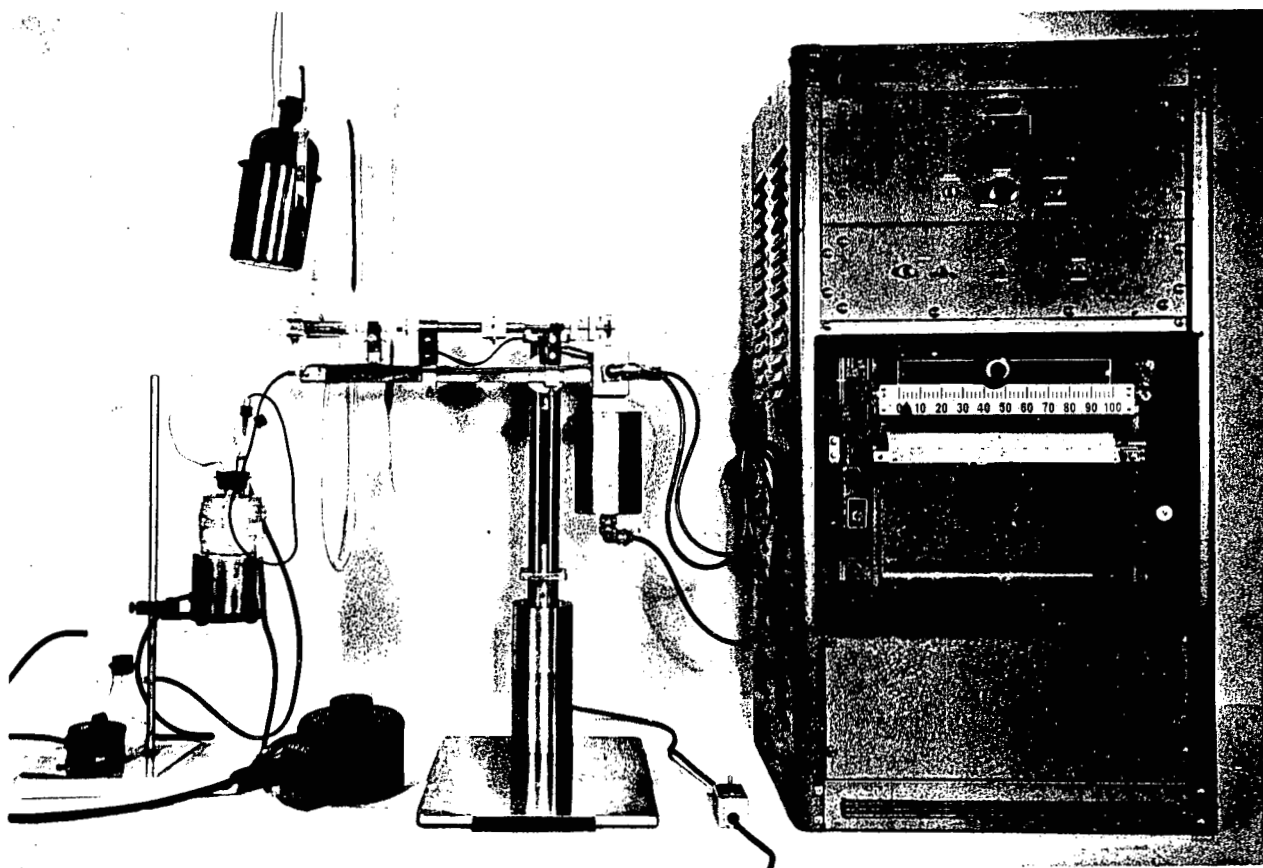


Figure 8. A servo-controlled potentiometric titrator, vintage 1960.

