Atomic Absorption
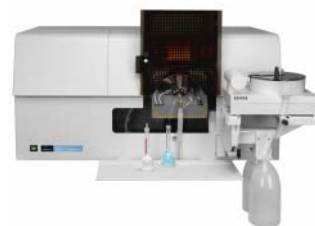

PerkinElmer
45

| AAnalyst 200 | AAnalyst 400 | AAnalyst 400+HGA 900 | AAnalyst 600 | AAnalyst 700/800 |

1

Evolution of analytical instrumentation: The PerkinElmer Story
SDI Global 7th Edition 2002-AAS
SDI Global 8th Edition 2004-AAS

2

-

HAc-MIBK   GFAAS

STPF

——

-

-
-
-

NBS   Pb

3

Pb Cd Cr

Pb—— 0.1NHNO_3 -NaI

4

——

Characterizing the Metal Adsorption Capability of a Class F Coal Fly Ash

EDTA EAAS

5

L vov

AAS
FCC

MIBK-

Na   Ca

6

Cu   Mn   Zn   Fe   Se

-

Cu^{2+}

Ultratrace Aluminum Analysis of Nutritional Intravenous Solution Components in 1-Propanol Using GFAAS
Occupational Exposure to Lead and Induction of Genetic Damage
PE AA800
Zeeman

-

SIMMA6000

7
GFAAS   Ag
                    GFAAS   Pb

            -

High-Temperature, Microwave-Assisted UV Digestion: A Promising Sample
Preparation Technique for Trace Element Analysis
            -

Speciation analysis. The future of atomic absorption spectrometry
Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite
On-line separation for the speciation of mercury in natural waters by FI-AAS
                    -

AAnalyst   AAnalyst   AAnalyst   AAnalyst   AAnalyst
  200   400   400+HGA 900   600   700/800

Evolution of Analytical Instrumentation The Perkin-Elmer Story

Horace G. McDonell

President
The Perkin-Elmer Corporation

H.G. McDonell Jr.

We all come to the Pittsburgh Conference to see what is new. There are always plenty of new things to see here. That is what is exciting about this meeting. The Pittsburgh Conference has become the showplace for the analytical instrument industry to display its new wares. A steady flow of new products has been the driving force behind the relentless expansion of the instrument industry. Therefore, it is not surprising that the growth of the Pittsburgh Conference has closely paralleled the growth of the instrument industry.

How about all these new products? There must be several hundred of them being shown in this hall this week. What is the source of all this new technology, and what is the nature of the analytical chemistry market that uses it?

There has been a remarkably successful marriage between the instrument designer and the instrument user. Together, they have built a 2-billion-dollar a year industry. This industry has emerged from initially nothing at the end of World War II, and shows no sign of slowing its growth.

Where does the technology come from and how does it get put to work? In the answer to this question, I think lies the key to our success as an industry.

Let us look for the answer in our history. The source of my own experience these last 27 years, and the data base to which I have access both lie within Perkin-Elmer. So, if you can forgive a somewhat polarized view of the subject, I will examine the history of the analytical instrument business at Perkin-Elmer.

Analytical Instruments at Perkin-Elmer

The history of analytical instrument techniques at Perkin-Elmer is summarized in Figure 1. I think it tells us a lot about the instrument business in its modern form. It is not a large industry as industries go, but it is incredibly diverse. While Perkin-Elmer covers more of the field of analytical chemistry than most other suppliers, we are a long way from covering it all. Yet, the number of technologies, or product lines, we are in today in order to cover just our segment of industry's total requirements is *sixteen* — and it's still growing. Within these 16 technologies, Perkin-Elmer offers more than 150 distinct instruments, not counting the thousands of accessories and configuration options we market.

As we say at Perkin-Elmer, "there are no large targets."

Another statistic one might glean from Figure 1 is the number of fields we have entered in the past, but which no longer survive in the company: that number is *eight*.

I think I can convince you that Perkin-Elmer has been a successful participant in the analytical instrument industry. Yet, I must point out that over the years almost one-third of our new product ventures have not survived.

To the instrument company, the fact that the targets are small means that if you don't hit them squarely, you won't survive. In this multiple small target array, the game has been played over and over again according to the rules of Darwin: only the fittest survive! The evolutionary selection process is not limited to sorting out the surviving species among the analytical techniques: it applies within a given technique as well.

Let us look at the genealogy of a few of these surviving 16 product lines to see how they have evolved to their present state. In the interest of brevity, I suggest that we limit our discussion to three techniques: infrared spectroscopy, gas chromatography and atomic spectroscopy. Let us retrace some history in these three product lines.
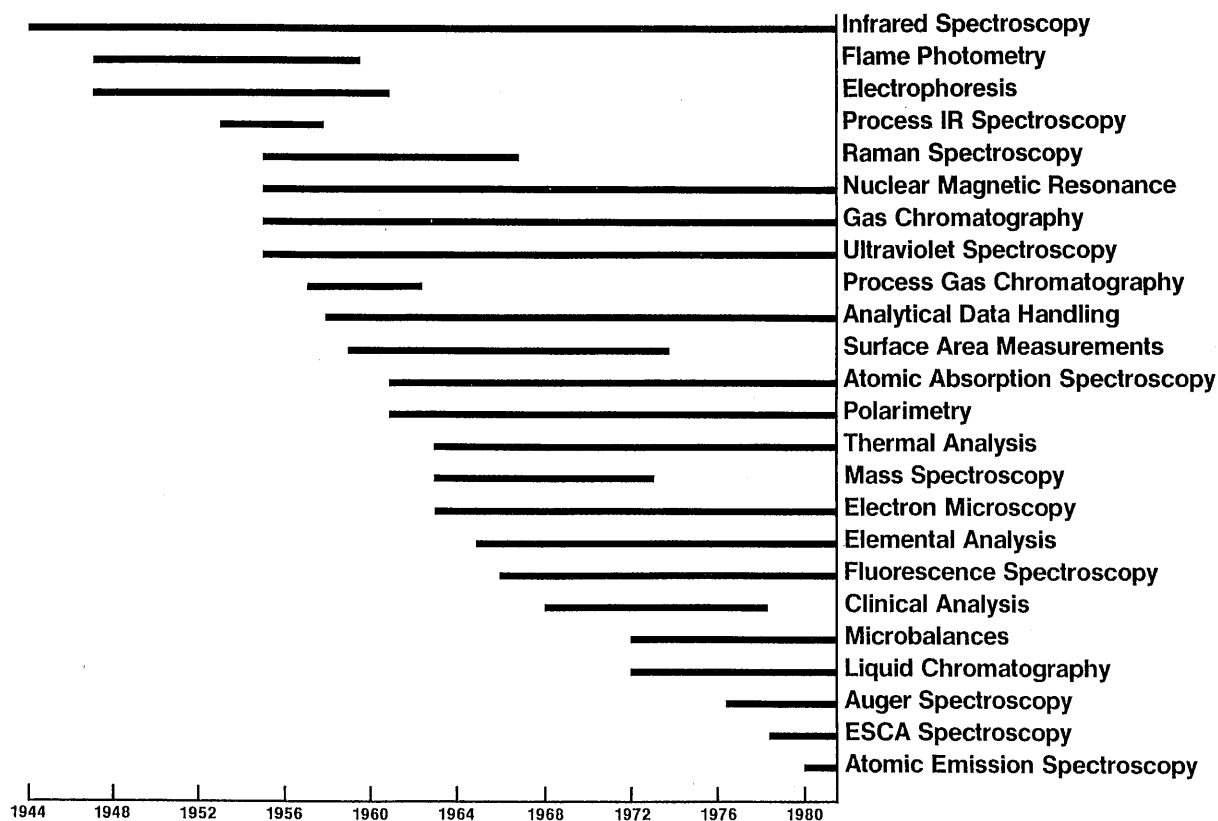
Figure 1. History of analytical instrument techniques at Perkin-Elmer
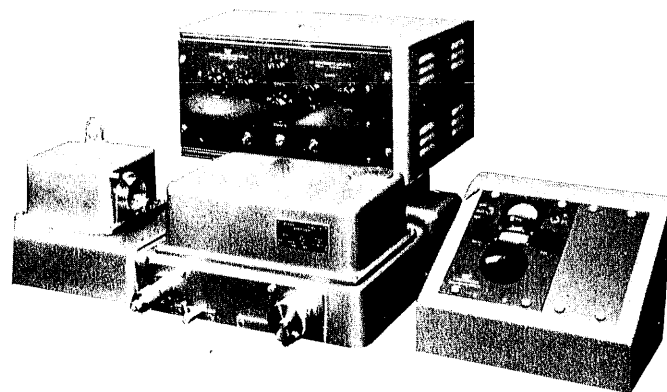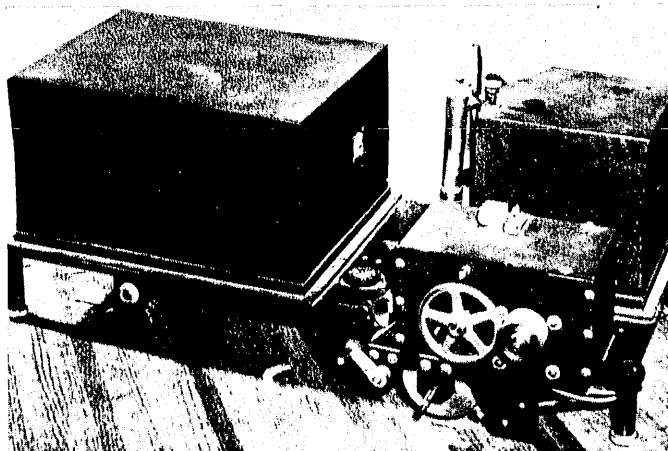
Figure 2. The prototype (left) and the commercialized version (right) of the Model 12 IR Spectrophotometer.
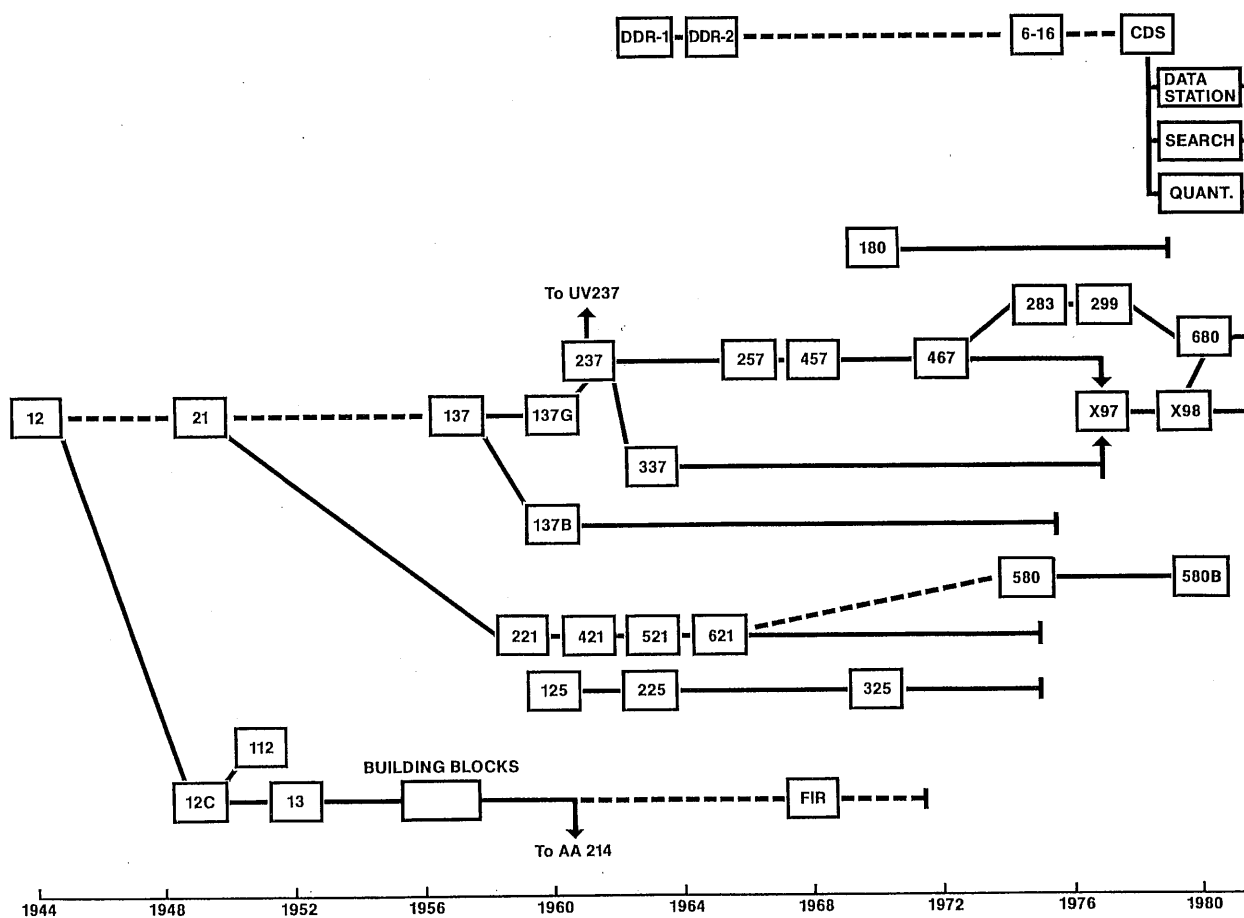
Figure 3. IR family tree at Perkin-Elmer
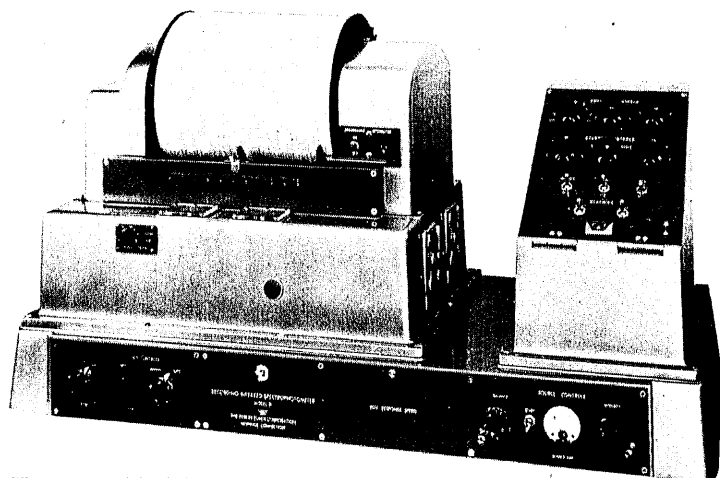
Figure 4. Model 21
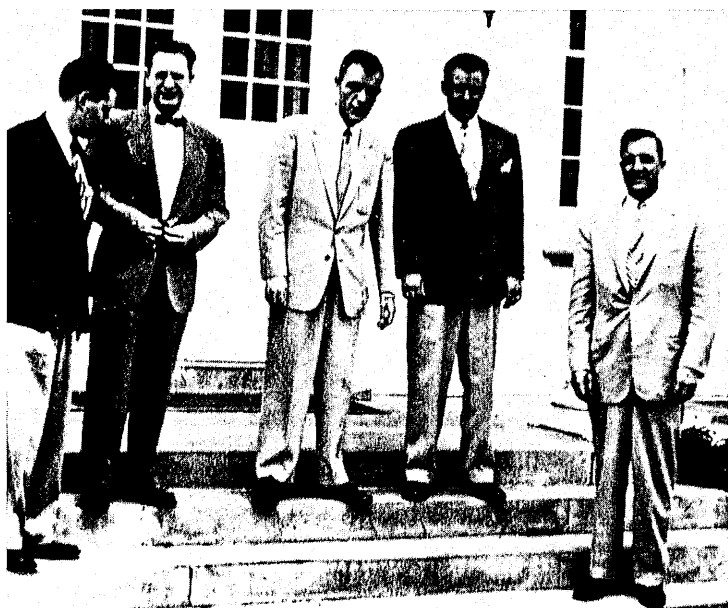
Figure 5. Leading people in the early 1950's. Right to left: Dr. V.Z. Williams, H.H. Hausdorff, S. Lindsley, Dr. A. Savitzky and W. Hargrave.

