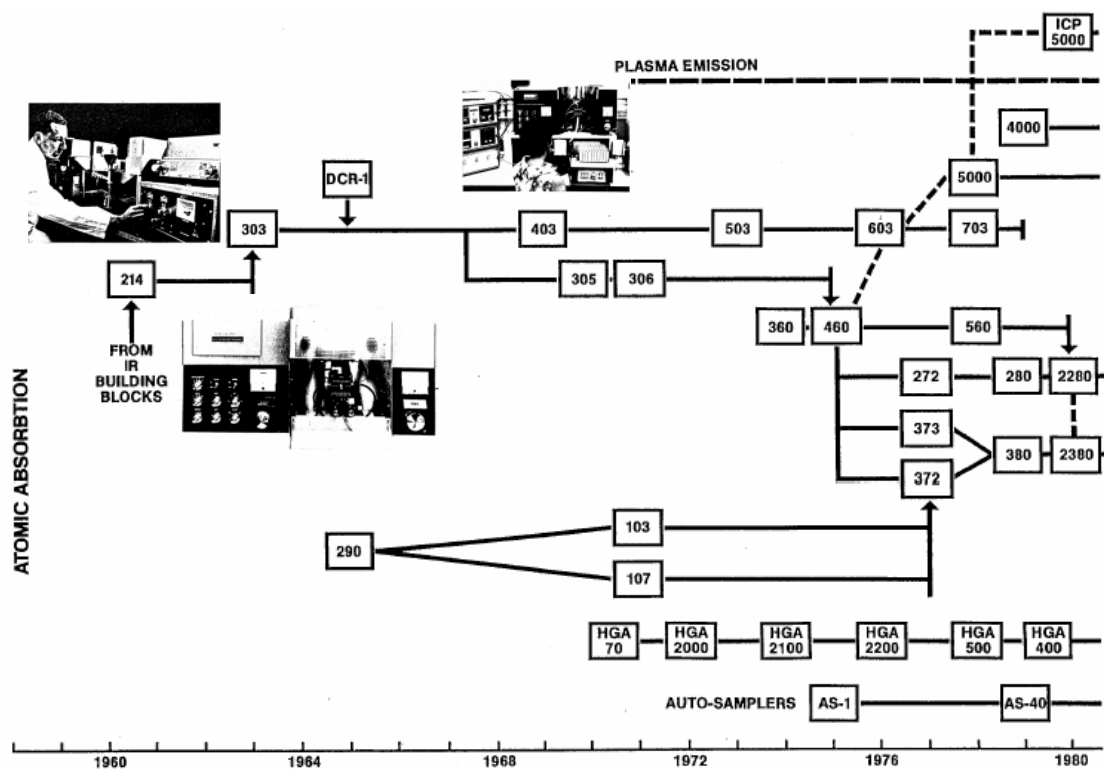


## Atomic Absorption



## 美国 PerkinElmer 公司 原子吸收 45 周年纪念



AAAnalyst  
200



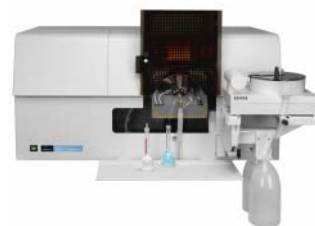
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AAAnalyst  
400+HGA 900



AAAnalyst  
600



AAAnalyst  
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AAAnalyst  
200



AAAnalyst  
400



AAAnalyst  
400+HGA 900



AAAnalyst  
600



AAAnalyst  
700/800

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# Evolution of Analytical Instrumentation

## The Perkin-Elmer Story

**Horace G. McDonell**

**President**

**The Perkin-Elmer Corporation**

Presented at the Symposium "Analytical Instrumentation — Evolution in the Last 40 Years", during the 31st Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 10-14, 1980.

Pittsburgh Conference Paper No. 379



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.*

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## 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.