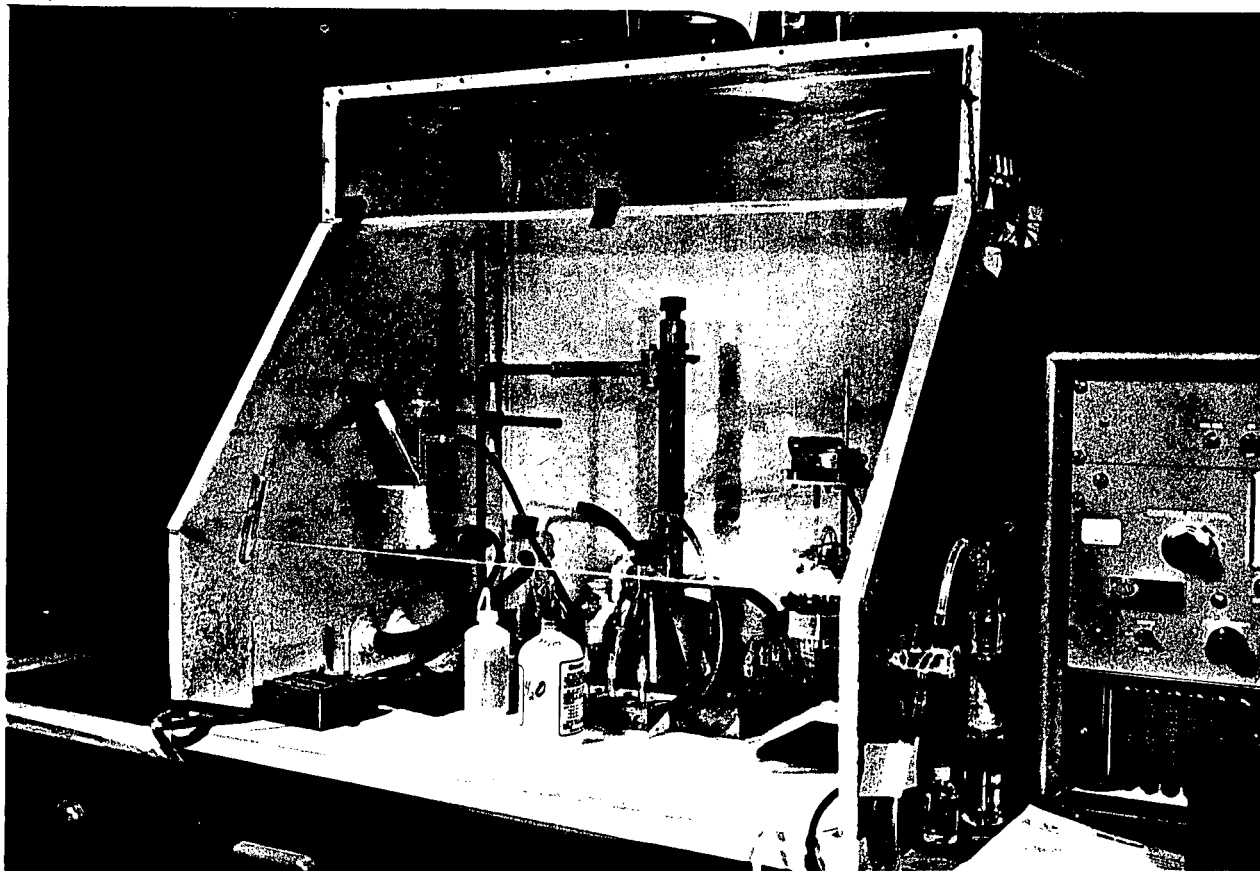


Figure 9. A titration box la-alutonium. vintage 1960. -----

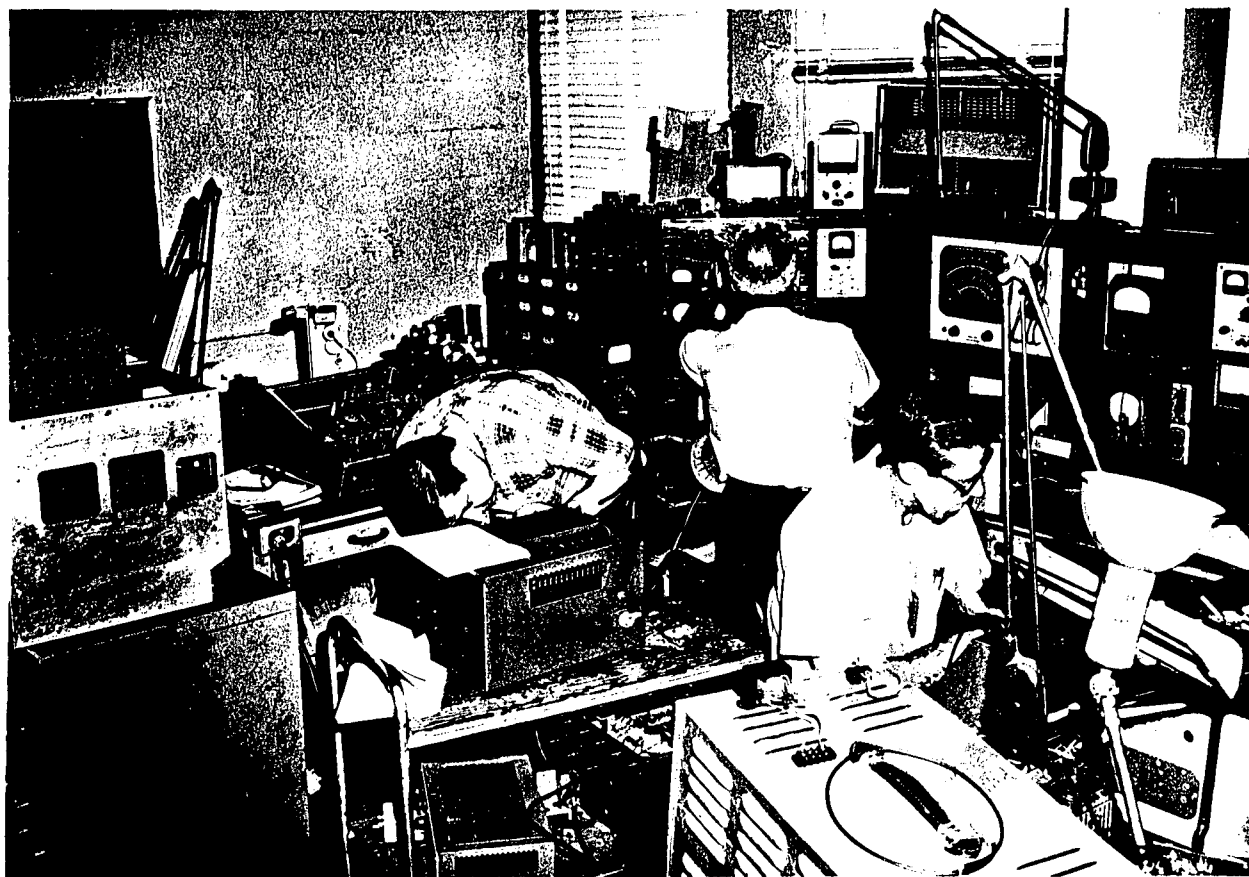


Figure 10. The operational amplifier era.