Figure 6. Laboratory exercises at Fisk. Lee Cahn is on the left, leaning on the instrument; J.E. Baudean is standing on the right. Sitting on the left: H.G. McDonell.

Infrared Spectroscopy

Perkin-Elmer's first analytical instrument grew out of a crash program supported by the U.S. Government during World War II to produce synthetic rubber through the polymerization of butadiene. This process required the analysis of C_4 hydrocarbon isomers, an analysis for which there was no commonly accepted method. It was recognized that *infrared spectroscopy* could satisfy this need if only a practical instrument could be made available to the chemical industry. Acting under this incentive, two industrial research laboratories set out to design such an instrument; they were the Shell Development Company, in Emeryville, California, and the research laboratories of American Cyanamid Company, in Stamford, Connecticut.

The Cyanamid design required an off-axis collimating mirror of particularly demanding optical quality. Perkin-Elmer, then a tiny optical shop, entered into this picture due to two highly unusual characteristics: it specialized in very-high-quality optics, and, like Cyanamid, it was located in Stamford.

It is a long story, the essence of which is that Perkin-Elmer made the optical elements for the Cyanamid prototype, built a few instruments for Cyanamid, and was then reluctantly induced into building still more instruments for other interested firms. Like most newborns, Perkin-Elmer was dragged kicking and screaming into the new world.

The instrument Perkin-Elmer built for Cyanamid became the Model 12, the commercialized version of this prototype (Figure 2).

It is an interesting footnote in this story that through a similar relationship to ours with Cyanamid, Beckman, at about the same time, entered into production of the instrument development by Shell: it became known as the Model IR-1.

The Model 12 was a successful instrument that was subsequently improved into the Models 12A, 12B, 12C and 112. This pattern of multiple tactical developments following on the heels of a single strategic success emerged early in the history of the instrument business. It is an important one, and fundamental. Every successful product line is made up of many tactical refinements of a few strategically important concepts: that is to say, the system is adaptive.

Figure 7. Graduating class at Fisk

Our next big step in infrared came in 1949 when we developed the Model 21. It borrowed liberally from the optical design of the Model 12, but added enormous utility from the user's point of view through the use of programmed slits, linear wavelength drive, and double-beam optics. It produced whole spectra that were repeatable and easy to read, and popularized infrared as a qualitative analysis tool. It also put Perkin-Elmer on the map as a leading supplier of analytical instruments. Figure 4 shows this instrument just off the production line.

The success of the Model 21 was also due to the fact that Perkin-Elmer was able to assemble a number of excellent people involved in the development of infrared spectroscopy and its applications. Some of Perkin-Elmer's leading figures during the heyday of the Model 21 are shown in Figure 5. Besides Dr. Van Zandt Williams, one of the great pioneers of the analytical instrument industry, the group includes Harry Hausdorff, Sy Lindsley, Dr. A. Savitzky and Bill Hargrave.

The success of the Model 21 was also accompanied by a significant expansion of Perkin-Elmer. Outgrowing its Glenbrook plant, the company moved in 1951 into new headquarters in then rural Norwalk and, in Fall 1952, opened its first branch office in New Orleans headed by Sy Lindsley. He holds the dubious distinction of having hired me into Perkin-Elmer as a service engineer at the New Orleans office.

The rapid expansion of infrared spectroscopy also necessitated the organization of courses to
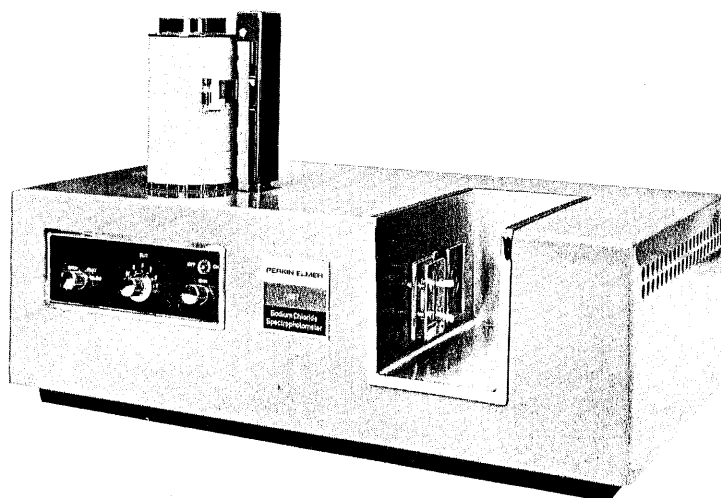
Figure 8. Model 137 IR Spectrophotometer

Figure 9. 1957 Pittsburgh booth
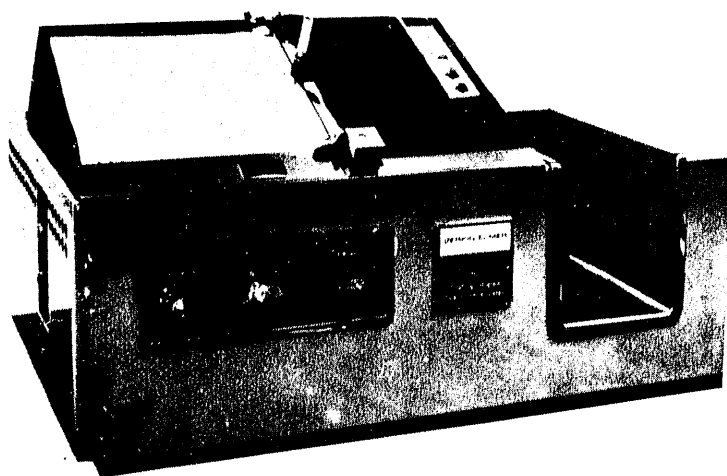
Figure 10. Model 257 IR Spectrophotometer
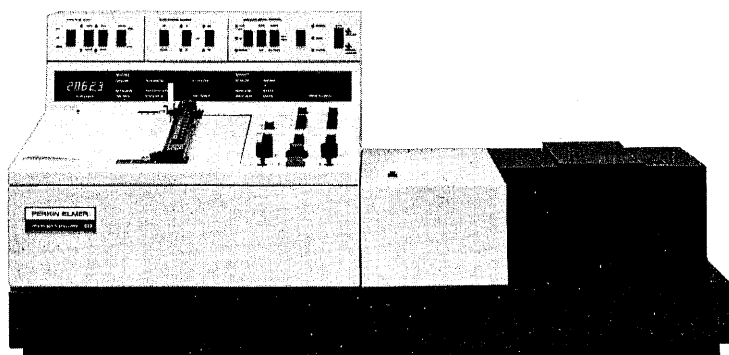
Figure 11. Model 283 IR Spectrophotometer

Figure 12. Model 154A Vapor Fractometer with H.H. Hausdorff

train spectroscopists. MIT and Fisk University in Nashville, Tennessee, pioneered in these during the early 1950's by organizing summer Infrared Institutes. Two photos are shown here from my first Fisk IR Institute. The first, (Figure 6) was taken during the laboratory exercises; among others, it shows Lee Cahn who led the design of the Beckman IR-4 and later the Cahn electrobalance, and from Perkin-Elmer, Jack Baudean and myself. The second (Figure 7) shows one of the early graduating classes. The Institute's founders are circled: Jim Lawson who later became president of Fisk University is on the left, and Nelson Fuson on the right. The white-haired gentleman in the middle of the first row is Professor Randall of the University of Michigan; Professor Randall had already retired years earlier; he was the "grandfather" of molecular spectroscopy in the country; Lawson and Fuson had studied under him. He visited the Institute to wish success to his former students.

After the Model 21, our next big event in infrared came at the 1957 Pittsburgh Conference when we introduced the Model 137 (Figure 8). Low-cost infrared was born. Some visitors in our Pittsburgh booth that year included Norman Wright and Clara Smith Craver with Perkin-Elmer's Jack Baudean (Figure 9).

The Model 137 infrared was introduced at a price of $3,800 (1957-dollars); at that time, the Model 21 was selling for about $13,000. With optical performance very close to the Model 21, the Model 137 was clearly a major engineering achievement. It became a popular instrument, but did not have the revolutionary impact on the market that some of us had hoped: its single slit program and small drum-chart recorder led it to be perceived as a limited-purpose instrument. It took two subsequent developments to alter that perception: *gratings* which greatly improved optical performance, even over large prism instruments, and *flow-chart recording* which greatly improved data presentation and operator convenience.

The Model 257 (Figure 10) was developed in England, at Perkin-Elmer Ltd., using the Model 137 optical system; it added flow-chart recordings and multiple slit programs. These relatively minor engineering developments altered the utility and perception of small infrared instruments in a dramatic way: the revolution hoped for with the Model 137 introduction got into high gear when the Model 257 came along.

The strain of instruments bred from the 137's optics and the 257's flow chart recorder was a hardy one, indeed, leading to at least a dozen later models as optical, mechanical and electronics improvements became possible. In fact, the basic optical design concepts of the Model 137 survive today, 23 years later, in modern instruments such as the Model 283 (Figure 11), as does the flow-chart recorder approach of the Model 257.

Other properties given to modern instruments, primarily through the use of microprocessors, give them greatly expanded functional capability, even though basic optical and mechanical concepts may change very little.

This evolutionary process is a driving force behind the expansion of the instrument industry. It is the means through which instrument companies are able to provide you with ever improving and easier-to-use instruments, with little, if any increase in cost.

There is another lesson to be drawn from the 137/257 experience. The flow-chart enhancement that triggered the Infracord success did not come out of Norwalk where the original Infracord was developed. I am convinced it never would have. Having given the world the Infracord, drum chart and all, we were convinced that the entire design was optimum and that it was then only a matter of convincing the world of the enormity of our accomplishment. On the other hand, the English, having no ego stake in the matter, simply went ahead and designed a flow-chart recorder, thereby saving our most lasting accomplishment from the shadows of mediocrity.

Because of this experience, and similar ones in other product lines, Perkin-Elmer organizes itself today so as to allow some degree of overlap, that is competition, among its manufacturing sites. We call this the *two-site concept*.

Gas Chromatography

Let us now shift to the field of gas chromatography.

Perkin-Elmer introduced America's first commercial gas chromatograph, the Model 154, in May 1955. We got an early start as the result of contacts made between Van Zandt Williams, then manager of Perkin-Elmer's Instrument Division, and A.J.P. Martin and others in England who

Figure 13. Model 154B Vapor Fractometer with G.N. Kelley

Figure 14. Light-hydrocarbon separation

Figure 15. GC lab at Esso in New Jersey

Figure 16. A.J.P. Martin (left) and R.S. Perkin

were working with home-made systems in their laboratory. Perkin-Elmer at that time was just starting up its Bodenseewerk subsidiary in Germany and was looking around for a suitable arrangement in England. It was probably because of these events, and of our infrared contacts in these European laboratories that Van happened on those important developments. At that time, gas chromatography was virtually unknown in the United States.

Immediately on his return from England, a prototype development was started and Harry Hausdorff began to investigate the possibilities of this new technique. From this effort, in a matter of months, the Model 154 was born and with it an

Figure 17. Consultants' meeting at Perkin-Elmer Ltd. On the left side of the table (left to right): R.D. Condon, H. Carter, C.G.S. Phillips and H. Bolz. In the right foreground: A.J.P. Martin, then A.I.M. Keulemans and J.E. Lovelock

Figure 18. M.J.E. Golay

instrument technology that was to alter fundamentally the analytical instrument industry.

Figure 12 records Harry Hausdorff with the Model 154-A, and Figure 13 the Model 154-B with the young designer who laid out the cabinet and controls for the instrument. In the end, he started a second career in the company: Gaynor Kelley now manages the world-wide analytical instrument business of Perkin-Elmer.
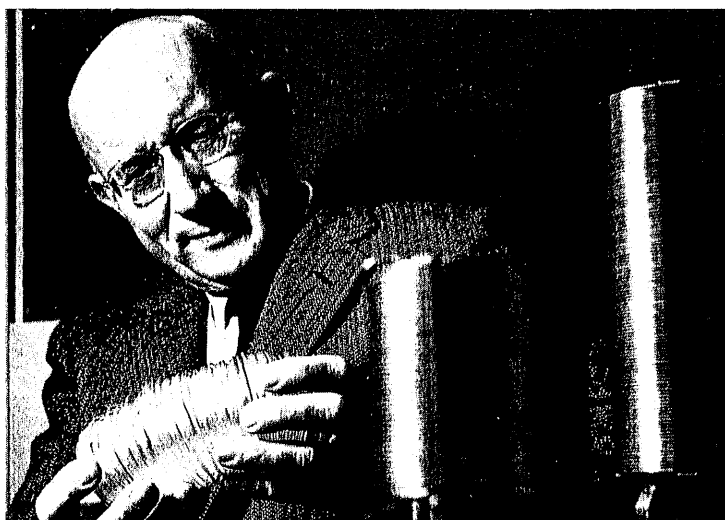
The introduction of the Model 154 was coupled with the publication of practical examples for its use. Chromatograms like the one reproduced in Figure 14 showing light hydrocarbon separation, created a sensation among analytical chemists. Soon, every large analytical laboratory included gas chromatography among the techniques em-

ployed and within a couple of years, major laboratories had practically wall-to-wall chromatographs such as the ESSO laboratory in New Jersey (Figure 15). The Model 154 was the hottest thing going. Competition soon entered the field. But for some years, Perkin-Elmer remained dominant.