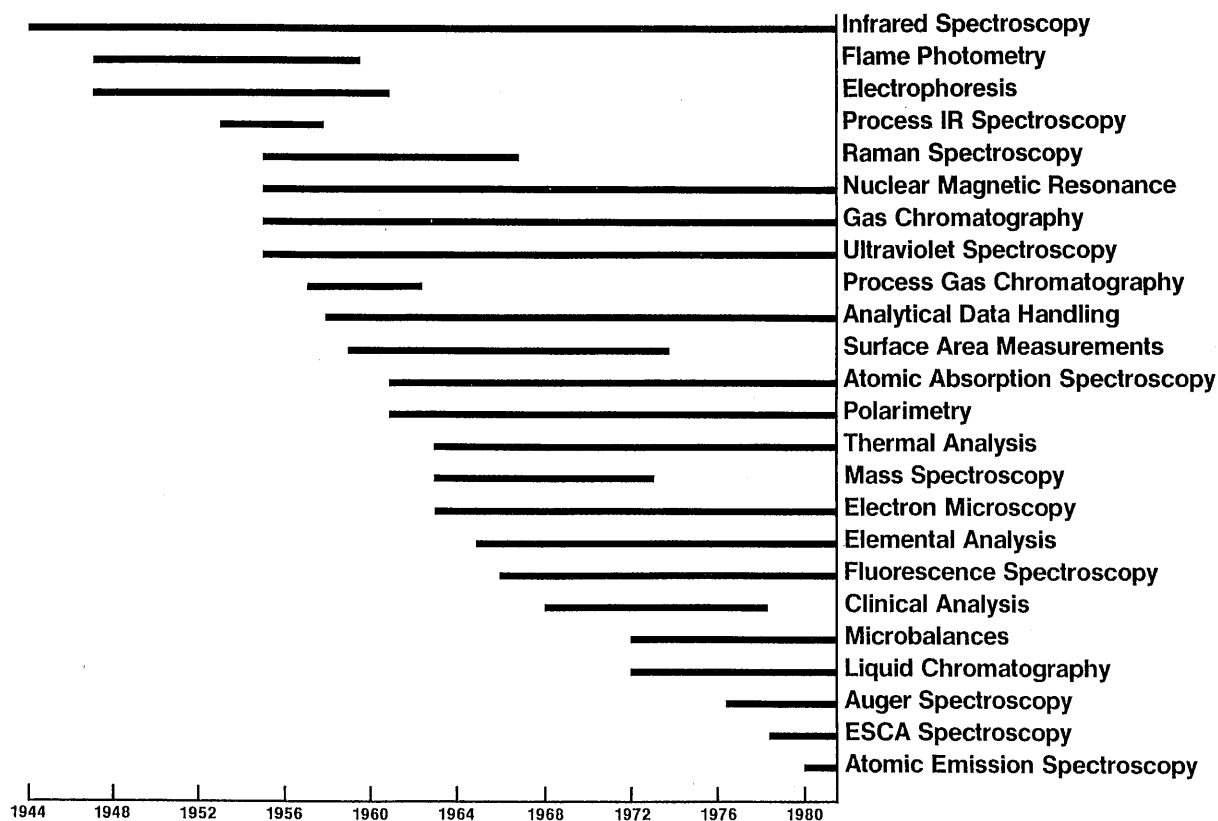
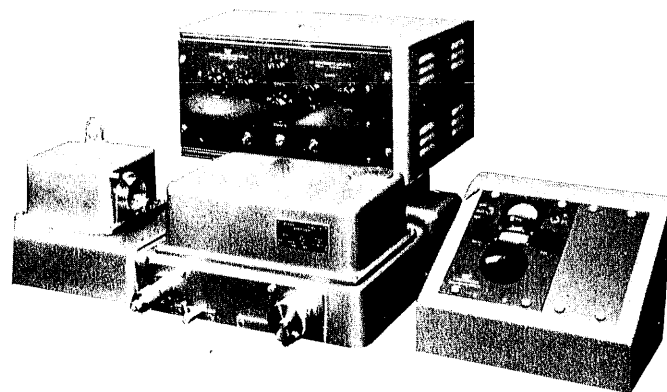
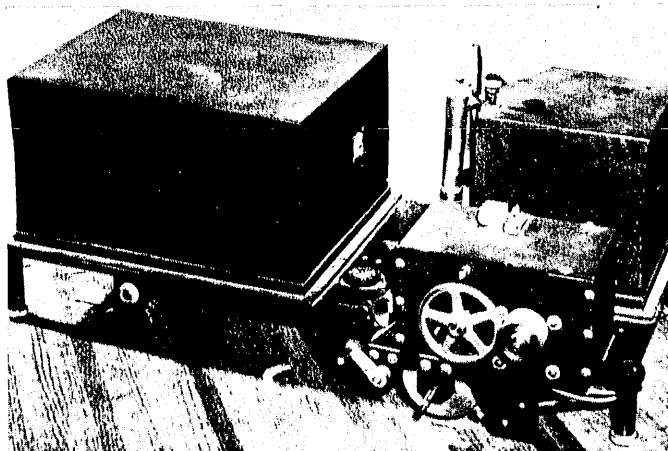
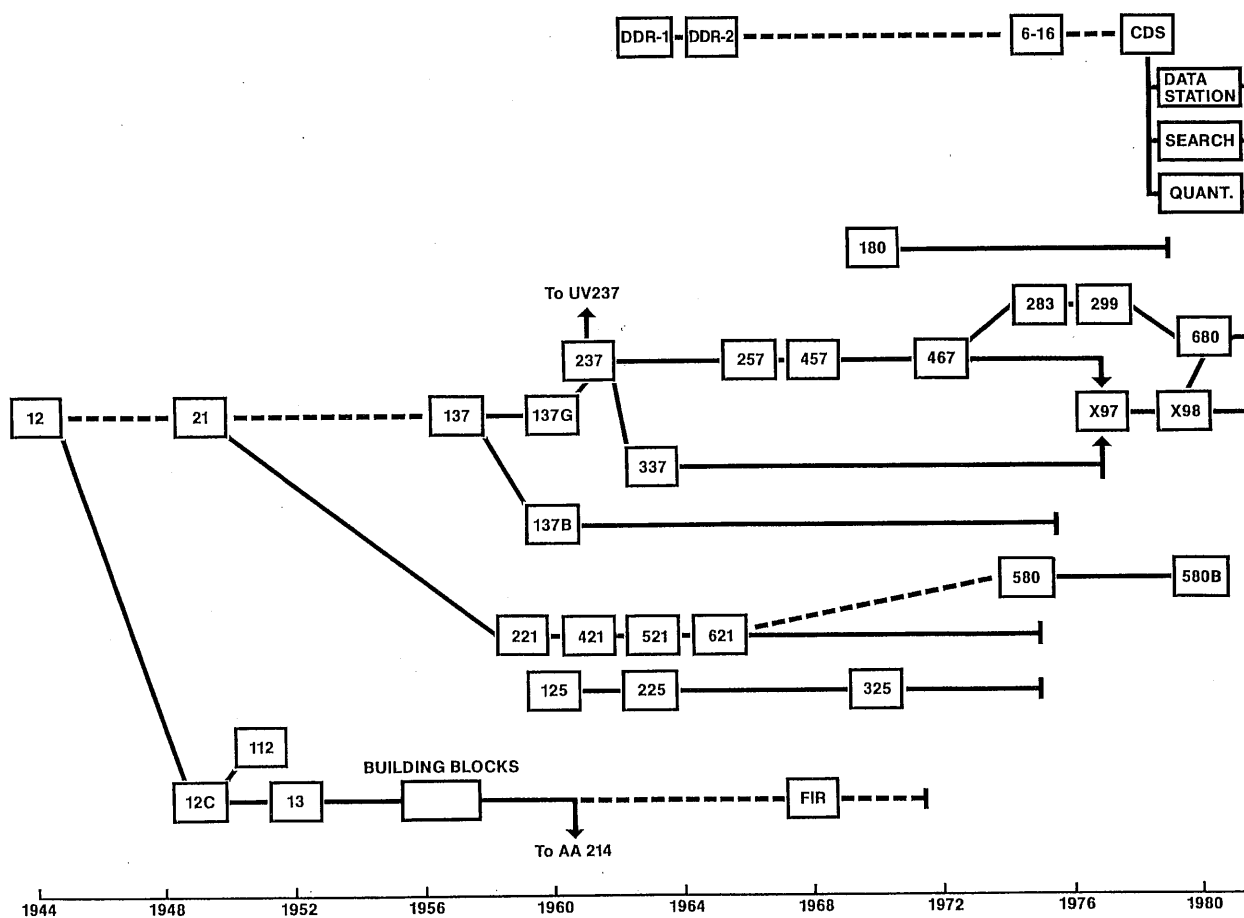