Figure 11. A laboratory minicomputer system of the 1970s.

A. Multiple-Fusion and fission Summary for
the Determination of Uranium by the Fluorometric Method

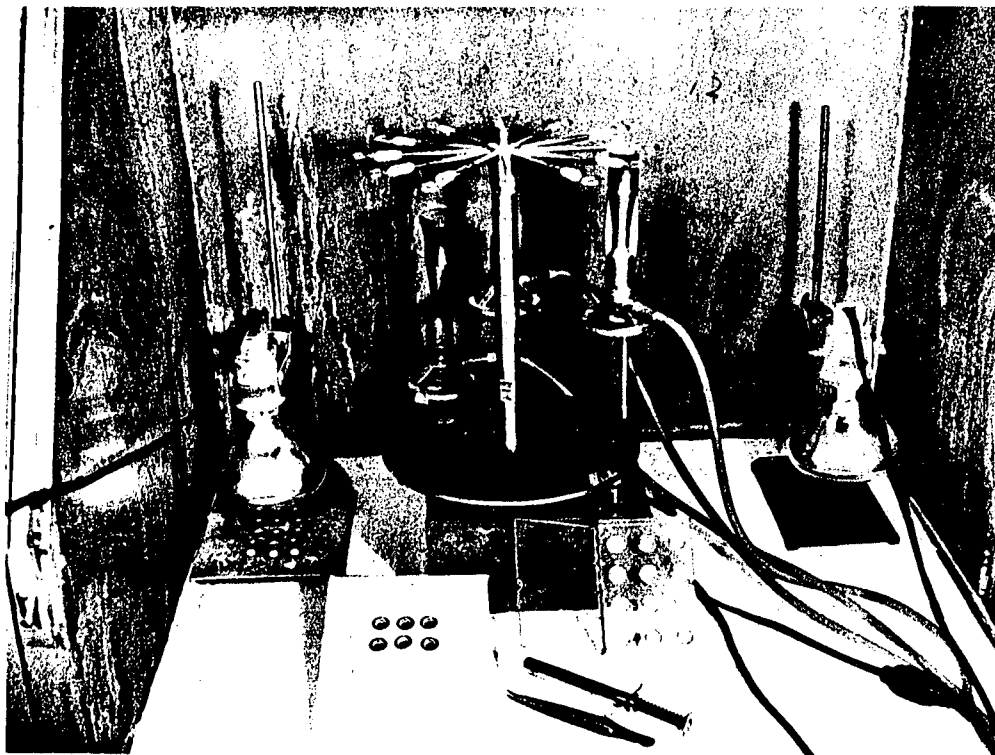


Figure 12. A pellet fusing device, vintage 1950.

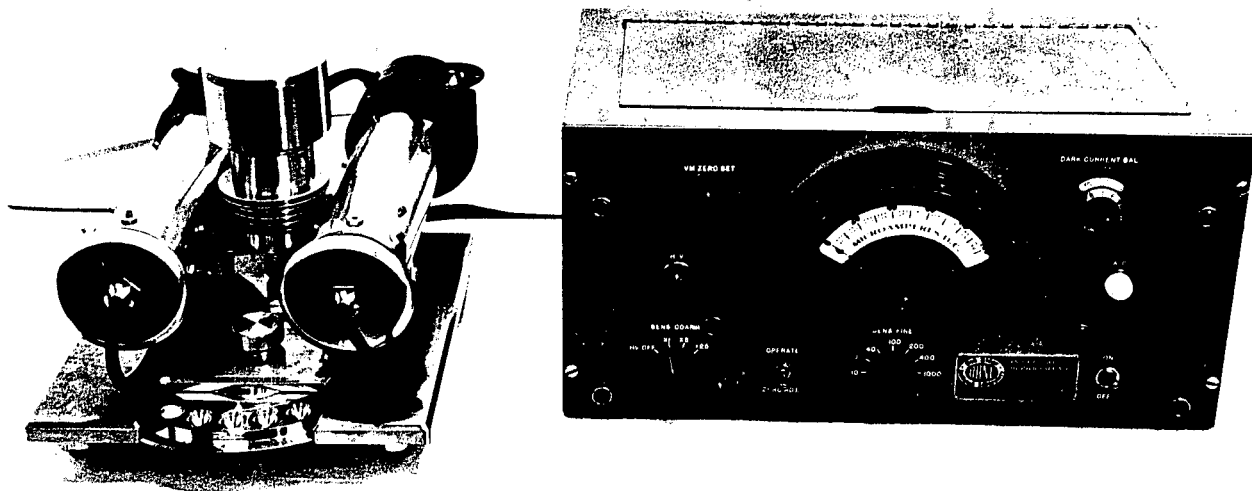


Figure 13. *An* early uranium fluorimeter.