In the early years of gas chromatography, technical advancement was at an incredible rate and scientific superstars emerged. We, at Perkin-Elmer worked by maintaining a continuous contact with them. A.J.P. Martin is shown with R.S. Perkin (Figure 16) when visiting Norwalk in 1959; and in Figure 17 a number of leading gas chromatography experts are grouped with Perkin-Elmer's specialists in 1960 at an advisory group meeting in Beaconsfield, England. Dick Condon of Perkin-Elmer Norwalk was later to lead the design effort for the Model 900; Harry Carter of Perkin-Elmer Ltd. was responsible for the F-11, F-17 and F-30 programs; and H. Bolz of Bodenseewerk has served until recently as the manager of their development group. Our guests included: C.S.G. Phillips of Oxford University, one of the

Figure 19. One of Golay's first chromatograms

Figure 20. Model 194 Digital Integrator

Figure 21. GC family tree at Perkin-Elmer

Figure 22. Model 226 Gas Chromatograph

Figure 23. Model F-11 Gas Chromatograph

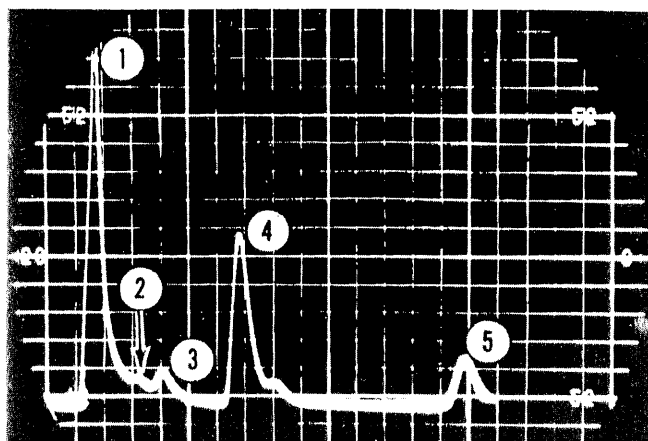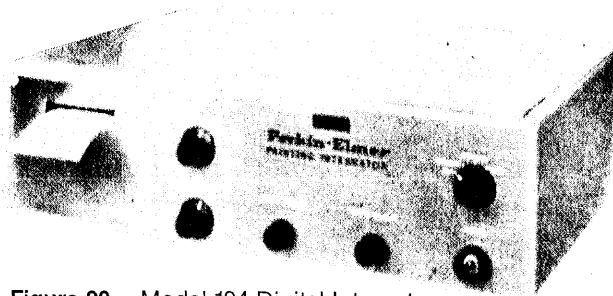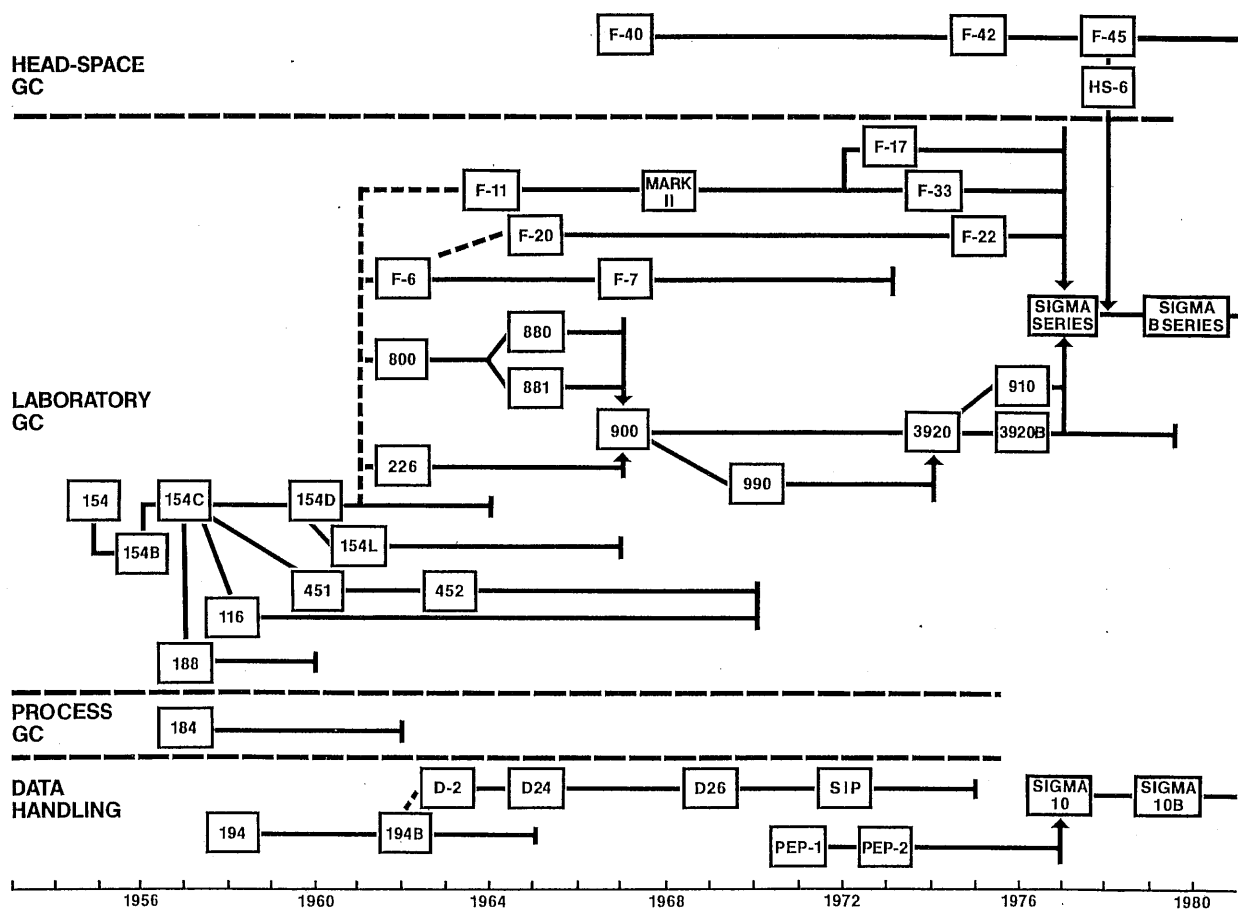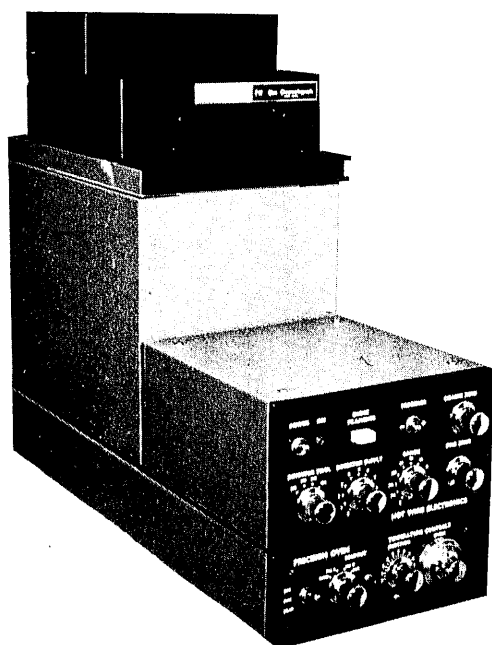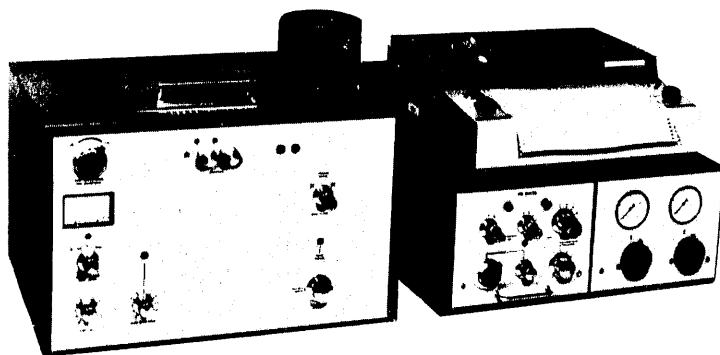**Figure 24.** Model F-20 Gas Chromatograph

earliest British scientists active in gas chromatography; A.I.M. Keulemans of Shell, Amsterdam, and the University of Eindhoven who played a key role in gas chromatography from its beginning; J.E. Lovelock then of Lister Institute, London, the inventor of the argon ionization and electron capture detectors; and A.J.P. Martin, the inventor of partition chromatography and Nobel laureate.

Major technical achievements at Perkin-Elmer in the first years of gas chromatography included the open tubular columns developed by M.J.E. Golay (Figure 18). His historical chromatogram (Figure 19) was included in his Engineering Report proving the superior performance of these columns. Another significant achievement was the development of the first digital chromatographic integrator, the Model 194, introduced in 1958 (Figure 20).

In the following years the Model 154 underwent a number of improvements and modifications both in Norwalk and in the two European sites, Bodenseewerk and Perkin-Elmer Ltd. and represented the basis of future gas chromatography development. Figure 21 represents the family tree of Perkin-Elmer's gas chromatographs. This development, however, was not without problems.

By 1958-59, the application of gas chromatography advanced so much that the chemists tried to analyze complex, wide-boiling-range samples. For these, however, the operating range of a single isothermal instrument was not enough. We bet on a three-oven approach each containing a column at a different temperature and this system represented the basis of the Model 188. Meanwhile, however, a little company called F & M Scientific (now part of Hewlett-Packard) came out with a new approach, based on Steve Dal Nogare's work at du Pont: temperature programming. They were right and we had guessed wrong.

We brought our first temperature-programmed instrument, the Model 226 in 1962 (Figure 22). Although an excellent instrument, it was rather expensive and came out two years behind our competition. These were tough times for Perkin-Elmer in gas chromatography. During the early 1960's we continued to grow in chromatography largely through products coming out of our European sites, like the F-11 from Perkin-Elmer Ltd. (Figure 23) and the F-20 from Bodenseewerk (Figure 24). Having a foot in Europe sustained us.

Perkin-Elmer's renaissance in the U.S. really began in 1967 with the Model 900 (Figure 25). It proved to be a first class instrument and a big success in the high-performance segment of the market. The Model 3920 (Figure 26) followed in 1974 and was very successful in the larger, medium-price part of the market. We were back in the ballgame. That was followed in 1977 by the Sigma series (Figure 27) the B version of which is being introduced here at this Exhibit. We shall come back to that product later. First, however, let's look at atomic absorption spectroscopy.

Atomic Spectroscopy

Perkin-Elmer's first efforts in atomic absorption came as a result of our experience in infrared. Toward the end of the 1950's we were approached by Alan Walsh of Australia, a past collaborator with Perkin-Elmer through his development of the double-pass monochromator which showed up in our Model 112 Infrared Spectrophotometer. He had since been working on the principle of atomic absorption which he viewed as a potentially attractive tool for trace metal analysis. The technology was available under license from C.S.I.R.O. in Australia — was Perkin-Elmer interested?

We concluded that we are cautiously interested, and undertook to test the waters. The vehicle chosen for testing the waters, the market as well as the technology, was the Model 214 (Figure 28). This was an expedient design based upon our

Figure 25. Model 900 Gas Chromatograph

Figure 26. Model 3920 Gas Chromatograph
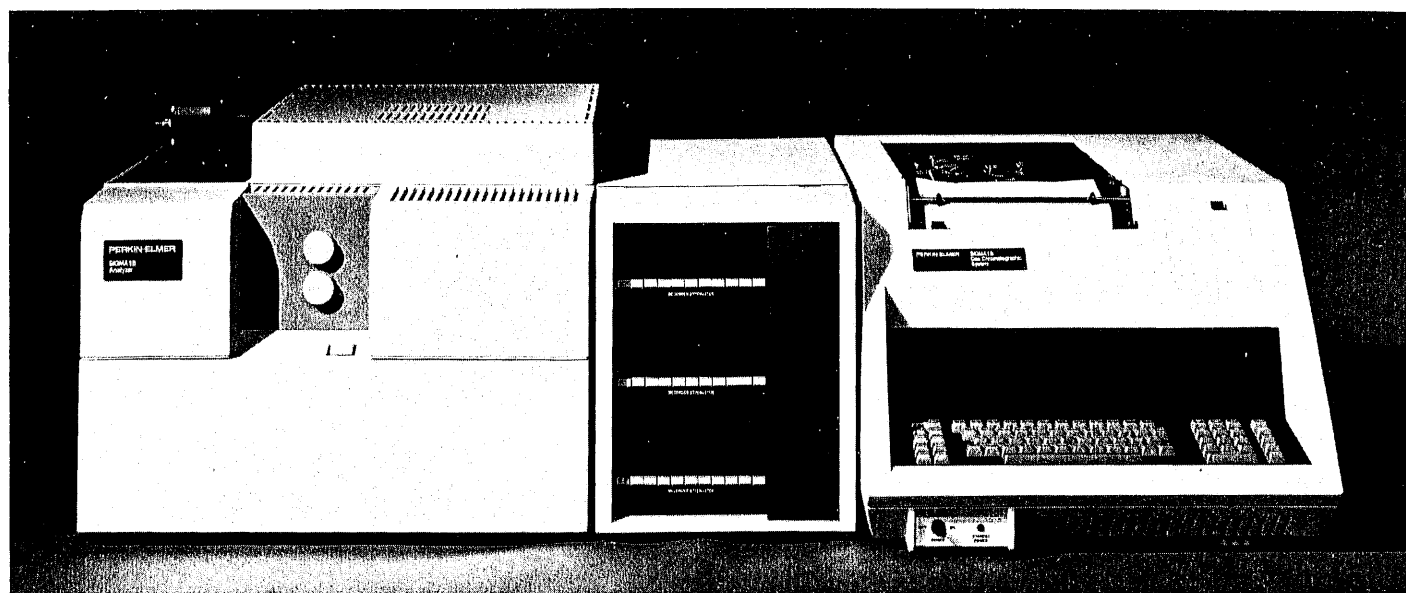
Figure 27. Model Sigma IB Gas Chromatograph

Figure 28. Model 214 Atomic Absorption Spectrophotometer
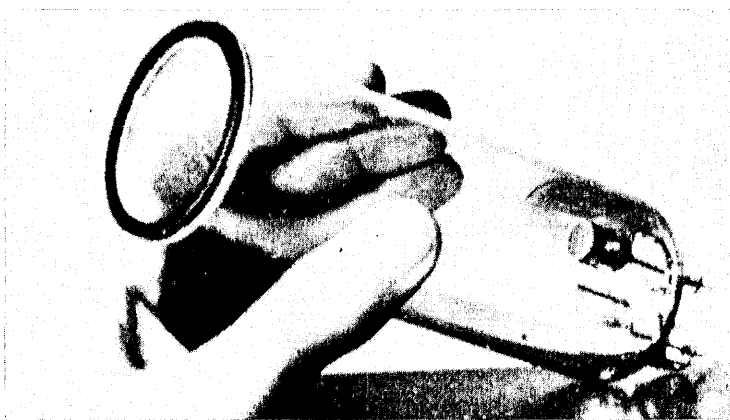
Figure 29. Hollow-cathode lamp

infrared building blocks, direct descendants of the Model 12, but with electronics and systems engineering directing themselves toward the functional requirements of atomic absorption. Our management approach was an "IWO", inventory work order, under which we could build short runs of instruments without the extensive documentation required of a production release. Our object was to learn about the technique.