Figure 1. History of analytical instrument techniques at Perkin-Elmer



**Figure 2.** The prototype (left) and the commercialized version (right) of the Model 12 IR Spectrophotometer.



**Figure 3.** IR family tree at Perkin-Elmer



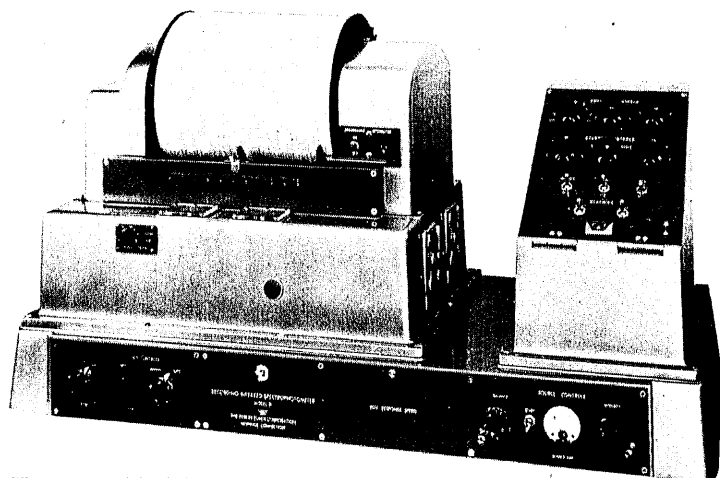


Figure 4. Model 21

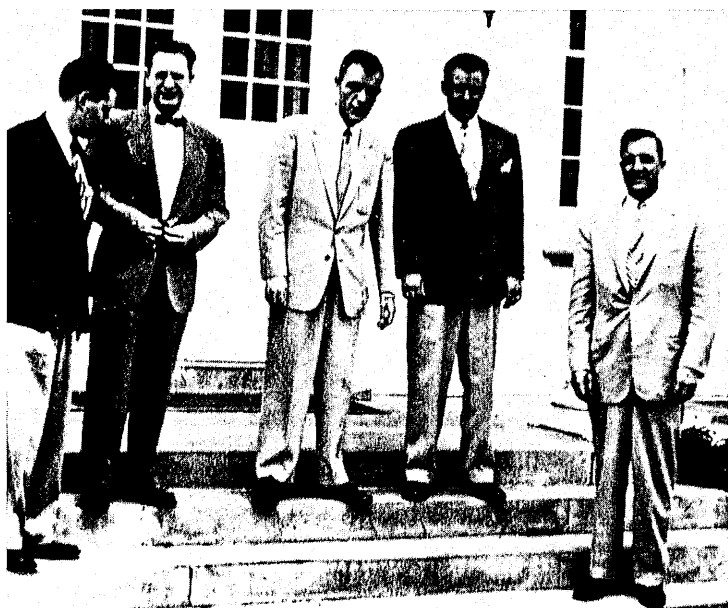


Figure 5. Leading people in the early 1950's. Right to left: Dr. V.Z. Williams, H.H. Hausdorff, S. Lindsley, Dr. A. Savitzky and W. Hargrave.



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

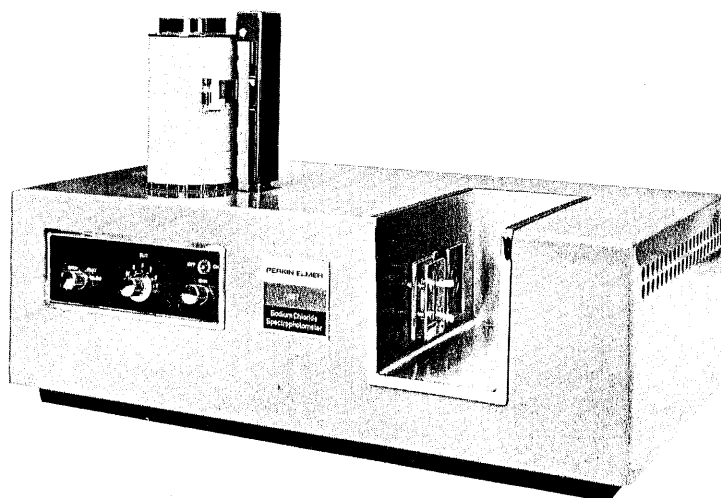


Figure 8. Model 137 IR Spectrophotometer



Figure 9. 1957 Pittsburgh booth

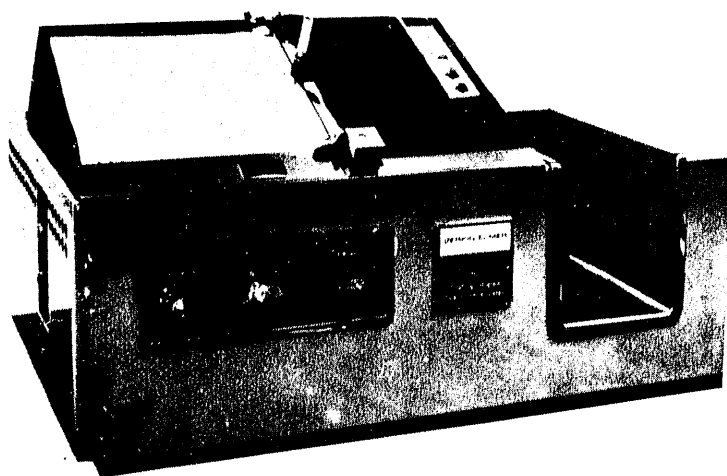


Figure 10. Model 257 IR Spectrophotometer

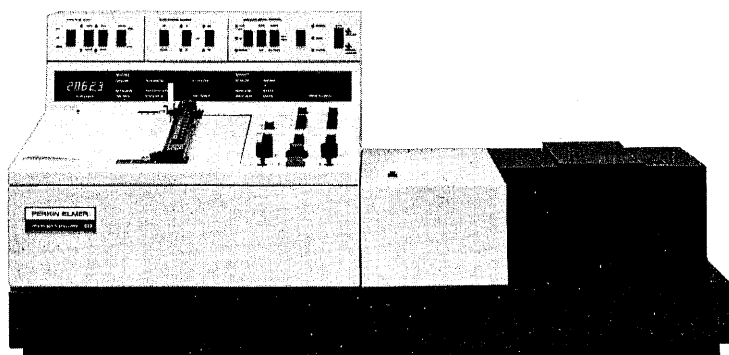


Figure 11. Model 283 IR Spectrophotometer



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.





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

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.