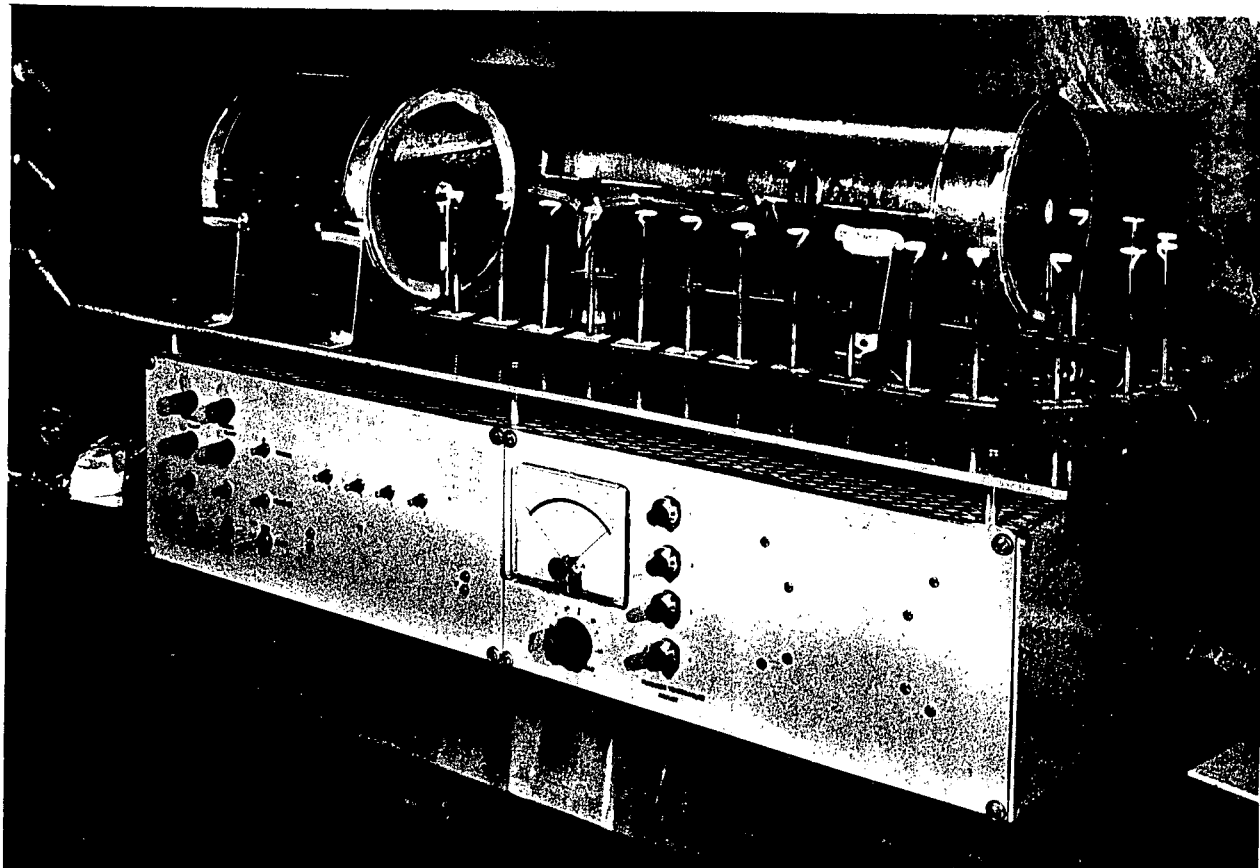


Figure 14. *An* advanced pellet fusing device, vintage 1970.