Among the technologies we had to master was how to make hollow-cathode lamps (Figure 29) but most importantly, we had to understand what one could do with atomic absorption. Walter Slavin conducted some of our first experiments in that direction.

Around the Model 214 coalesced a small team that was to build, experiment with, and sell our first 35 atomic absorption instruments. Besides Joe Borden and Walter Slavin others of the team included Horace Siegler, Dick Reiss, Herb Kahn, Dave Manning and Fred Johnson. Then came the difficult decision: should we commit to the development of an instrument especially for atomic absorption and to the considerable expense of manufacturing it? The decision was to fall to the then new general manager of our Instrument Division Chester W. Nimitz, Jr., shown on the right in Figure 30 with Dick Perkin. Needless to say, he decided in the affirmative and, as is his manner, with great enthusiasm. We were underway in atomic absorption.

Figure 30. Richard S. Perkin (left) and Chester W. Nimitz Jr.

The instrument that resulted was the ubiquitous Model 303 (Figure 31) which was an instant and enormous success — and, like the Models 12, 21 and 154, a benchmark development.

More than with any marketing effort heretofore undertaken, strong applications support was central to our strategy. Our "software" strategy was to prove as successful as the hardware.

Much as gas chromatography took off in the late 1950's, atomic absorption took off in the mid-1960's. As the market blossomed, so did the technology. The digital concentration readout (DCR-1) used with the Model 303 (Figure 32) showed that it was possible electronically to make a general-purpose instrument that reads the analytical "answer" directly — and that the user viewed this as a property of value.

The Model 303 was the start of a continuously improving line of atomic absorption instruments. In the next instrument, we encompassed a number of technical improvements including a built-in DCR. This was the Model 403 (Figure 33). It became a highly successful instrument; atomic absorption became a major product line at Perkin-Elmer.

The two-site principle served as well in atomic absorption by providing a heated graphite sampling furnace, an important supplement for both liquid and solid samples. The HGA-products, as we call them were pioneered by Bodenseewerk, in Germany, based upon the work of L'vov and Massman; Figure 34 shows an HGA furnace.

After the Model 403 and the HGA, our AA product line was to proliferate into several new branches, and many new products, not unlike the pattern shown in our earlier experience with infrared and gas chromatography. Figure 35 is a family tree of atomic spectroscopy instruments. Most recently, this proliferation has led us to the ICP-5000, an instrument for plasma emission as well as atomic absorption (Figure 36).

New Instruments at the 1980 Pittsburgh Conference

Now, let me address myself to those three new instruments being introduced this week at the 1980 Pittsburgh Conference.

Let us start with the Model 680 (Figure 37). This is an attractive new infrared instrument, with
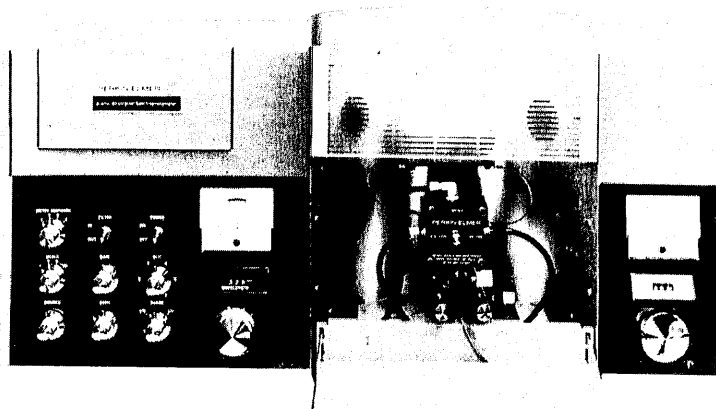
Figure 31. Model 303 Atomic Absorption Spectrophotometer
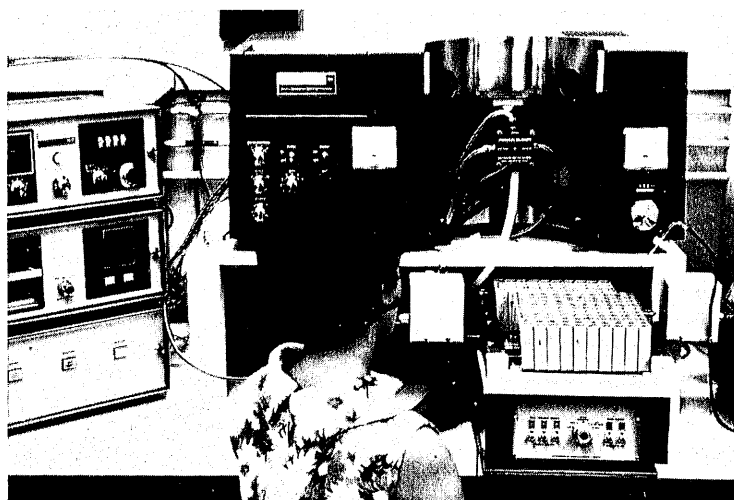
Figure 32. Model DCR-1 with the Model 303 AA Spectrophotometer
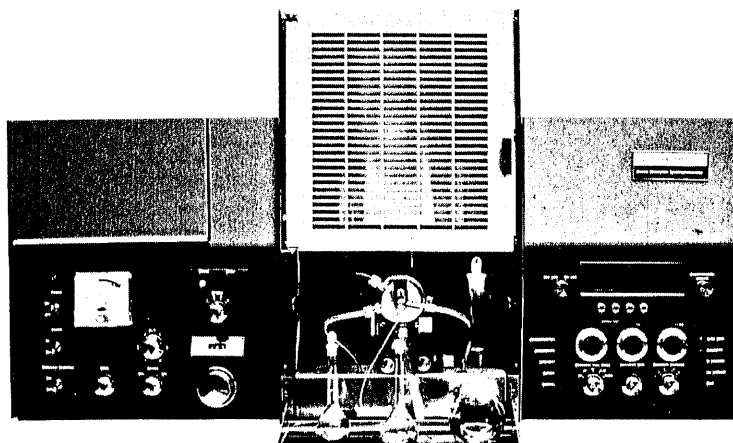
Figure 33. Model 403 Atomic Absorption Spectrophotometer
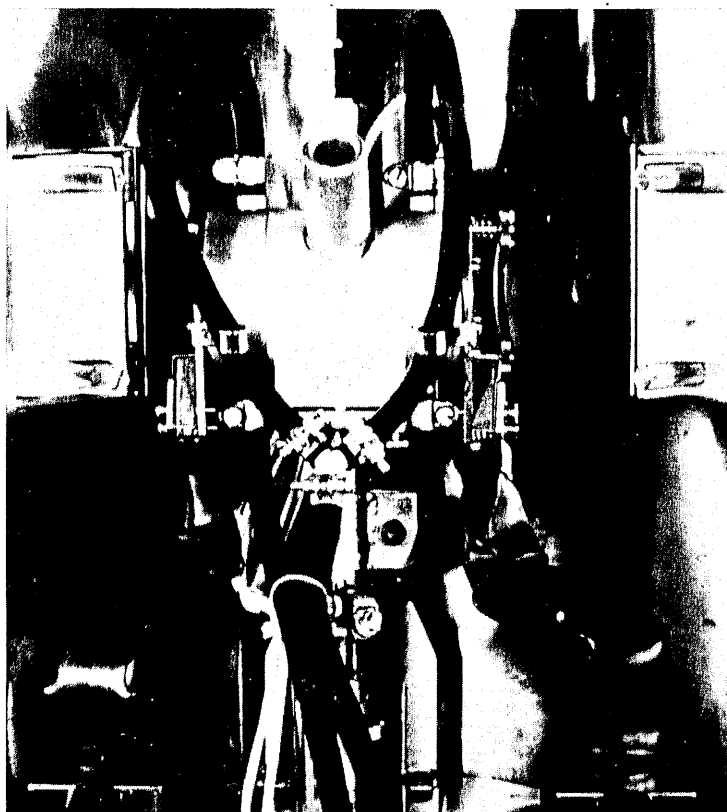
Figure 34. HGA furnace

a very high-performance-to-price ratio, and technologically modern in every sense. It offers enhanced microprocessor hardware and software first developed for the 28X instruments; it has a ratio-recording system similar to that of the Model 580; the optical bench and mechanical design are similar to the X98 series. In other words, it is a hybrid. The Model 680's breeding can be followed on from early IR development: Its origins can be traced through a marriage of cousins between the X98 and 280 series; its lineage is then traceable through the 467 and 457 to the 257, 237, and 137, and then, "by marriage", to the 21 and, finally, to the Model 12. Think of that: over 35 years and at least 13 new designs, technological continuity was never broken.

The second instrument first shown here is the Sigma 1B gas chromatograph shown in Figure 27. This is a chromatograph with more memory, more methods storage, and improved data communications capability than previously available. Obviously, its immediate predecessor is the Sigma 1 first introduced in 1977. Beyond that, as you can follow in the gas chromatography family tree (Figure 21), it is traceable through the 3920 and the 900 to the 800 and the 226 (again, a
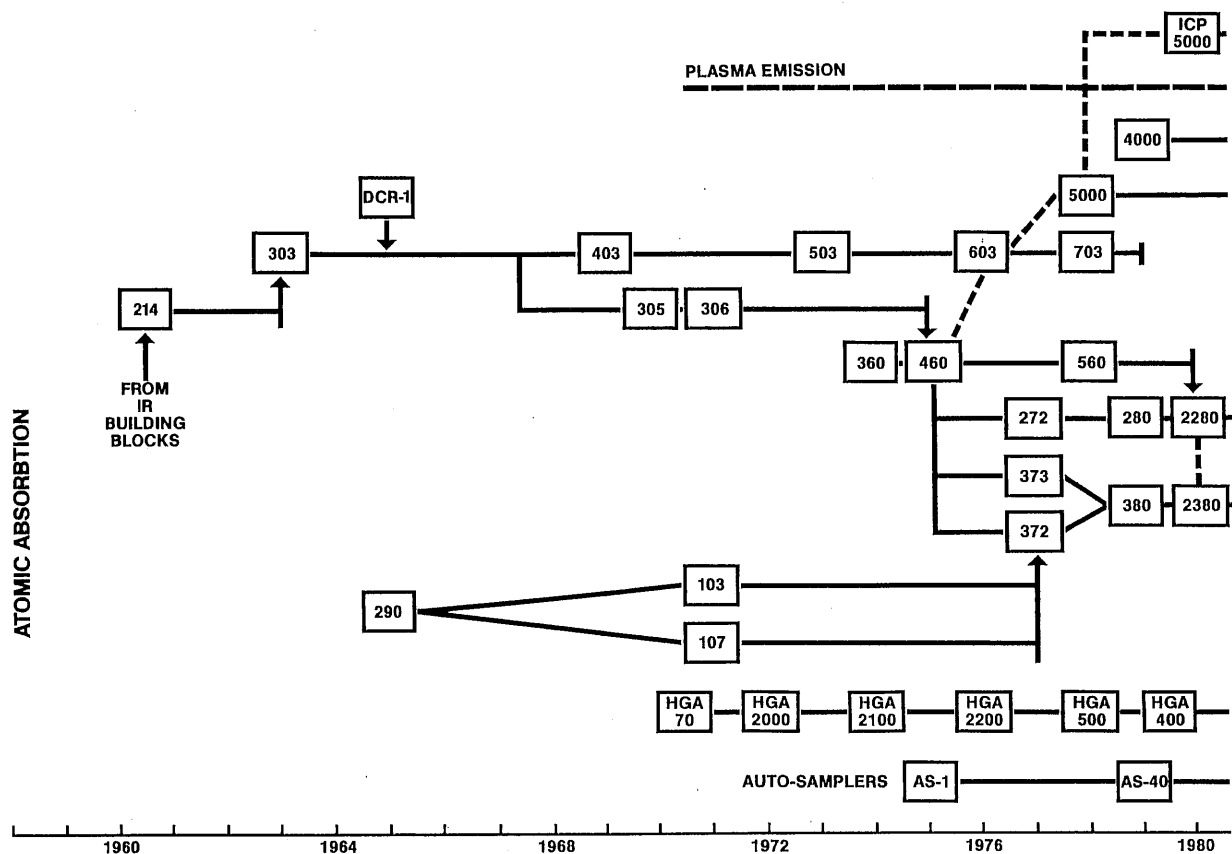
Figure 35. Atomic spectroscopy family tree at Perkin-Elmer
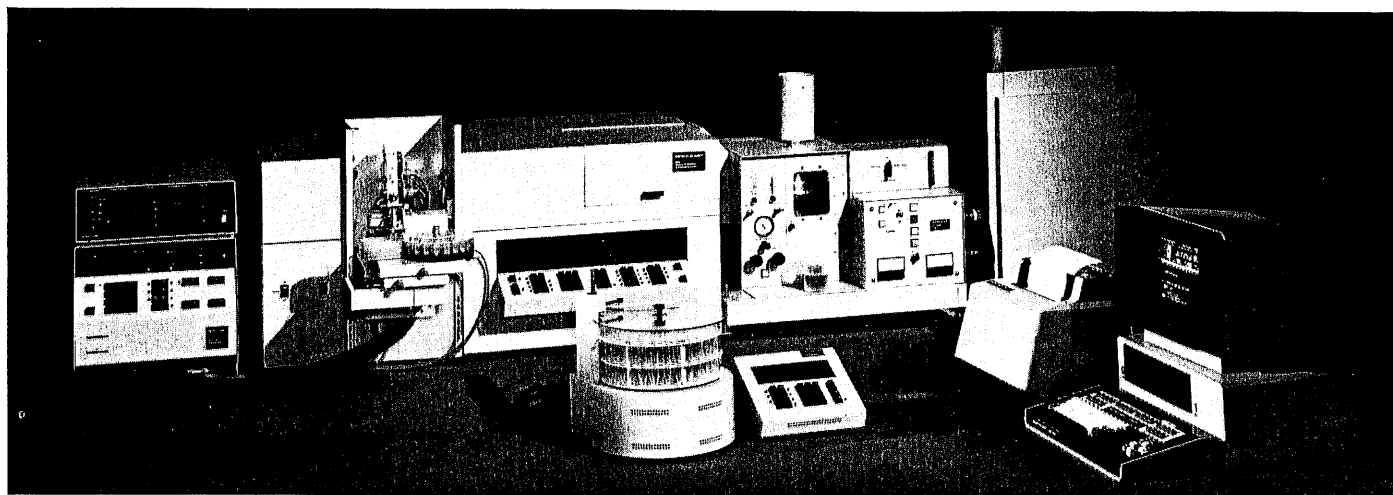
Figure 36. Model ICP-5000 Plasma Emission/Atomic Absorption Spectrophotometer

marriage of cousins), then to the 154D and back to the original 154. This time 25 years and 12 embodiments, still no break in the evolution.