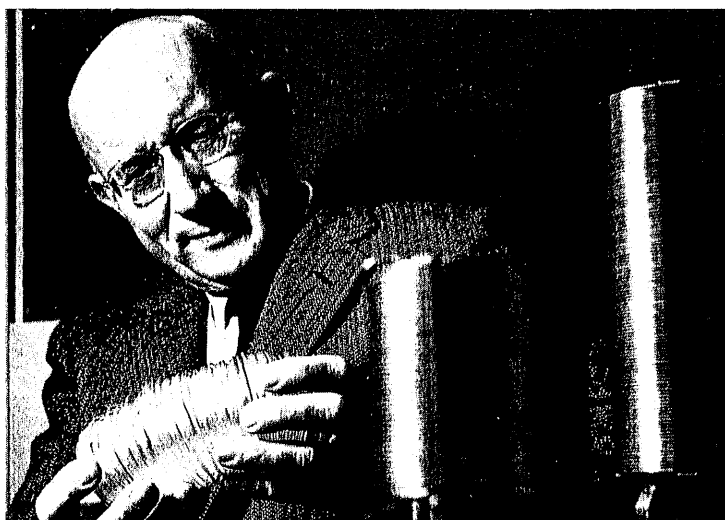


Figure 18. M.J.E. Golay

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

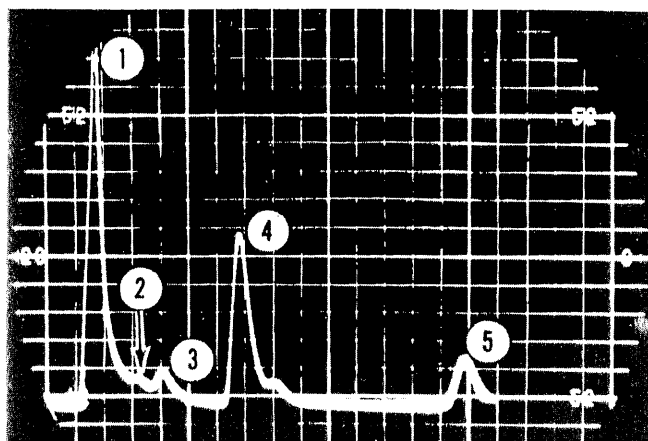


Figure 19. One of Golay's first chromatograms

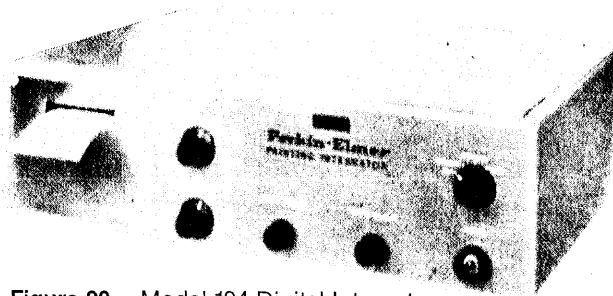


Figure 20. Model 194 Digital Integrator

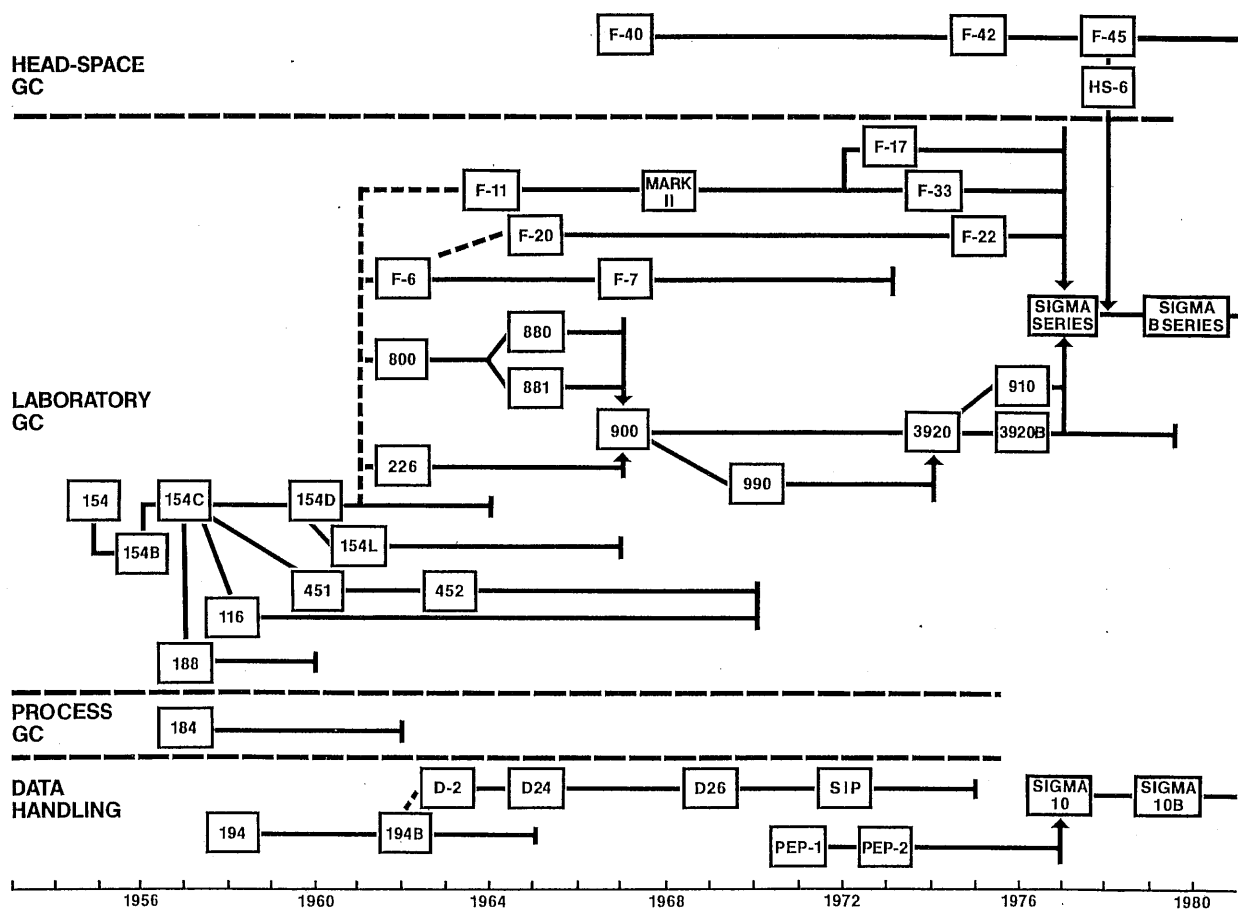


Figure 21. GC family tree at Perkin-Elmer



Figure 22. Model 226 Gas Chromatograph

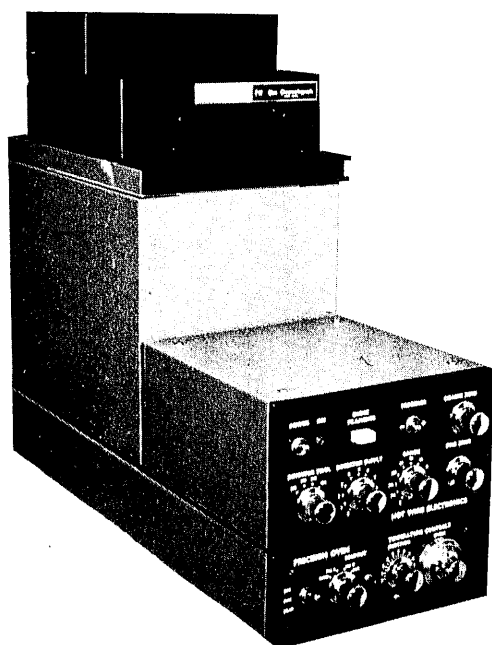