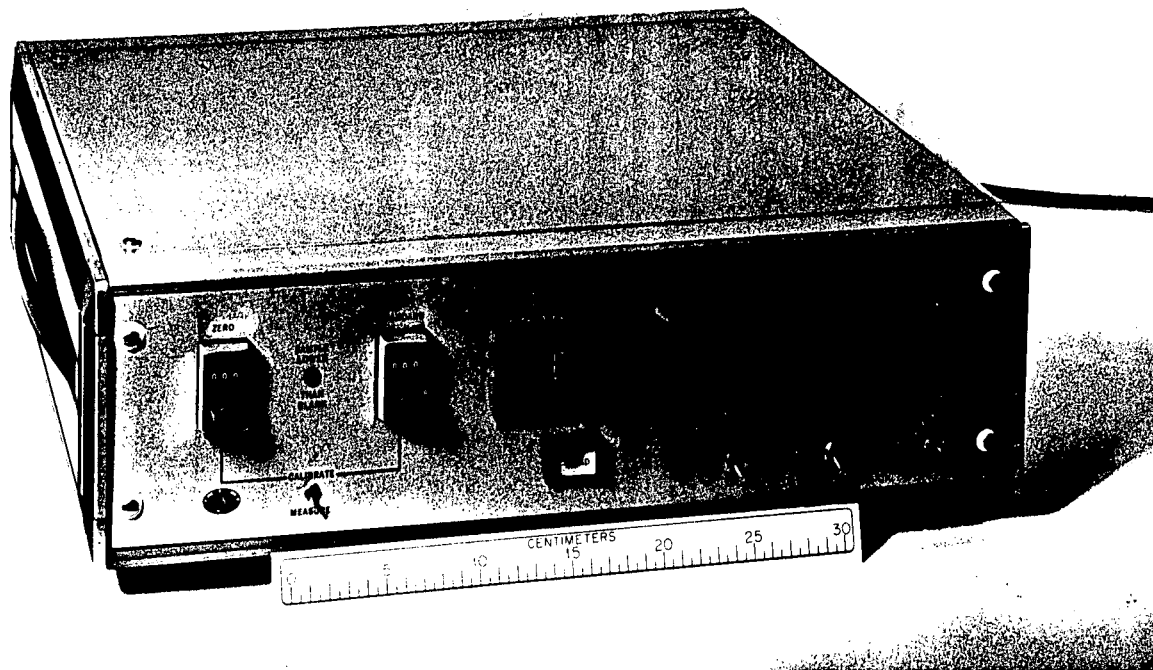


Figure 15. An advanced fluorimeter, vintage 1970.

LASER-BASED FLUORIMETRY

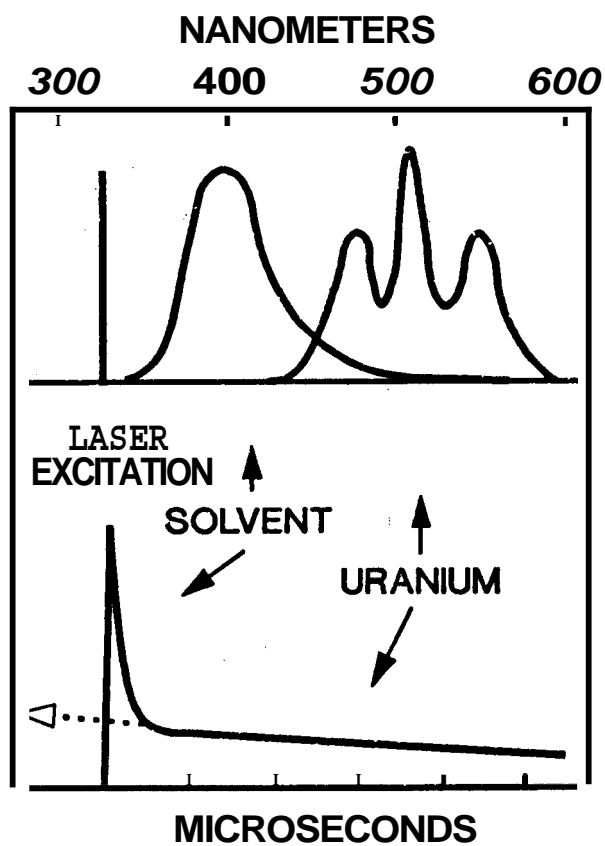


Figure 16. Laser-excited fluorescence of uranium.