The third instrument, the ICP-5000 (Figure 36) is an interesting case. Will the ICP-5000 mutate to found a new dynasty of emission instruments as did its ancestor, the Model 214, in atomic absorption? We are not sure; the picture hasn't evolved yet. But if we check the family tree of atomic absorption instruments shown in Figure 35, there is no doubt where the ICP-5000 came from. Its father is the AA Model 5000 and its grandfather the Model 603; from there, it is traceable through the X03's to the 303, then to the 214, and, through it, across "political boundaries" into the field of infrared. Then, through the building blocks and the Model 13 it finally finds its origin with the Model 12, the tap root of Perkin-Elmer's presence in the instrument business.
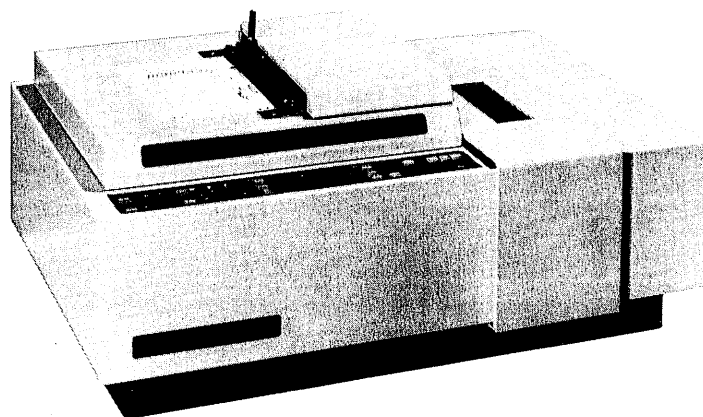
Figure 37. Model 680 IR Spectrophotometer

Conclusions

After investigating the evolution of these three instrument lines, it seems to me that there is a pattern that recurs consistently — at least in Perkin-Elmer's history.

Analytical instrument technology has developed in an evolutionary way. The market is a honeycomb of small pockets with special requirements. None, or at least few, of these pockets are large enough to reward enormous investment of capital or technology to be amortized in that target alone. Yet, the technological demands of each segment are very high. The system, therefore, favors the adaptive organization. Communi-

cations is in the forefront and users and suppliers must know each other very well to be effective.

To the instrument maker, I offer the following advice:

- Changes must be innovative, but gradual.

- Develop strong "breeding" strains and stick with them as long as possible; yet, be at the forefront of the newest technologies. Microprocessors are an example of this.

- Be prepared to lose some bets — it is certain that you will.

- Learn from your experience and know your customer.

- Make the commitment. Be part of the analytical chemistry community. Live in it!

I am sure that Perkin-Elmer's experience is not very different from that of Beckman, Varian, Hewlett-Packard, Technicon, or the scores of fine instrument companies represented here at the 1980 Pittsburgh Conference. So, let me address the key to our success as an industry: where does the technology come from and how does it get put to work?

The technology comes from dedicated professional teams repeatedly putting one brick on top of another.

Its useful employment derives from the extraordinary respect and rapport that has grown up between the instrument builder and the instrument user.

From this I draw the personal conclusion: there could be no more rewarding place to spend one's career than the analytical instrument industry.

PERKIN–ELMER

B. Atomic Absorption

1. Technology Description

Historically, spectroscopy as a science began with the observation of absorption lines in the solar spectrum in the early 19th century. When light from the sun is broken into its component frequencies, certain frequencies are missing, leaving dark lines in a photographic spectrum. These lines correspond to frequencies of light that are absorbed by the solar atmosphere, and can effectively 'fingerprint' the elements in it. The existence of the element helium was first discovered by means of absorption lines in the solar spectrum. This elemental fingerprinting is not limited to sunlight. If light is shone through a volatilized sample, the elements in the sample will absorb certain frequencies of light. The amount of absorption can be measured, which can then be used to determine the amount of an element present in the sample. This forms the basis of atomic absorption, or AA, spectroscopy.

Figure XII-6: Perkin Elmer AAnalyst 200

The actual operation of an AA spectrometer is relatively simple. First, a flame or graphite furnace is used to volatilize the sample. Light from a Hollow Cathode Lamp (HCL) is then passed through the atomized sample. HCLs that emit the spectrum of a specific element are typically used. A photomultiplier tube detects the intensity of the transmitted light. The fraction of light that is absorbed yields the concentration of that element in the sample. One drawback to AA spectroscopy is that, in general, different lamps must be used for each

Figure XII-7: Varian SpectrAA Duo

element. However, some vendors now produce lamps with cathodes that contain multiple elements. These can be used to detect up to ten elements.

As mentioned, there are two primary types of AA spectrometers, which are differentiated by the method in which the sample is volatilized. Flame AA spectrometers, which use an acetylene flame to heat the sample, are used exclusively with solutions, whereas graphite furnace AA spectrometers can be used with liquids, pastes or solids. In graphite furnace AA, the sample is placed in a graphite tube, which is electrically heated. Graphite furnace spectrometers have several advantages over flame, including a smaller sample size, a more repeatable heating process, and detection limits that are as much as a thousand times better for some elements. Graphite furnace AA's are, however, about four times as expensive as flame AA's.

2. Product Segmentation

The overall market for AA instruments is quite stable. The technology is mature and most of the recent improvement in instrumentation have been focused on providing instruments of smaller size at lower cost. In particular, flame spectrometers are now on the market with prices not much

Table XII-2: AA Worldwide Demand by Product Forecast 2001-2006 ($ Millions)

	2001		2002		2006		CGR
	$ Mil	Percent	$ Mil	Percent	$ Mil	Percent	'01-'06
Initial Systems							
Graphite Furnace	*211*	*56%*	*212*	*56%*	*218*	*56%*	*0.7%*
Flame	*97*	*26%*	*97*	*26%*	*95*	*24%*	*-0.4%*
Total Initial Systems	308	82%	309	82%	313	80%	0.3%
Aftermarket	37	10%	38	10%	44	11%	3.5%
Service	31	8%	31	8%	34	9%	1.9%
Total Market	**376**	**100%**	**378**	**100%**	**391**	**100%**	**0.8%**

over $10,000. Although the sales volume remains relatively constant, the total revenue generated is shrinking slightly. The price of graphite furnace AA's has been more stable than for furnace AA's, and the market for them is increasing slightly.

Another reason that the market for AA is stagnant is the increasing competition from other spectroscopic techniques, which are better suited for performing multiple element analysis. Foremost among these techniques is ICP.

The aftermarket for AA, which includes replacement lamps, AA standards and fuel gases, is the market segment with the highest long-term growth prospects. Although initial system sales are sluggish, the large installed base of AA's is contributing to the aftermarket for AA. Hollow Cathode Lamps, in particular, are an important factor in the maintenance costs of AA. Each lamp costs several hundred dollars, and a separate lamp is required for each element.

Figure XII-8: AA Worldwide Demand by Product Type, 2001

Flame 34%

Graphite Furnace 66%
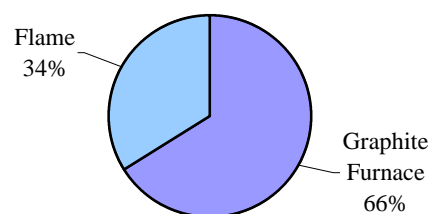
$ 376M

Table XII-3: AA Worldwide Unit Sales

Product Type	Units Shipped	Price Range
Graphite Furnace	3800	$40K to $70K
Flame	5000	$11K to $30K
Total	**8800**	

Although more flame AA spectrometers are sold than graphite furnace AA's, the higher cost of the latter results in them accounting for roughly two-thirds of the AA market for initial systems. Although the decreasing price appears to have had a negative effect on revenue, it has also allowed these instruments to penetrate new markets, particularly in the less industrialized countries of the world.

3. Application Segmentation

Nearly half of the AA market is concentrated into three main industries with similar needs. The environmental market is the most important, accounting for 16% of the total. AA is one of the established methods for detecting levels of various elements, mainly heavy metals, in water and soil samples. Many of the laboratories run by government and utilities have many environmental applications that re-

Figure XII-9: AA Worldwide Demand by Industry, 2001

quire the use of atomic spectroscopy. Wastewater facilities are perhaps the most important of these, as levels of mercury and lead are monitored for the public health reasons. The EPA standards recognize AA as the recommended technique for this sort of analysis. University laboratories are the next largest consumer of AA products. These labs come from a wide variety of disciplines in which elemental analysis is important. Quality control and analysis of alloys is an important function for AA in the metals industry. Food and beverage manufacturers are a growing segment for AA sales, mostly in terms of product safety by examining them for harmful trace elements. To comply with environmental regulations, manufacturing and industrial facilities in many industries maintain onsite testing laboratories that use AA to test waste products and other samples for levels of toxic elements.

Since atomic absorption spectroscopy is so closely related to elemental analysis in many industries, nearly half of these products are used for basic analytical functions. Government, corporate and independent environmental testing labs are the largest contributors to this category. The next largest category, quality control, accounts for roughly a fifth of the market. Basic research and development accounts for a smaller, but significant, fraction of the global market. The remaining functional groups total to 14% of the market.

Figure XII-10: AA Worldwide Demand by Function, 2001
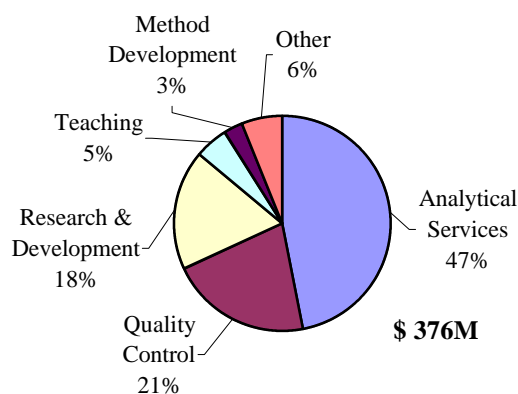
4. Regional Market Demand

Although North America and Europe are responsible for the lion's share of AA sales, they are projected to be the regions with the slowest growth. Indeed, North America, which is primarily a replacement market, is contracting, despite having the strongest aftermarket sales. The greatest opportunities for growth are to be found in the developing countries, where awareness and interest in water safety is increasing the demand. The lower price of introductory instruments is also helping vendors to extend their reach into new regional markets. The formation of a new Japanese Ministry of the Environment in 2001 (with a concomitant increase in environmental spending) should help boost sales there, for at least the short term.