Figure 23. Model F-11 Gas Chromatograph

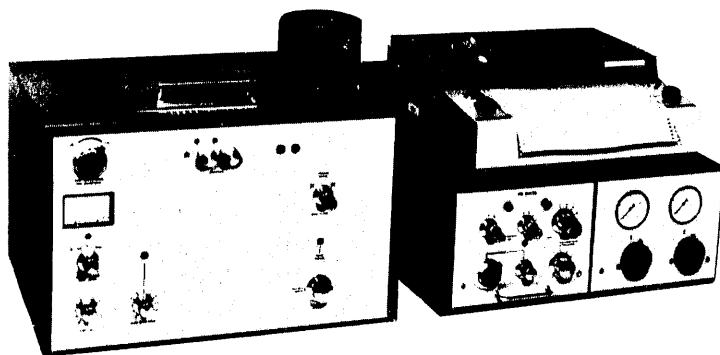


Figure 24. Model F-20 Gas Chromatograph

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

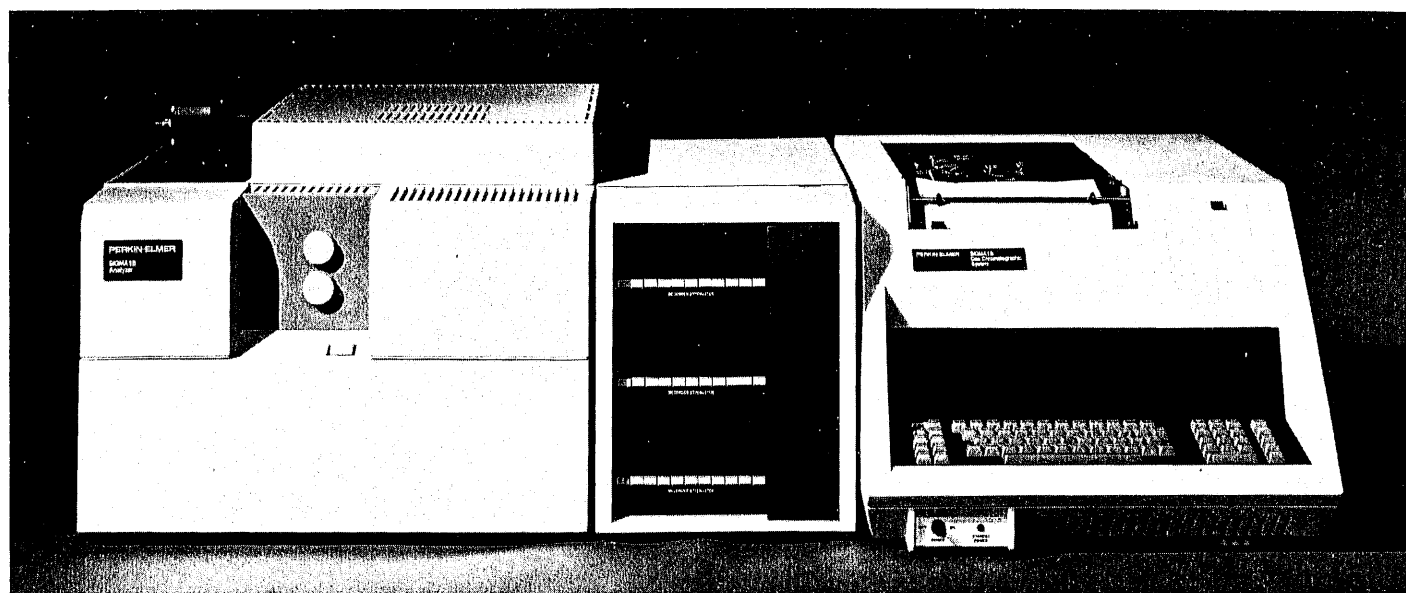


Figure 27. Model Sigma IB Gas Chromatograph





Figure 28. Model 214 Atomic Absorption Spectrophotometer

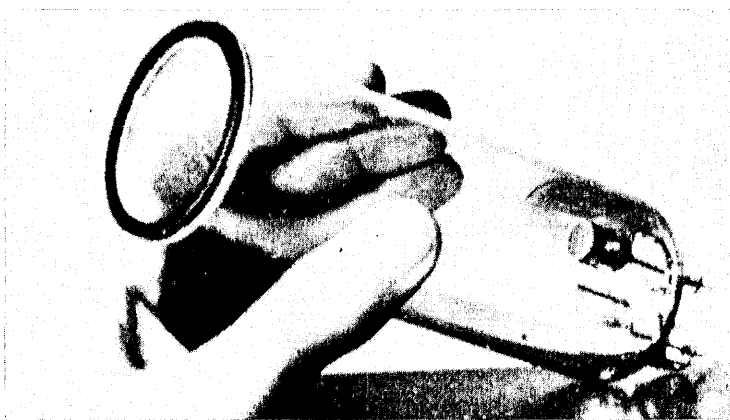


Figure 29. Hollow-cathode lamp

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

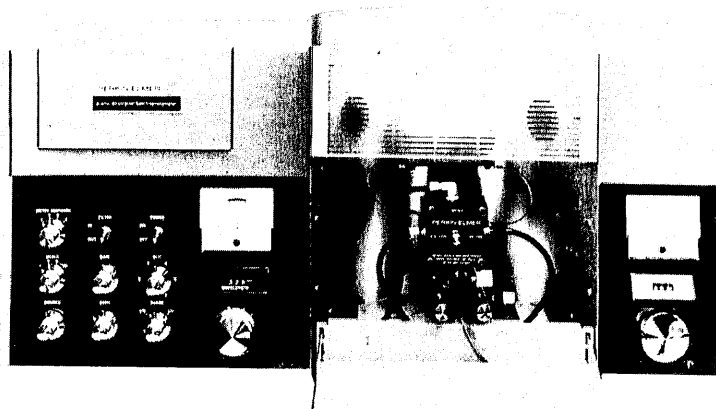