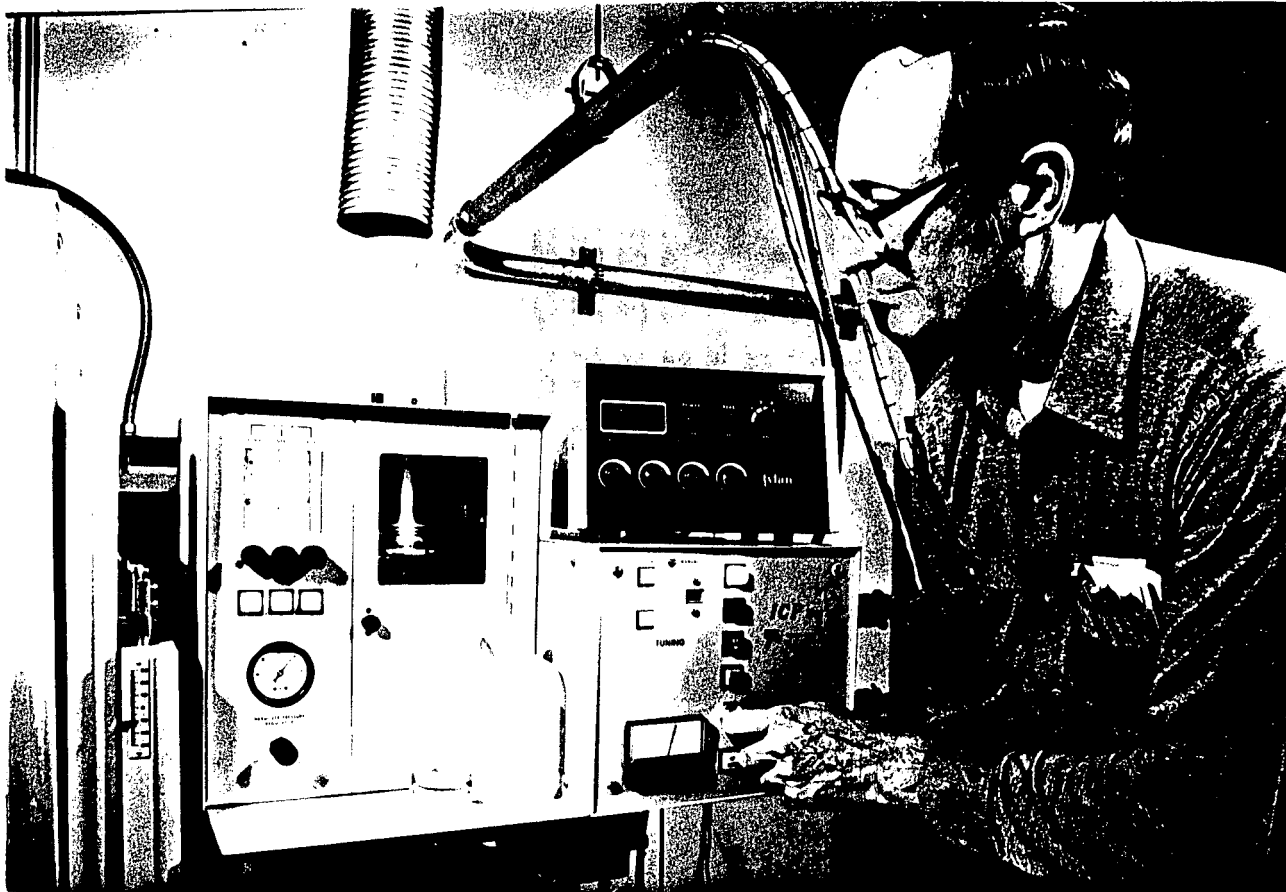


Figure 17. An inductively coupled plasma source for atomic emission spectrometry, vintage 1980.

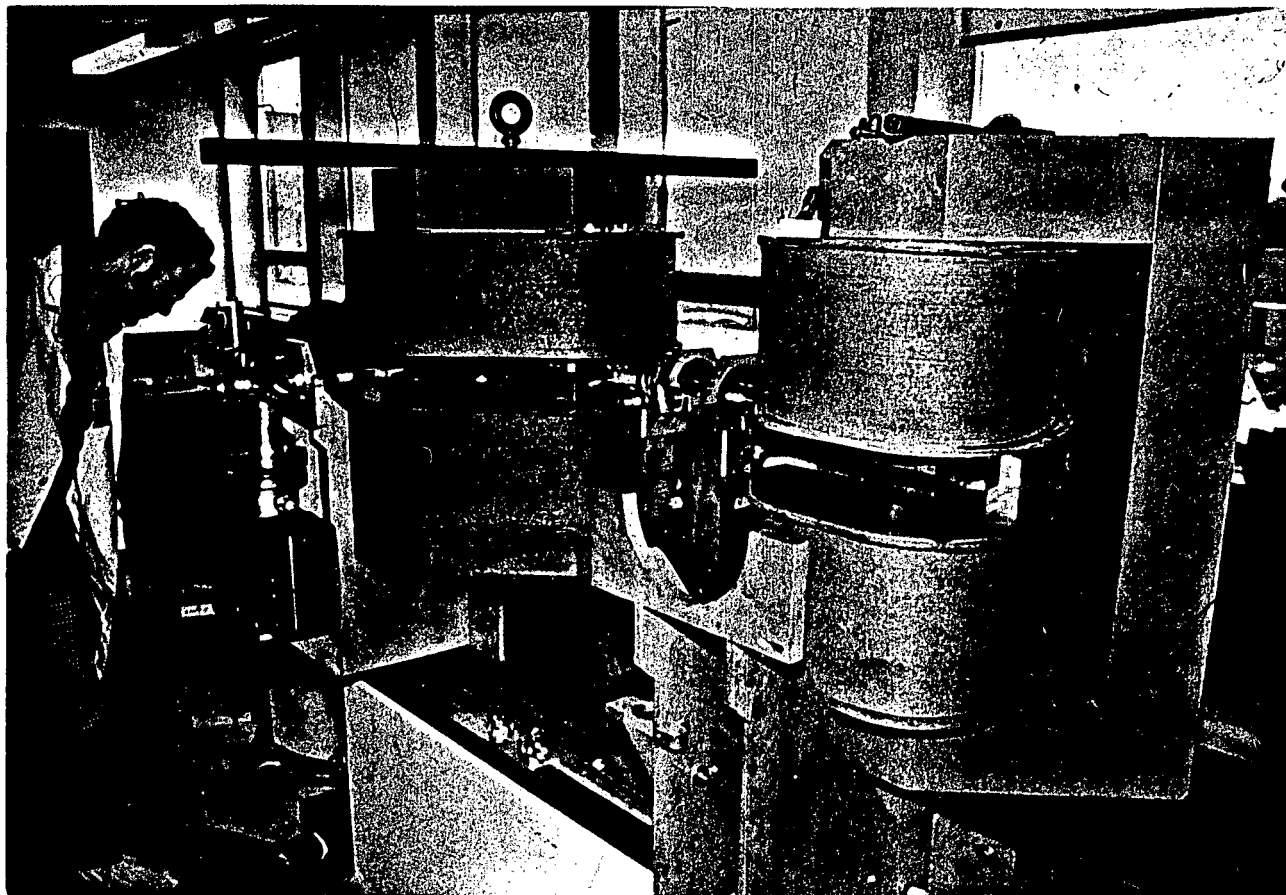


Figure 18. A two-stage mass spectrometer, vintage 1975.