Figure XII-11: AA Worldwide Demand by Region, 2001

Rest-of-World 8%
Latin America 7%
Asia Pacific 9%
Japan 15%
North America 32%
Europe 29%
$ 376M
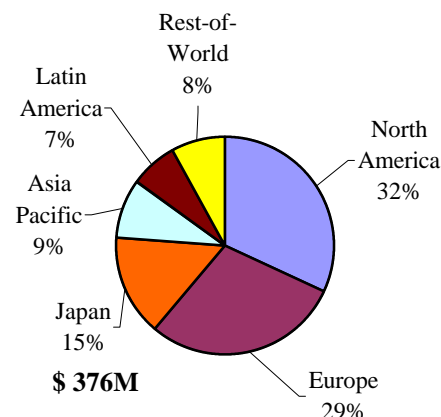
Table XII-4: AA Worldwide Demand by Region Forecast 2001-2006 ($ Millions)

	2001		2002		2006		CGR
	$ Mil	Percent	$ Mil	Percent	$ Mil	Percent	'01-'06
North America	120	32%	120	32%	116	30%	-0.8%
Europe	109	29%	110	29%	111	28%	0.3%
Japan	56	15%	57	15%	60	15%	1.2%
Asia Pacific	34	9%	34	9%	38	10%	2.3%
Latin America	26	7%	26	7%	32	8%	3.8%
Rest-of-World	30	8%	30	8%	35	9%	3.3%
Total	**376**	**100%**	**378**	**100%**	**391**	**100%**	**0.8%**

5. Competitive Situation

In the AA market, there are relatively few active participants with a major market share. Foremost among them is PerkinElmer, with twice the sales of its closest competitor, Varian. Both of these companies retain their positions through refinement of their instruments and a broad array of instrument options. Thermo Elemental is the third largest vendor, with 10% of the market. In addition to instruments, Thermo has a large involvement in the supply of aftermarket items for AA spectrometry. Shimadzu has more limited product offerings, but is strongly positioned for the Japanese and Asian markets. Hitachi has a strong pres-

Figure XII-12: AA Worldwide Vendor Share, 2001

Shimadzu 7%
Hitachi 5%
GBC 4%
Analytik Jena 2%
Photron 1%
Aurora 1%
Buck 1%
Varsal 1%
Lumex 1%
Hamamatsu 1%
Thermo Elemental 10%
Varian 17%
Perkin Elmer 34%
Other 15%
$ 376M
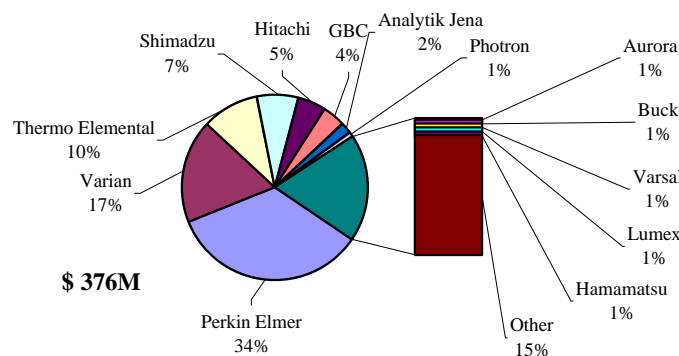
Table XII-5: AA Worldwide Vendor Participation, 2001

Vendor	Graphite Furnace	Flame	HCL; Aftermarket
Analytik Jena	◆	◆	◆
Aurora Instruments	◆	◆	
Buck Scientific	◆	◆	◆
CETAC	◆	◆	
GBC	◆	◆	
Hamamatsu			◆
Hitachi	◆	◆	◆
Lumex		◆	
Perkin Elmer	◆	◆	◆
Photron			◆
Shimadzu	◆	◆	◆
Thermo Elemental	◆	◆	◆
Varian	◆	◆	◆
Varsal		◆	

◆ Major Activity
◆ Moderate Involvement

ence in Europe, where its Scientific Instruments division is based. GBC Scientific, an Australian firm, is still a small vendor, but is increasing its market share. Analytik Jena has also been growing at a rapid pace, and has been particularly successful in Europe. Photron and Hamamatsu are important manufacturers of Hollow Cathode Lamps for AA. In addition to their direct sales, their OEM contracts with vendors are a reliable source of business. The remaining companies in the list of vendors are small manufacturers of instruments.

6. Recent Developments

Table XII-6: AA Worldwide Market – Recent Events 2000-2002

Date	Company	Development
Oct-01	Varian	SpectrAA Duo is introduced.
Oct-01	Thermo Elemental	S Series of instruments released.
Apr-02	Analytik Jena	NovAA 300 released.
Jun-02	Perkin Elmer	AAnalyst 200 introduced.

The maturity of the technology and the stability of the competitive situation means that there are few important business developments. All of the major vendors have released new products or lines over the past two years. Of them, Varian's SpectrAA Duo is notable for being easily convertible from flame to furnace mode. Perkin Elmer's AAnalyst 200 has many technical improvements, including touchscreen control and a compartmentalized electronics module that makes repair and replacement of parts much simpler for consumers.

7. Future Prospects

Historically, Atomic Absorption has been the largest of the product segments in atomic spectroscopy. However, its dominance appears to be on the wane, as it is replaced by more versatile technologies, such as ICP. Consequently, market growth will be relatively flat for the foreseeable future.

B. Atomic Absorbance Spectroscopy (AA)

1. Technology Overview

Atomic Absorption (AA) spectroscopy is the earliest spectroscopic technique to be developed, and still remains one of the most common. The basic technique dates to the 19th century and the discovery of dark lines in the solar spectrum at particular frequencies. These lines are the result of atoms in the solar atmosphere absorbing some of the light passing through them. The particular pattern of frequencies absorbed corresponds to the elements present in the gas.

Figure XII-6: Shimadzu 6300 AA

The actual operation of an AA spectrometer is based on these observations. In order to simplify matters, the sun's light is not used as the source. Rather, lamps that emit the spectrum of a particular element are used. In the most basic design, the sample is volatilized into a gas, and light from a lamp is shone through the gas. A detector, either a photomultiplier tube (PMT) or solid state device, measures the light passed through the sample and calculates the amount of the element present in the sample by how much of the light is absorbed. More sophisticated instruments use multiple lamps and/or lamps that can detect multiple elements to make analysis faster. This dependence on lamps makes AA particularly suited for applications where only a small number of elements are of interest, e.g. the detection of mercury in water.

There are two major types of AA spectrometers, differentiated by the method by which the sample is volatilized. Flame AA spectrometers use an acetylene flame to heat the sample, and are used exclusively with solutions. Graphite furnace AA spectrometers can be used with liquids, pastes or solids. In graphite furnace AA, the sample is placed in a graphite tube, which is electrically heated. A graphite furnace has two major advantages over flame: smaller samples are used, and the gas is more concentrated. This leads to detection limits that are roughly one hundred times lower than for flame. Graphite furnace instruments are, however, significantly more expensive than flame instruments.

Figure XII-7: Analytik Jena NovAA 300

2. Product Segmentation

Table XII-2: AA Demand by Product

	2003		2004		2005		2008		'03-'08
	$ Mil	Percent	$ Mil	Percent	$ Mil	Percent	$ Mil	Percent	CGR
Initial Systems									
Flame	*92*	*24%*	*93*	*24%*	*91*	*24%*	*85*	*21%*	*-1.5%*
Graphite Furnace	*192*	*51%*	*194*	*51%*	*197*	*51%*	*213*	*52%*	*2.2%*
Total Initial Systems	284	75%	287	75%	289	75%	299	73%	1.1%
Aftermarket	48	13%	49	13%	52	13%	58	14%	4.1%
Service	45	12%	45	12%	46	12%	51	12%	2.4%
Total	**376**	**100%**	**381**	**100%**	**387**	**100%**	**408**	**100%**	**1.6%**

AA remains a relatively flat market, although some improvement in revenues should be evident in the coming years. One reason is that higher-end AA systems are becoming better able to compete with ICP spectrometers with regard to performance, while maintaining a lower cost.

Figure XII-8: AA Demand by Product Type

Flame 31%
Graphite Furnace 69%
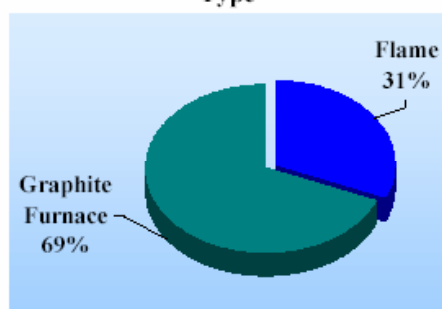
Graphite furnace, which includes all of the high performance instruments, will experience more growth than flame instruments, which are actually declining slightly, although instrument sales are relatively flat, due to lower priced units accounting for a larger share of the market. Another important segment of the market is the aftermarket. Perhaps the greatest contributors to aftermarket sales are Hollow Cathode Lamps (HCL). HCLs are used as the light sources in AA, and require regular replacement at a cost of a few hundred dollars each. Multielement and boosted lamps are also an active portion of the market, with new light sources offering analytical advantages. Standards, burners, furnaces and fuel gases are other components of the aftermarket, which comprises 13% of the total market for AA.

Although many AA spectrometers are designed to work with either flame or graphite furnace, the former configuration is far more common in initial system sales, though some of these are upgraded to

Table XII-3: AA Prices and Unit Volumes

Product Type	Price Range	Units Shipped
Flame	$10K-$30K	4300
Graphite Furnace	$35K-$85K	3300
Total		**7600**

graphite furnace systems later. Average prices for flame systems are slightly decreasing, while those for graphite furnace systems are stable. All together, about 7,600 AA spectrometers were shipped in 2003.

3. Application Segmentation

AA instruments are most commonly found in environmental laboratories, which SDi includes among independent testing laboratories. The independent test category includes not only the environmental labs, which make up the bulk of that segment, but also other independent laboratories that perform all types of analytical services for customers. In total, these labs account for 22% of the demand.

Figure XII-9: AA Demand by Industry

Like the independent test laboratories, utility and government labs are also highly focused on environmental applications. These include analysis of mercury and lead in wastewater and monitoring heavy metal levels in drinking water. EPA standards in the US recognize AA as a standard technique for these applications. Combined, the top three industrial consumers of AA account for roughly one-half of the total market.

Metal manufacturing and processing (including mining) is the source of the next largest industrial demand. Quality control of processed alloys and analysis of raw materials are the primary applications. Many tests of metals focus on a particular element, and inexpensive, dedicated AA instruments are ideal for such measurements.

Because AA is a general, inexpensive tool for the analysis of the atomic composition of materials, it is found in laboratories from many disciplines within academia, which represents about 8% of the total market. The semiconductor and electronics industry is also an important niche application, with applications that center on the purity of ultrapure water and other materials, including raw silicon materials.

Figure XII-10: AA Demand by Function
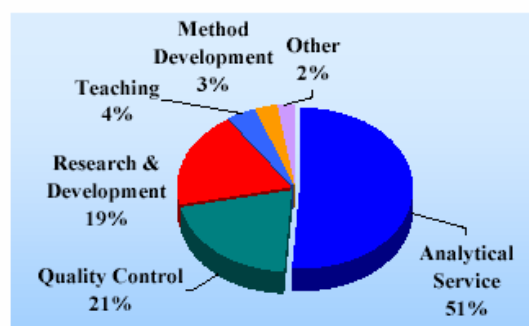
Petrochemical, chemical and pharmaceutical applications are the remaining significant ones. Basic analytical service is the function of the majority of AA spectrometers, while quality control and R&D form the two next most important functions. Other functional categories are not major components of the marketplace.

4. Regional Demand

North America and Europe represent almost equal shares of the market, each accounting for 31% of the total. However, neither region will be a source of growth as initial system sales decline while aftermarket and service hold steady. Nevertheless, these regions account for almost two-thirds of the market and are a source of replacement sales. Eastern Europe is the only growth opportunity. All the emerging markets are experiencing good growth, and this will be where most suppliers will be focusing their attention.

Figure XII-11: AA Demand by Region
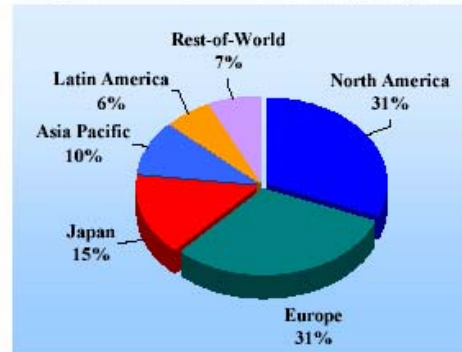
Table XII-4: AA Demand by Region

	2003		2004		2005		2008		'03-'08
	$ Mil	Percent	$ Mil	Percent	$ Mil	Percent	$ Mil	Percent	CGR
North America	116	31%	117	31%	117	30%	110	27%	-1.0%
Europe	118	31%	116	30%	116	30%	120	29%	0.4%
Japan	56	15%	57	15%	58	15%	64	16%	2.5%
Asia Pacific	38	10%	40	11%	43	11%	55	13%	7.8%
Latin America	23	6%	24	6%	25	6%	28	7%	4.7%
Rest-of-World	26	7%	27	7%	28	7%	31	7%	3.0%
Total	**376**	**100%**	**381**	**100%**	**387**	**100%**	**408**	**100%**	**1.6%**

5. Competitive Situation

Two main competitors dominate the AA market, PerkinElmer and Varian. PerkinElmer is by far the larger, with an estimated 41% market share. Varian is roughly half that size, with 19% market share. Not only do these two companies account for most of the new initial system sales, but they both also manufacture their own hollow cathode lamps, and other aftermarket items. Basically, all HCLs manufactured today conform to either the PerkinElmer or Varian lamp designs. Consequently, both manufacturers reap a great deal of benefit from having set the standard.

Figure XII-12: AA Vendor Market Share
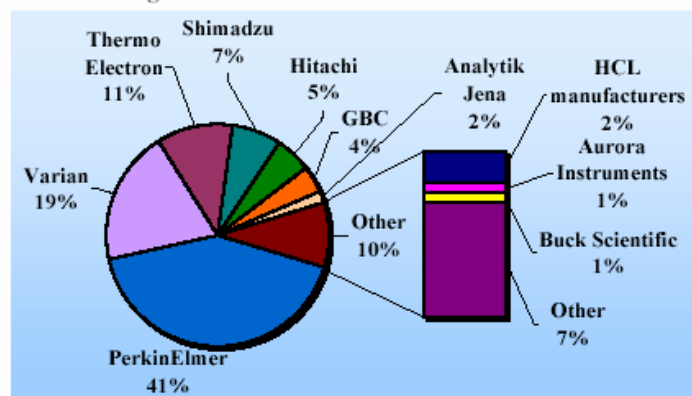
Thermo Electron holds the number three position, and the Thermo Elemental SolAAr series of instruments combine technical improvements with stylish design. Shimadzu released its 6300 AA model last year, and is trying to get better market penetration outside the Japanese market.

In the next tier of vendors are Hitachi, GBC Scientific and Analytik Jena. Analytik Jena had a rather poor year in 2003, despite excellent growth in recent years. The high euro and the lack of German spending are largely to blame.

Manufacturers of HCLs form the next largest contribution to the market. The total market for HCLs is in excess of the amount shown in the vendor share, but much of it is hidden within the sales of instrument manufacturers. However, some companies (e.g. Photron and Cathodeon) only participate in this market through their involvement in the manufacture of lamps. Smaller competitors in the AA market include Aurora Instruments, Buck Scientific, Lumex, SAFAS and Beijing Rayleigh Analytical, which is important in the Chinese market.

Table XII-5: AA Vendor Participation

Vendor	Flame	Graphite Furnace	Aftermarket
Analytik Jena	Minor	Moderate	
Aurora Instruments	Minor		
Beijing Rayleigh	Minor		
Buck Scientific	Minor		
GBC	Moderate	Moderate	
HCL manufacturers			Moderate
Hitachi	Moderate	Minor	
Lumex	Minor		
PerkinElmer	Major	Major	Major
SAFAS	Minor		
Shimadzu	Moderate	Moderate	
Thermo Electron	Major	Major	Moderate
Varian	Major	Major	Major

Key:
- ■ Major Involvement
- ■ Moderate Involvement
- □ Minor Involvement

6. Recent Developments

Table XII-6: AA – Recent Events 2003-2004

Date	Company	Development
Feb-04	Leeman Labs, Teledyne	Teledyne acquired Leeman Labs, which has become part of Teledyne's instrumentation division.
Feb-04	Cathodeon, Heraeus Noblelight	Heraeus Noblelight acquired Cathodeon, a maker of Hollow Cathode Lamps (HCL).
Mar-04	Leeman Labs, Hitachi	Leeman Labs (Teledyne) and Hitachi entered into a distribution deal, with Leeman offering Hitachi's AA spectrometers to complement its own products.