Figure 31. Model 303 Atomic Absorption Spectrophotometer

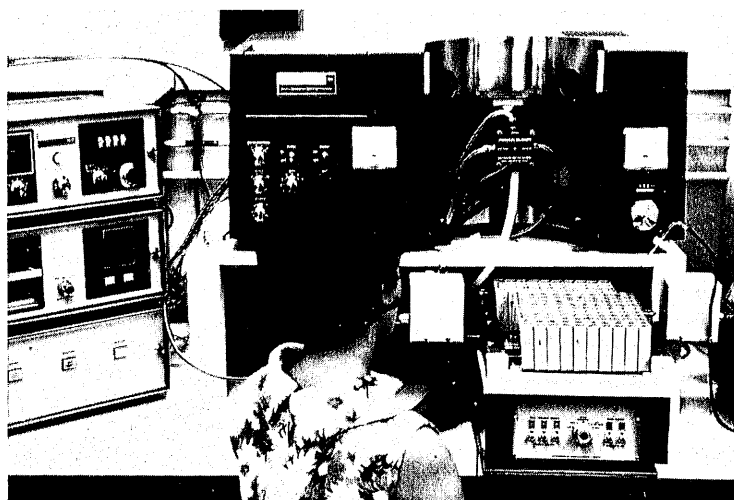


Figure 32. Model DCR-1 with the Model 303 AA Spectrophotometer

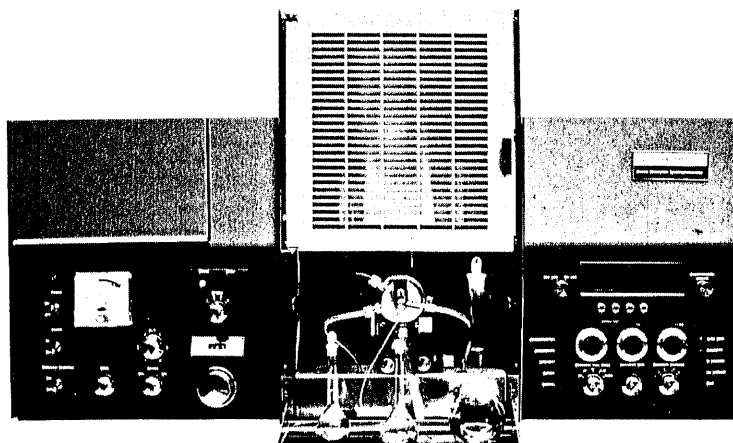


Figure 33. Model 403 Atomic Absorption Spectrophotometer

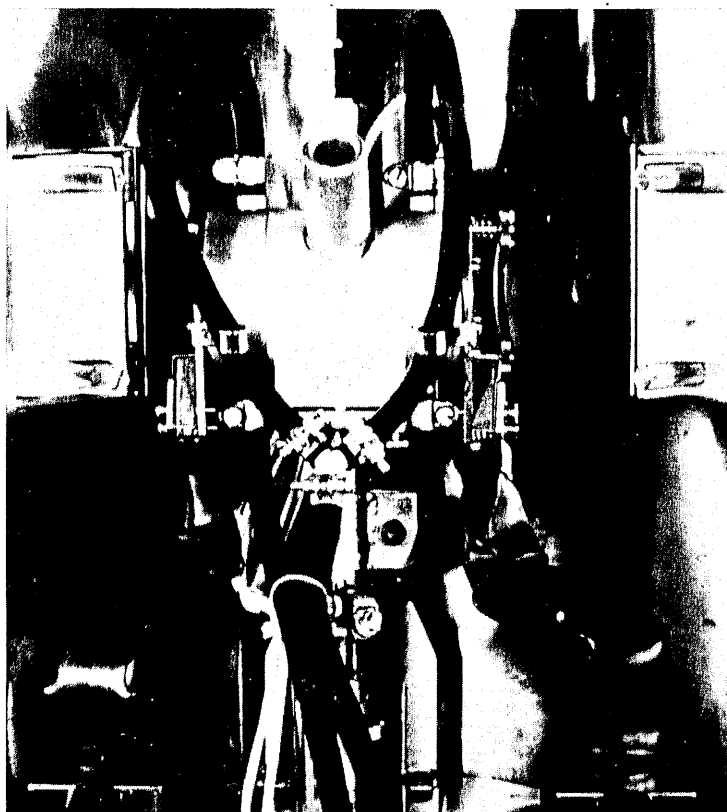


Figure 34. HGA furnace

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

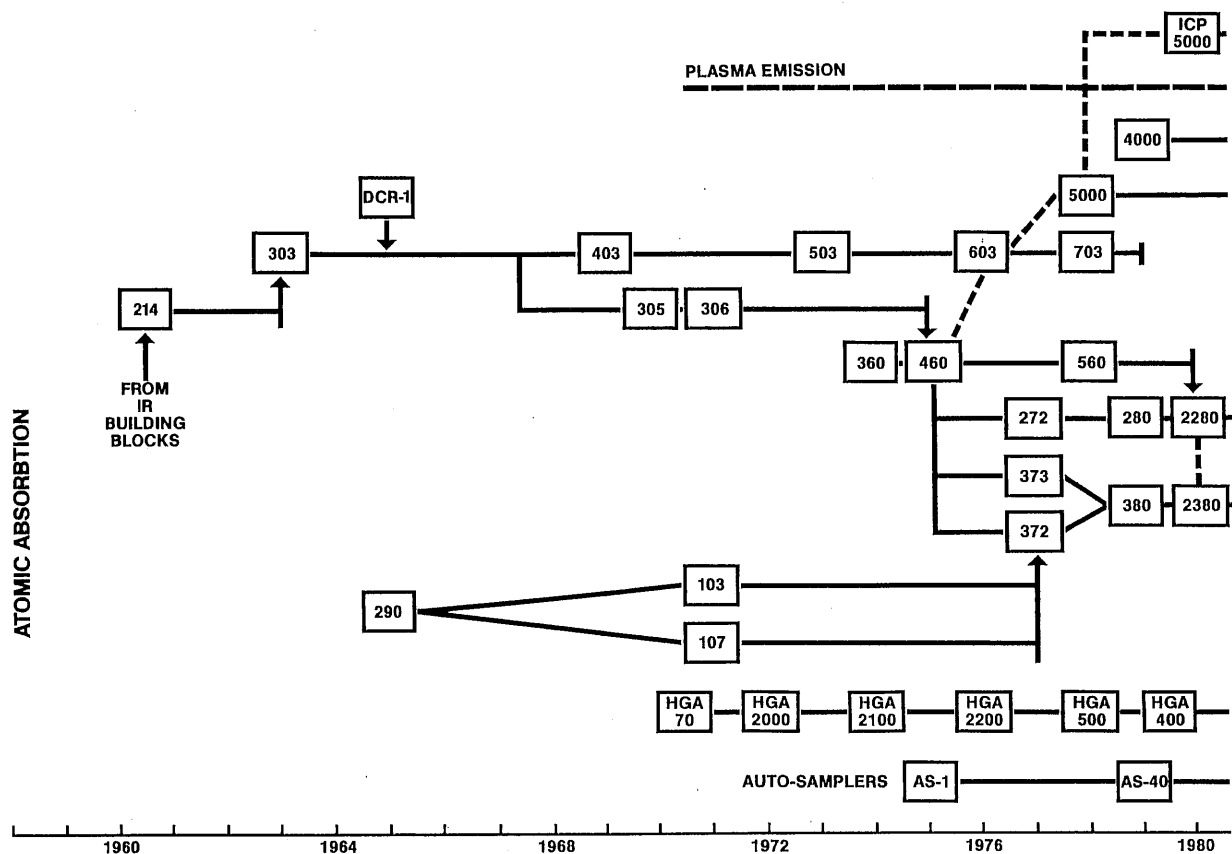
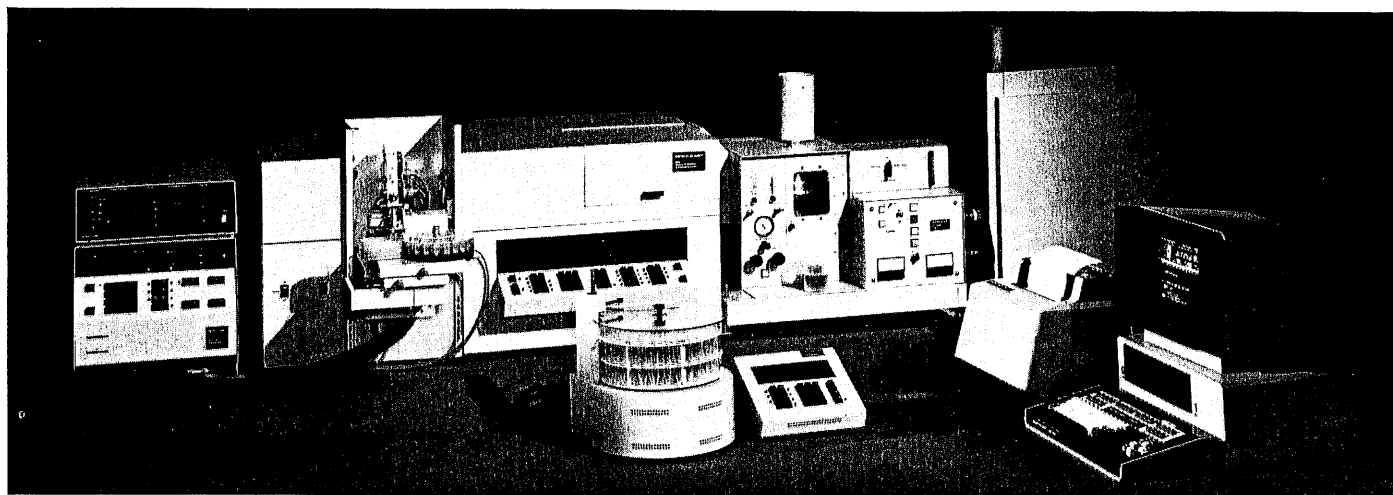