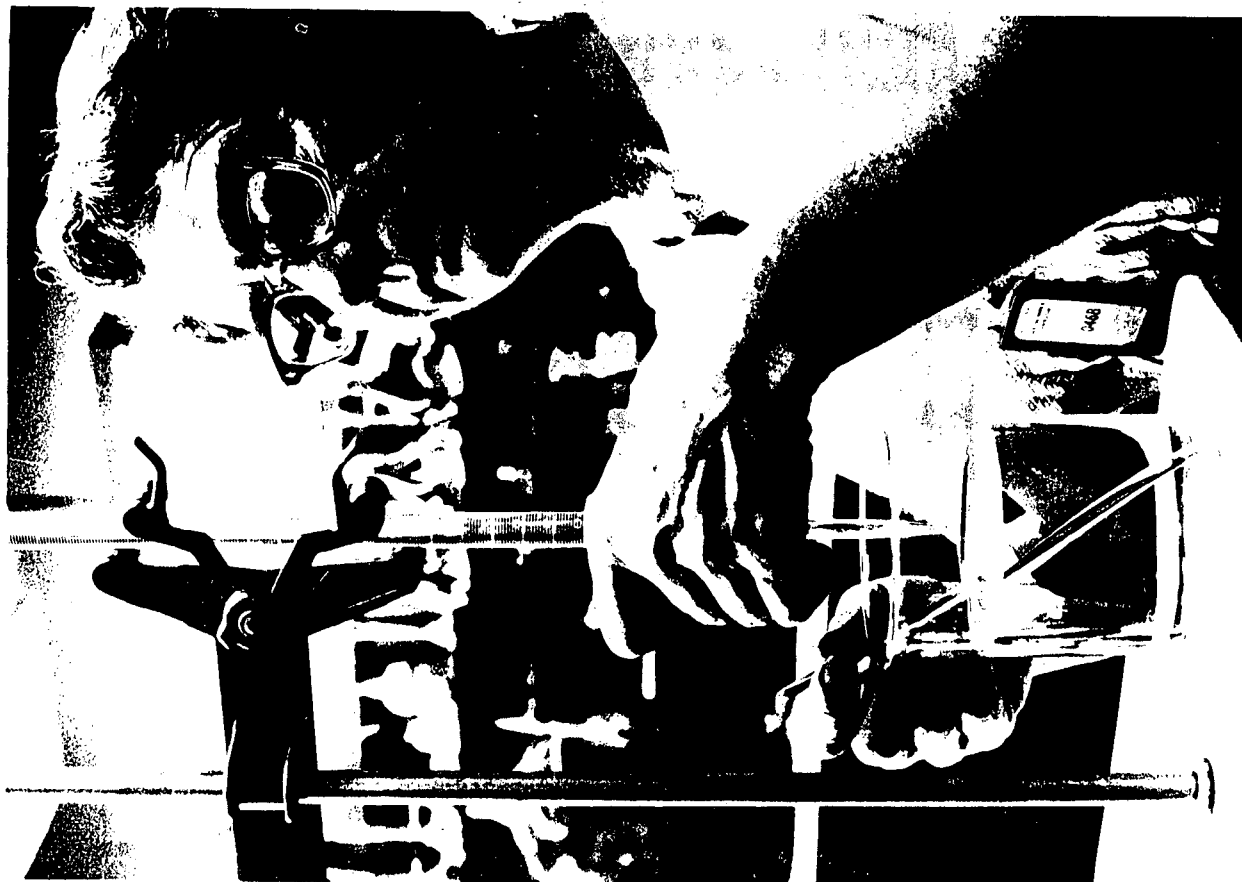


Figure 19. Analytical chemistry, vintage 1950.