7. Future Prospects

High performance, multi-element graphite furnace instruments will impact the ICP market more and more. Flame AA will remain ubiquitous in the lab, but no significant technical advancement can be expected for these instruments; consequently, sales of flame AA are expected to decline in the coming years, except in the developing countries. Vendors will largely focus on speed of analysis, light sources and automation.

石墨炉原子吸收光谱分析仪器技术的现状与发展

The Current Status and Future of the Technology of GFAAS Instrumentation

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【摘要】 本文从原子化器，多元素同时测定石墨炉原子吸收光谱分析法和石墨炉空间分辨光谱技术的研究等三方面论述了石墨炉原子吸收光谱分析仪器技术的现状与发展，指出石墨炉原子吸收光谱分析法虽面临挑战，但却是进入一个新的发展时期。

【Abstract】 The current status and future of the technology of GFAAS instrumentation is discussed, through three aspects: atomizer, multi-element simultaneous measurement GFAAS and spatial resolution spectroscopy. Our viewpoint is that although the GFAAS analysis is confronted with challenge, it has entered a new stage of development.

关键词： 石墨炉原子吸收　原子化器　多元素同时测定　空间分辨光谱技术

Key Words： Graphite furnace atomic absorption　Atomizer　Multi-element simultaneous measurement　Spatial resolution spectroscopy

自 1970 年美国 PE 公司推出世界上第一台石墨炉原子吸收分光光度计商品仪器以来，石墨炉原子吸收光谱（GFAAS）分析法已经成为一种非常普及的方法。由于这种测定方法的灵敏度高，选择性好，能测定约 60 种元素，与其他超痕量分析方法相比，其仪器结构简单，费用较低。这一系列的特点使石墨炉原子吸收光谱分析法在超痕量分析中发挥了重要作用。此法已成为与质谱法和中子活化分析法并列为超痕量分析的主要方法，广泛应用于冶金、地质、环境和生物试样以及半导体材料的分析中。

虽然三十余年来的研究工作，使石墨炉原子吸收光谱分析技术日趋完善，但 80 年代末以来，整个原子吸收光谱分析法的发展不仅不能保持平台式前进，且有下降趋势。尤其是 ICP-AES 法的兴起，ICP-MS 法的灵敏度已达到了 GFAAS 的水平，其多元素同时测定的功能又是目前 GFAAS 法所望尘莫及的。难道 AAS 法真是到了山穷水尽的地步？作者认为 GFAAS 法的发展确实面临着挑战。但另一方面，以横向加热石墨炉为原子化器的 GFAAS 商品仪器的出现，能同时测定 4-6 个元素 GFAAS 商品仪器的问世，新光源半导体二极管激光器的快速发展，CCD、CID 等新型光电检测技术的引入，标志着石墨炉原子吸收光谱分析法的上升时期正在开始。本文将从三个方面论述。

1 原子化器的发展

1.1 横向加热石墨炉（Transversely heated graphite furnace）

B.L'vov 在 1959 年提出石墨炉原子吸收光谱分析法时，其指导思想一是在恒温条件下原子化，二是样品完全原子化。而在将石墨炉原子化器推向实用化商品化时，他却支持 H.Massmann 的在升温过程中原子化的方案。在 1978 年提出在 Massmann 炉中放置平台的思想是要实现恒温条件原子化。横向加热石墨炉进一步将实现恒温条件原子化提高到了新的水平。纵向加热石墨炉原子化器具有严重的温度梯度和在升温过程中原子化的缺点。而横向加热石墨炉克服了这些缺点。

所谓横向加热石墨炉是指在与石墨管长度相垂直的方向对其加热，即电流流过的方向与石墨管长度方向正交。最为人们熟知的是在 70 年代 Varian 公司生产的 9mm 长碳棒原子化器就是横向加热石墨炉，因其长度太短，无法显露其优越的性能而不被人们认识。80 年代初开始了这一课题的研究，比较出色和成功的是瑞典 Frech 教授和荷兰 de Galan 教授。1990 年 PE 公司推出世界第一台横向加热石墨炉原子吸收分光光度计商品仪器（4100ZL 型），其石墨炉原子化器是在上述实验室成果基础上研究开发出来的。

当今，有两种类型横向加热石墨炉原子吸收光谱仪器商品，纵向磁场中的横向加热石墨炉方式和普通横向加热石墨炉方式，即 PE 公司的 4100ZL 型和 4110ZL 型，AI 公司的 AI1000 型和 AI1100 型，Leeman Labs 公司的 Analyte5 型，Carl Zeiss 公司 5EA 型。图 1、图 2 为四种横向加热石墨炉结构示意图。

从前面理论分析可知，横向加热石墨炉温度梯度大幅度减小及恒温区大幅度扩大。其分析性能要比传统的 Massmann 炉优越，但 1990 年以来的实践表明，可能由于受到一些条件的局限，THGF 尚未完全显露出其应该具有的良好分析性能，这也是目前原子光谱分析工作者的热点研究课题之一。

1.2 非热方式原子化器（Non-thermal typical atomizer）

顾名思义，是不用加热的办法而使样品原子化的一种原子化器。显然，这种原子化器不受温度因素的影响，化学干扰要比石墨炉小得多。研究较多并已商品化的是辉光放电方式，即阴极溅射法。其实早在 1960 年 Walsh 就提出过用空心阴极型溅射进行原子化的方案，由于技术的原因没有成为实际应用的分析手段。辉光放电是一种在低气压下放电现象，它是利用正离子轰击阴极表面，使
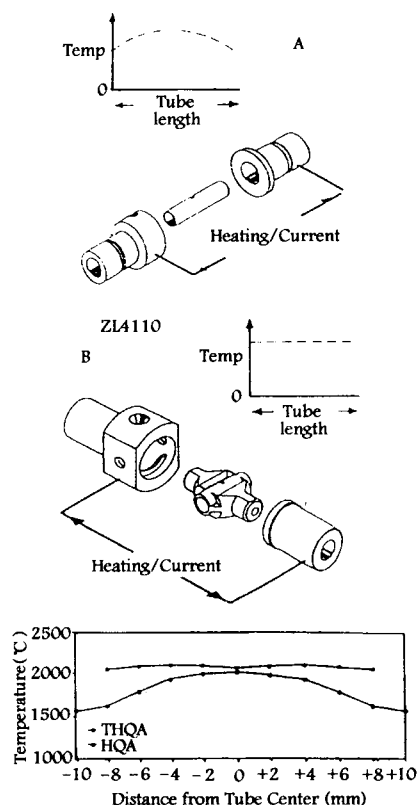
图1 PE公司 Massmann 型炉(A)和 THGF(B)结构图和温度分布曲线图
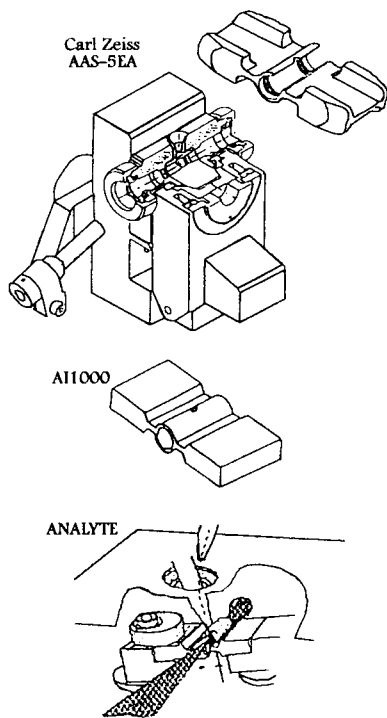
图2 Aurora公司 AI1000型、Carl Zeiss公司和 Leeman Labs 公司的 THGF 结构示意图

样品表面待分析元素成为原子蒸气。所以说辉光放电具有可以从固体表面直接

将分析物转化为原子蒸气的特点,是理想的原子光谱"原子库"和质谱分析的"离子源",也是当前的研究热点。

1987年美国 Analyte 公司推出第一台具有阴极溅射原子化器的原子吸收分光光度计商品仪器,称这种原子化器为原子源(Atomsource)。这种原子化器的特点是专门用于分析固体样品,图3为其原子化器(即阴极溅射原子化器)工作原理图。1997年 Leeman Labs 公司在上海 BCEIA 会议上展出了具有这种原子化器,可快速程序分析30个元素的 A30型 AAS 仪器。这类原子化器有下述特点:①原子化与温度无关,与石墨炉原子化器相比,其记忆效应、高温气相化学反应产生的干扰及难熔炭化物的形成都已基本消除;②原子化时间较长,有利于多元素同时测定;③线性范围宽;④能进行固体样品表面逐层分析。不仅可分析高纯材料中的杂质元素,还能分析基体金属元素的含量。由于是在10毛氩气气氛中,也能分析硫、碳、磷等元素。对于金属样品中的杂质分析将是一个十分有效的原子化器。
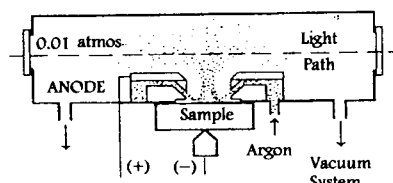
图3 阴极溅射辉光放电原子化器示意图

2 石墨炉多元素同时测定原子吸收光谱分析法

2.1 发展过程简述

自1970年 GFAAS 商品仪器问世以来,分析工作者就开始了多元素同时测定 GFAAS 法的研究探索。至今已解决了一个又一个难点,由锐线光源(HCL)、连续光源(Xe 弧灯等)、半导体激光器等光源,光栅单色器,中阶梯光栅单色器(高分辨系统)傅立叶变换光学系统,以及光电倍增管(PMT)、LPDA、CCD 等光电器件组成了七种多元素同时测定 GFAAS 系统:①多个 HCL 加多个检测系统;②连续光源,为分辨分光系统和多个 PMT 检测系统;③连续光源,程序快速扫描分光系统和单个 PMT 检测系统;④连续光源,高分辨分光系统,以及 LPDA 或其它一维 TV 型光电检测系统;⑤连续光源,傅立叶变换系统和 PDA、CCD 或其它光

电检测系统;⑥多阴极 HCL 和单个 PMT 检测系统;⑦半导体激光器光源,多路光纤和光电器件检测系统。上述⑥、⑦两个系统没有分光系统。

2.2 主要技术难点和进展

在原子吸收光谱法中,单元素逐一分析时所具有的优点,对多元素同时测定却成了技术障碍。

(1)GFAAS 法可为每个待分析元素提供最佳原子化温度,而多元素同时测定时石墨炉所提供的原子化温度只能是各待测元素最佳原子化温度的折衷,显然不能获得最佳的分析结果。在70至90年代的研究工作中,大都选用折衷温度的办法。80年代末期,随着 LPDA 等固体多道光电检测器件和计算机高速数据采集技术在 GFAAS 法中的应用,可以获取精确的波长—温度(或时间)—吸光度之间的三维信号曲线图,为在原子化阶段快速升温过程中准确测量各待分析元素的最佳吸光度值提供了可以实现的机会。作者在这方面做了初步的工作。

(2)光源 至今研究较多的要数连续光源氙灯,其波长覆盖范围宽,由紫外到近红外。主要问题是紫外能量差,而 GFAAS 法大部分的元素分析线集中于此。经过不断的努力,已向短波长推进到了 Co 240.7nm。可调染料激光器系统不仅价格昂贵,其稳频、稳强度性能不够理想,波长覆盖范围有限,难以实现多元素的同时测定。异军突起的半导体二极管激光器体积小,功耗低,立即引起了原子光谱学家的关注。用它可实现多个光源和单个光电器件检测系统由光导纤维组成的袖珍的多元素同时测定仪器,遗憾的是用于 AAS 的工作波长还只在600nm 以上。令人鼓舞的是波长420nm 的蓝光半导体激光器的研究工作已取得了重大突破。

(3)其它 GFAAS 分析中的基本干扰问题,已经有了横向加热石墨炉原子化器、较为通用的基体改进剂 Pd 盐和流动注射使之减轻。

LPDA、CID 或 CCD 光电检测器件的引入,可使多元素 GFAAS 同时测定具有了定性和定量分析的功能。傅立叶光学系统的一个重要优点是光能量大,无光学孔径限制,又可引入激光参考波长进行标定,但工作向紫外区移动时,技术困难较大。

1989年日立公司推出的 Z-9000型为能同时测定四个元素的 GFAAS 仪器,

而 1994 年 PE 公司的 SIMAA6000 型亦为能同时测定六个元素的 GFAAS 仪器,但此仪器的结构设计把多元素同时测定 GFAAS 仪器提高到了一个新的水平,图 4 为其光学系统和固体检测器结构示意图。其分光系统省去了扫描机构,待分析元素的分析线已经定位于固体检测器的不同部位,由计算机控制电子扫描获取信息,一旦合适的光源研究成功,这套系统即可完成多元素 GFAAS 同时测定。
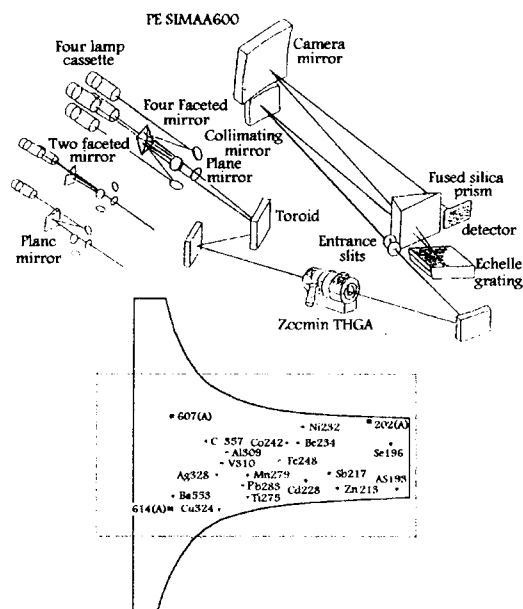
图 4 SIMAA6000 型多元素同时测定 GFAAS
仪器的光路图及固体检测器受光面示意图