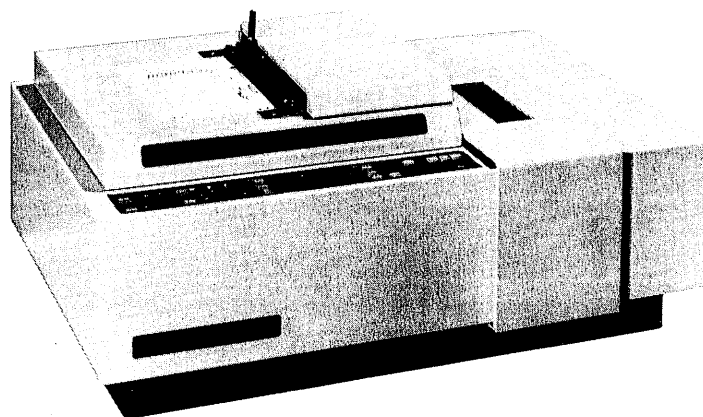
Figure 35. Atomic spectroscopy family tree at Perkin-Elmer



**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-

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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. Micro-processors 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**

**Perkin-Elmer Corp., Analytical Instruments**, Main Ave. (MS-12), Norwalk, CT 06856 U.S.A. Tel: (203) 762-1000

**Bodenseewerk Perkin-Elmer & Co., GmbH**, Postfach 1120, 7770 Ueberlingen, Federal Republic of Germany, Tel: (07551) 811

**Perkin-Elmer Ltd.**, Post Office Lane, Beaconsfield, Bucks HP9 1QA, England Tel: Beaconsfield 6161

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## 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 19<sup>th</sup> 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.

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-6: Perkin Elmer AAnalyst 200**



**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)**

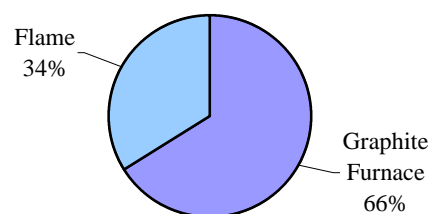
	2001		2002		2006		CGR '01-'06
	\$ Mil	Percent	\$ Mil	Percent	\$ Mil	Percent	
Initial Systems							
<i>Graphite Furnace</i>	211	56%	212	56%	218	56%	0.7%
<i>Flame</i>	97	26%	97	26%	95	24%	-0.4%
Total Initial Systems	308	82%	309	82%	313	80%	0.3%
Aftermarket	37	10%	38	10%	44	11%	3.5%
Service	31	8%	31	8%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

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**



\$ 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
<b>Total</b>	<b>8800</b>	

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

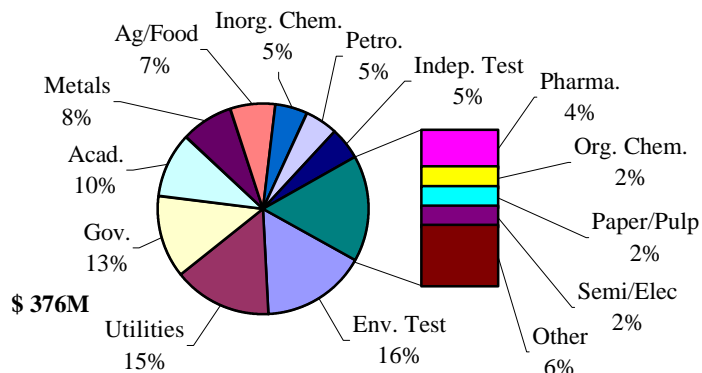
price appears to have had a negative effect on revenue, it has also allowed these instruments to penetrate new markets, particularly in the less industrialized countries of the world.

### 3. Application Segmentation

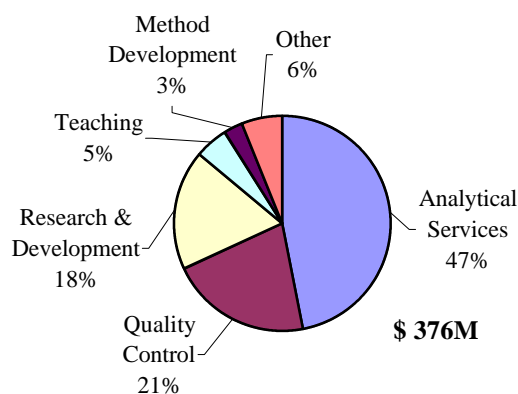
Nearly half of the AA market is concentrated into three main industries with similar needs. The environmental market is the most important, accounting for 16% of the total. AA is one of the established methods for detecting levels of various elements, mainly heavy metals, in water and soil samples. Many of the laboratories run by government and utilities have many environmental applications that require 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-9: AA Worldwide Demand by Industry, 2001**