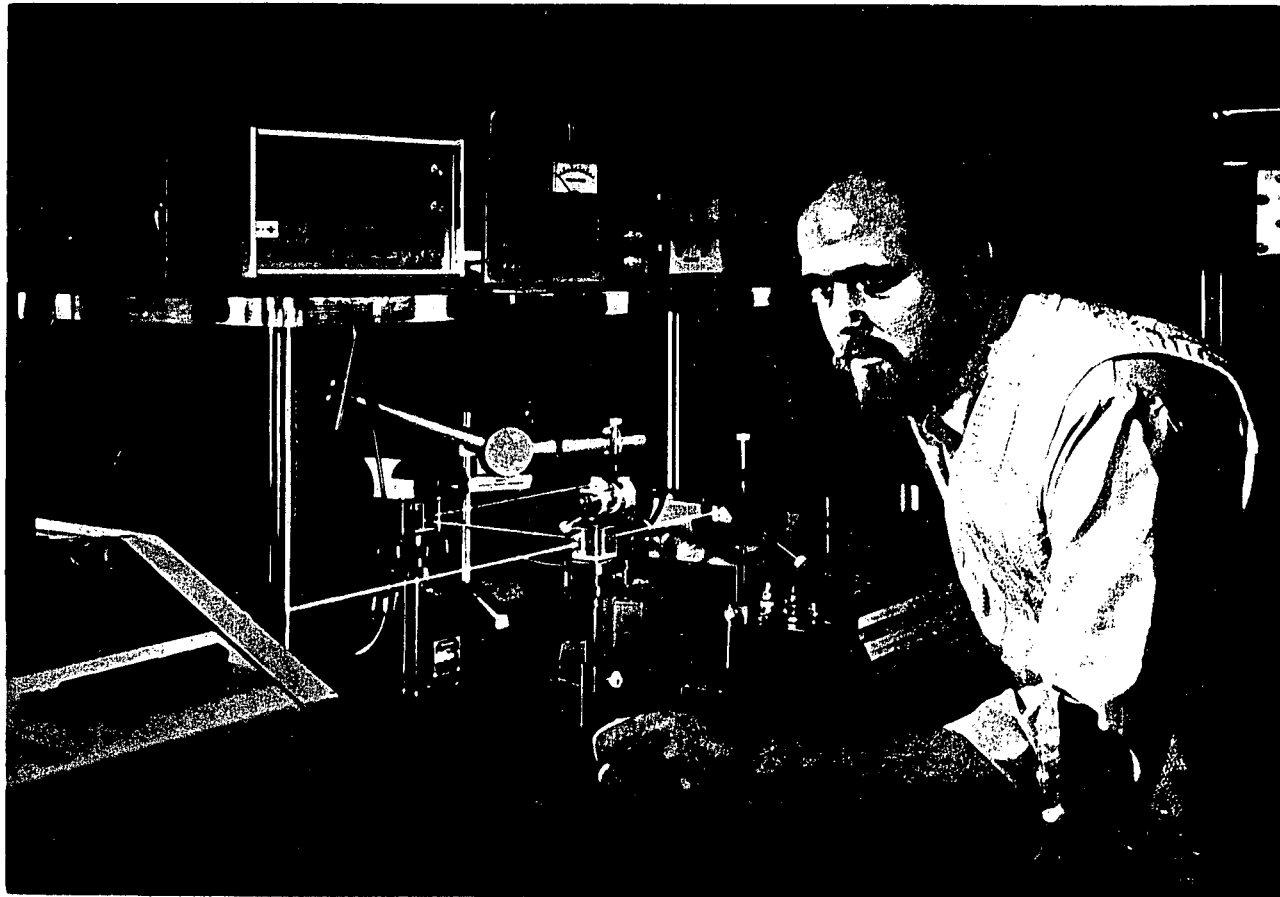
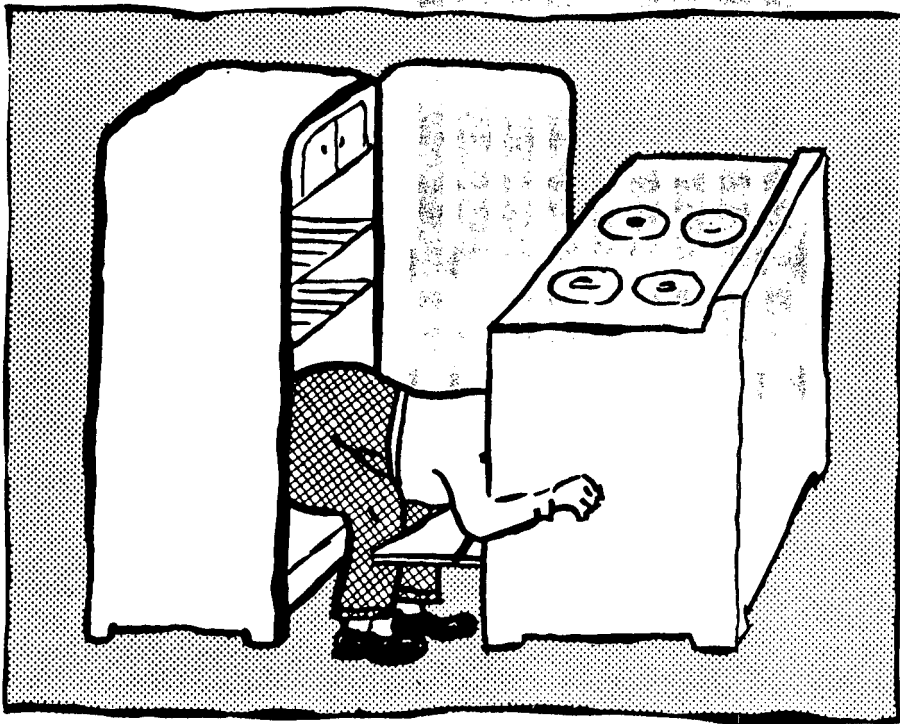


Figure 20. Analytical chemistry, vintage 1989.

AVERAGES CAN BE MISLEADING



"ON THE AVERAGE, HE FEELS FINE!"

Figure 21. The law of averages.