此外,目前各大公司推出的 AAS 仪器,如 Analyte 100/700/800(PE 公司),SpectrAA-220FS(Varian 公司),Z-5000(Hitachi 公司),6800(Shimadzu 公司)等都已具有对同一个样品程序地测定 8-10 个元素的功能。这表明 AAS 仪器走向多元素同时测定方式的速度已经加快。半导体激光器光源是最具诱惑力,因为它的研究应用成功标志 AAS 仪器进行一次变革。

3 石墨炉空间分辨光谱技术研究

最近关于 GFAAS 法原理的研究指出,在原子化过程中,在原子化器内待分析元素自由状态原子与辐射光源的特征波长光束之间的相互作用应包括两个方面:一是光源特征谱线与待分析元素原子吸收谱线轮廓之间重叠部分的相互作用;二是原子化器内光源辐射光束强度的空间分布与待分析元素原子蒸气浓度

分布之间的相互作用。第一部分已广为人知,是原子吸收光谱法的原理基础。第二部分乃鲜为人知的问题。俄罗斯学者 Gilmutdnov 在从理论上研究 AAS 法工作曲线的线性的论文中指出,上述第二部分是引起工作曲线在高浓度弯曲的主要原因,而这个问题目前 GFAAS 仪器仍无法解决。

至今 GFAAS 仪器都是用光电倍增管作光电检测元件,利用带有狭缝的单色仪将待分析元素的特征谱线进行选择分离,能对 GFAAS 信号进行时间分辨测量,但不能对石墨炉内光源的辐射光束强度进行空间分辨测量。也不能对石墨炉内样品原子、分子蒸气浓度的空间分布进行测量,获得的测量信号只是石墨炉截面与狭缝相对应的空间部分所包含的样品原子、分子蒸气产生的吸收信号。如果光源的辐射光强度不变,待分析元素的原子总数相同而空间分布不同,所获得的吸光度值应该是不同的。且这种差异随着浓度的增加而增大,在石墨炉中吸收信号的空间分辨是 GFAAS 仪器无法完成的。

在石墨炉内光源辐射光束光强度和原子、分子浓度的空间分布测量已有许多报导,比较成功的方法是 Gilumtdinov 提出的暗影光谱照相(Shadow Spectral Filming)技术,它是通过测量石墨炉内横截面上,光源辐射光束强度经不同程度衰减后的空间分布信号,反映待分析原子或分子的分布状态。此法又为 Chakrabarti 进一步发展和改进用 CCD 检测系统代替其中的电影摄影机,并用此法研究了 GFAAS 法的原子化机理。如通过原子化过程中,时间和空间分辨原子或分子光谱信息研究指出,Al 原子是由其先兆产物 Al_2O_3 和 Al_4C_3 生成的。

可以预计通过对在原子化过程中石墨炉内,空间时间分辨信号的测量及瞬变过程图象的观察和研究,必将有力促进 GFAAS 法的深入发展。如果说在 50 年代吸光度值是浓度的函数 $A = f(x)$。GFAAS 产生的 70 年代,变数又增加了一个,即时间 t,$A = f(c, t)$,而在今天,变数还要增加空间 x,即 $A = f(c, t, x)$。但是要把 $A = f(c, t, x)$ 推向应用尚有较多的技术难题需要研究解决。

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Application of Atomic Absorption Spectrometry to Environmental, Medicine and Foodstuff Analysis

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Abstract: The application of atomic absorption spectrometry to the analysis of environment, medicine and foodstuff in China is reviewed.

Key words: Atomic absorption spectrometry; Environmental monitoring; Foodstuff analysis; Medicine analysis; Clinic diagnosis

1

1955   ,   ,   ,

。   A. Walsh   Б. В. Лレвов   ,

1991   1997   27   30   (CSI)

CSI 。1961   Perkin-Elmer

,1970   ,

。   ,   45   30

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,   、   ,

。《   》   2000

,   30   。   30

、   。

2

,   ,

。   、

。   ，

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2. 1

。   [1]   FIA- FAAS

，   ，   。   [2]

Cu、Cd、Pb Zn。   [3] SO_4^{2-} $BaCrO_4$ CrO_4^{2-}

，   。   [4]   ，

Zn、Cu、Pb、Cd、Fe、Ni、Mn   ，   200，   ，

，   ，   50 。   [5]   ，

，FAAS   。

，   。   [6]   N205   、

P204   、   ， pH = 9   ，   ，

FAAS   。   250。   [7]   3 000 r/min   ，   P204   P507+

+   ，   (W/O)   ，   ，

，   180。   [8]   (2—   )   (P204)   ，

，   ，   ，   ，

100，   ，   。

。   [9]   ，

，   40 ，   0. 002 μg/L。   [10]

，8—   —5—   ，   ，

23，FAAS   0. 2 ng/L。   [11]

，   60~ 100   732   90 min，

2 mol/L   ，FAAS   ，   0. 5 μg/L，   12 ，   30   /h。

[12]   ，   DDTC

，   9 μl C18   ，   64，   80 μl   ，

，   4. 5 ng/L，   。   [13]

DDTC- Zn   ，   ，   ，   M IBK

FAAS   ，   40 s   ，   2. 7 μg/L，   、

。

，   。   [14]

，FAAS   ，   35 ，

。   [15,16]   FAAS   ，

40，   81 。   [17]

(Al₂O₃   )，FAAS   ，   192   ，

7 463 。

，   。   [18— 20]

，   。

Cd、Pb、Cu、Co、Ni、V、Se、As、Mn、Cr

, (1) ; (2) ,

Cl⁻ ; (3) ; (4) H₂、CO、C

, 。 Б. М. Седых

, , , [21-23]。 [24] STPF

Cu、Pb、Cd , 、 、

、 。 [25] D— β—1,4,

, —NH₂ , pH=

8 Cd²⁺,1 mol/L ,FAAS Cd²⁺。

[26] AAS 。

,

。 , — ,

, 。 [27]

— — — 4 , As

(V)0.51 ng,As(Ⅲ)0.43 ng,MMA 0.38 ng DMA 0.67 ng。

, 、 As(V) , As(Ⅲ) , 。

[28] , 4 ,GFAAS

, As(V)0.89 μg/L,As(Ⅲ)0.94 μg/L,MMA 0.94 μg/L DMA 0.26

μg/L, 0.90 μg/L。 [29]

, — Cr(Ⅵ) Cr(Ⅲ)。

[30] (DPCI) Cr(Ⅵ) ,

, Cr(Ⅵ), 0.6% K₂S₂O₈ Cr(Ⅲ) Cr(Ⅵ), ,

Cr(Ⅲ) Cr(Ⅵ)。

2.2

[31,32] ,

, 。 ,

, 0.2 ng/m³。

[33] [34-37] ,

, (CH₃)₄Pb、(C₂H₅)₄Pb、(CH₃)₂(C₂H₅)₂Pb、(CH₃)₃(C₂H₅)Pb、

(C₂H₅)₃(CH₃)Pb 5 , , 30 pg。 [38,39]

,GFAAS , 、

, 21.5 pg 1.86 pg。

2.3

[40] FIA—AAS Cu、Zn、Fe、Mn、K、Na、Ca、Mg,

514 /h,RSD 1%;

, Hg⁰ 100

, 0.06 μg/L, 200 /h[41]。 [42] GC-GFAAS

、 、 , 0.14 ng 0.28 ng。

[43]   , PdCl₂   ,   ,   1.5× 10⁻¹³ g。

[44]   。

[45- 47]   ,

,   ,   。   [48]

Cu、Ni、Cr。   [49, 50]

、   、   ,   ,   、

。   ,

24   。   [51]   Ir、Te   ,   Ag,

0. 051 μg/g。   [52]   C

,   。

[53]   。

[54]   HGAAS- FIA   ,   4. 0× 10⁻¹¹ g。

[55]   ,

。   [56]   ,

,   。   [57]   [58]

,   4   As(V)、As(Ⅲ)、DMA   MMA。

3

、   、

,   ,

。   ,   。

3. 1

,   [59]、Mg、Cu、

Fe、Mn、Ca、Zn、Se[60, 61]、Hg[62]、Zn、Cu、Fe、Ca、Mg、Mn[63]、Ni[64]、Co[65]、   [66]   。   [67]、

[68]   ,   21. 5 pg   11. 69 pg。

[69]   (TBABr)   ,   TBA+   —

R   ,   ,

。   ,

。   [70]   。   2. 17

× 10⁻⁴ μg/L,   7. 7 。   [71]   —

,   、

。

[72]   316   、、   ,   ,

、、   ,   。

,   。   [73]   GFAAS

Cu、Zn、Fe、Mn、Ca   Mg   Cu/Zn   ,

,   ,   0. 01< α< 0. 05   ,   、、

。

3. 2

，   ，

[74]、   [75]、   [76- 78]、   [79] [80, 81]、 、 、 [82] 。   ，

[83- 85]   ，

、 、 、 、   ，

[86]   ，   ，   ，

，   Cd   Pb,   95% ~ 104%。   [87]

NH₄NO₃   (NH₄)₂HPO₄   , 5 000   ，

8. 3× 10⁻¹¹ g。   [88]   0. 2% T riton   4   ,

，   1 000 ℃ ,   。

[89]   ，   1 400 ℃ ,   ，

28 pg。

[90]   、   ，   9. 1× 10⁻⁵ m g• L⁻¹/1% ,

10 g/L   ，   5 。   、 [91] ，

[92] 。   [93]   Cu   Zn,

3   2 。   [94]   GFAAS   7   ，

2. 0× 10⁻¹¹ g,   α2   (0. 93± 0. 27) μg

(0. 22± 0. 06) μg。   [95]   —   —   ，

，   ，   ，   。

[96]   116   ，

(18. 88± 3. 30) μm ol/L。   [97]

。   30   ，   0. 769~ 1. 247 m g/L,

(81. 95± 9. 55)%。   ，   ，

，   。   [98]

、   ，   ，

，   。

[99]   A PDC   。   [100]

，   、   、 ，

。

[101]   ，   P t-   C   ，

，   ，   2. 23 μg/L。

3. 3

[102]   GFAAS   ，

，   ，   98% ~ 104%。   [103]   ，

。   0. 15 m ol/L   50 m m ol/L T ris- H Cl   (pH = 7. 4)

3 ,   。 FAAS   34   30

。   ，   。 [104]

70   Ni、Zn、Cu、Fe、Cr、Mn、Cd   Mg,
            。   ,
          。   。   FAAS   Zn、Cu、Fe   Mg,   GFAAS
    Mn、Ni、Cr   Cd。   [105]   BaF₂   ,   GFAAS   ,
            1 800 ℃,   ,   ,   94. 7% ~
104%。

          [106]   ,   ,
    1 200 ℃   1 600 ℃,   K、Na、Ca、Mg   ,
          。
        [107]   ,   ,   1, 2—   ,
FAAS   Cu、Zn、Cd   Fe。   [108]   Al₂O₃
            ,   B₁₂,   8 。   [109]
    Nafion   (SOD)   Cu²⁺   Zn²⁺,   GFAAS
            ,   2. 2 μg/L   0. 2 μg/L。   SOD
        1∶ 1,   SOD   Cu²⁺   Zn²⁺   2. 02× 10⁻⁷   2. 02×
10⁻⁷。

3. 4
          [110]   ,   、   、   、
            ,   ,   BIBK   ,   。
[111]   Ι⁻   -   (Ι)   ,   MIBK   ,   。
                              。   [112]   Triton X- 100
            ,   ,   Triton X- 100。   [113]
[Co(SCN)₄]²⁻   2∶ 1   ,   pH = 2. 0   ,
        ,   。   [114]   N, N   ,
                                      ,   FAAS
    ,   。   [115]   +   ,
800 ℃   1 200 ℃,   ,   0. 3 μg/L。
          ,   900 ℃   ,
        1. 5   ,   900 ℃   ,   Sn、SnCl₂   SnO₂
            ,   Pd- Sn   。

4
4. 1
                                          [116],   [117],   [118]   [119],   、
            ,   4   [120]。   [121]   BO₃⁻   BF₄⁻   IO₃⁻   Ι⁻,
1, 10—   ,   ,   ,
        0. 016 mg· L⁻¹/1%   0. 028 mg· L⁻¹/1%。   [122]
          -                            、   ,   0. 4 pg/g。

[123,124]   HSO$_4^-$, Ba^{2+} HSO$_4^-$,
                                                                                                              [125]
(CH$_3$)$_2$Se   (CH$_3$)$_2$Se$_2$,   0.3 ng   0.04 ng。
    [126]   [127]   ,   ,
       、   、   、   ,   ,   、
    、   [128]   ,   H$^+$ 。
95%   ,   [129]   [130]
                                      、   ,   ,
       , CN$^-$ CuS   Cu(CN)$_4^{3-}$,   ,
    。

4. 2
                   [131]   。   —   —   (1+ 0.05+ 4)
              ,   ,GFAAS   、   [132]。
                         ,   ,   、   、   [133]   [134]
                    ,   ,   25 pg, $RSD < 7\%$,
                   , FAAS   、 、 ,   GBW－080193
    , RSD 0.32% ~ 0.85%[135]。
          [136]   ,   ,
                        ,   91% ~ 104%。   [137]
       ,   。

4. 3
                                                                         [138]
                  ,   As、Pb、Cu。   [139,140]
Pd(NO$_3$)$_2$－Triton X- 100   ,   40 ℃   1 200 ℃ ,
                              [141]
    ,   ,   0.1 mg。   [142,143]
               ,   ,   ,
    ,   、   、   、   。
          [144]   -   4
       。   [145]   Pd/Ca
    ,   ,   8.2 ng。   [146,147]   —
                        ,   ,   Cu-
          ,   ,   。
       ,   。
          [148]   FAAS   、   Pb、Cu   Cd
    ,   FAAS   110、39、 150 。   [149]   ,   、
       、   ,   96.3% ~ 102%。   [150]
    , FAAS   、   、   、   。

[151]   、   ,

8 pg/1%   9 ng/1%。   [152]   ,   2. 5× 10⁻¹¹

g。

:

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1993, 9(6): 14.

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1988, 8(6): 39.

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1369.

[11]   ,   ,   .   -   [J].   ,
1999, 13(3): 135.

[12]   .   [J].   , 1997, 13(1): 34.

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          , 1997, 16(1): 22.

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(6): 103.

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8(4/5): 26.

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     , 1995, 15(3): 91.

[24]   ,   .   -   Cu、Pb、Cd   [J].   ,
1991, 7(6): 24.

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361.

[147]   ,   ,   .   (III)   [J].   ,
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