**Figure XII-10: AA Worldwide Demand by Function, 2001**

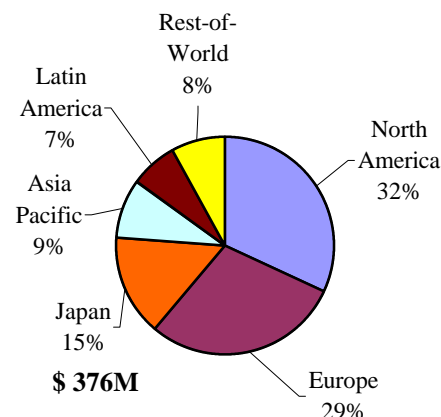




#### 4. Regional Market Demand

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**



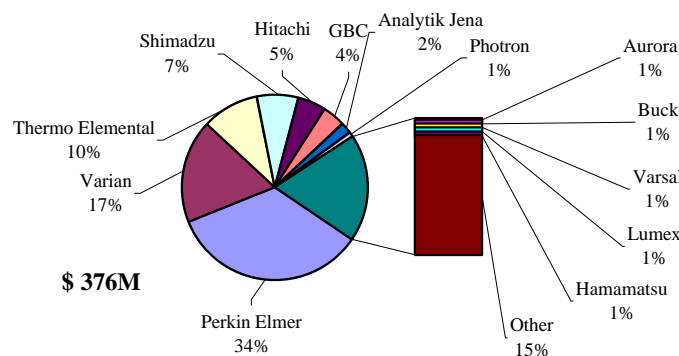
**Table XII-4: AA Worldwide Demand by Region Forecast 2001-2006 (\$ Millions)**

	2001		2002		2006		CGR '01-'06
	\$ Mil	Percent	\$ Mil	Percent	\$ Mil	Percent	
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%
<b>Total</b>	<b>376</b>	<b>100%</b>	<b>378</b>	<b>100%</b>	<b>391</b>	<b>100%</b>	<b>0.8%</b>

#### 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**



**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	AAAnalyst 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 19<sup>th</sup> 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.

Key Market Dynamics	
•	AA is a Mature Replacement Market
•	Technical Innovation Helps AA Hold Ground Against ICP Competition
•	New Products Offer Faster Analysis Times and Improved Light Sources
•	PerkinElmer Continues as Market Leader by a Wide Margin

**Figure XII-7: Analytik Jena NovAA 300**



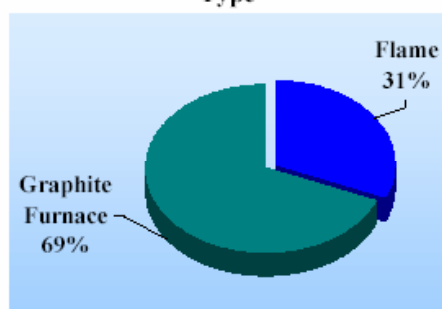
## 2. Product Segmentation

Table XII-2: AA Demand by Product

	2003		2004		2005		2008		'03-'08 CGR
	\$ Mil	Percent	\$ Mil	Percent	\$ Mil	Percent	\$ Mil	Percent	
Initial Systems									
<i>Flame</i>	92	24%	93	24%	91	24%	85	21%	-1.5%
<i>Graphite Furnace</i>	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%
<b>Total</b>	<b>376</b>	<b>100%</b>	<b>381</b>	<b>100%</b>	<b>387</b>	<b>100%</b>	<b>408</b>	<b>100%</b>	<b>1.6%</b>

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



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 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.

Table XII-3: AA Prices and Unit Volumes

Product Type	Price Range	Units Shipped
Flame	\$10K-\$30K	4300
Graphite Furnace	\$35K-\$85K	3300
<b>Total</b>		<b>7600</b>



### 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.

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-9: AA Demand by Industry

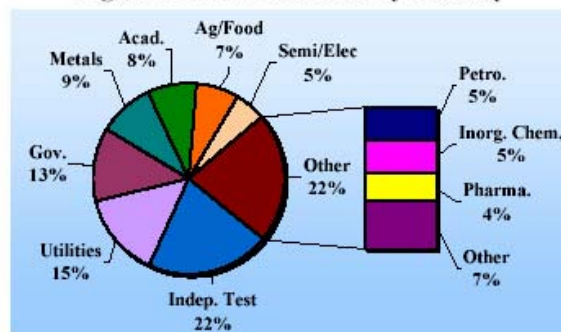
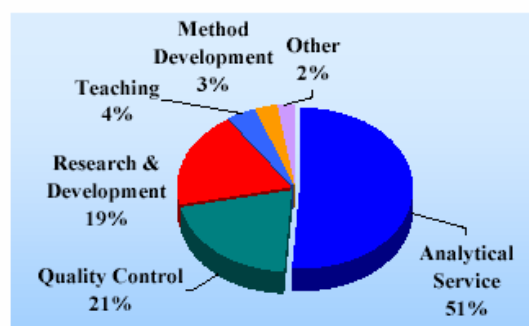


Figure XII-10: AA Demand by Function



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

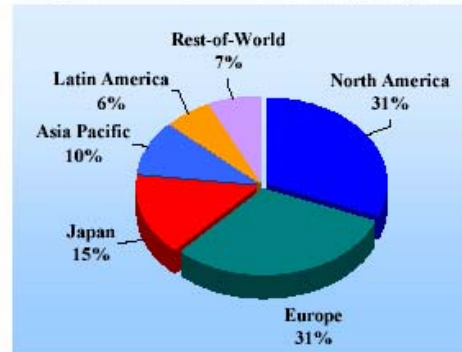


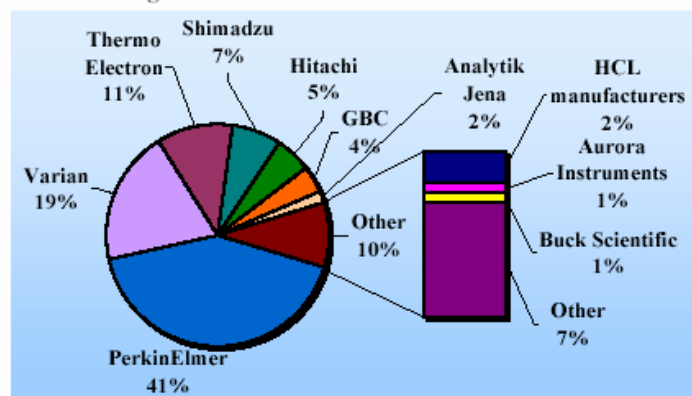
Table XII-4: AA Demand by Region

	2003		2004		2005		2008		'03-'08 CGR
	\$ Mil	Percent	\$ Mil	Percent	\$ Mil	Percent	\$ Mil	Percent	
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%
<b>Total</b>	<b>376</b>	<b>100%</b>	<b>381</b>	<b>100%</b>	<b>387</b>	<b>100%</b>	<b>408</b>	<b>100%</b>	<b>1.6%</b>

#### 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.

## 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.

Table XII-5: AA Vendor Participation

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

Key:   
 Major Involvement   
 Moderate Involvement   
 Minor Involvement

# 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

陈江韩 何志荣 何华焜\*

(中国广州分析测试中心 广州 510070)

**【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SEA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年以来的实践证明,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



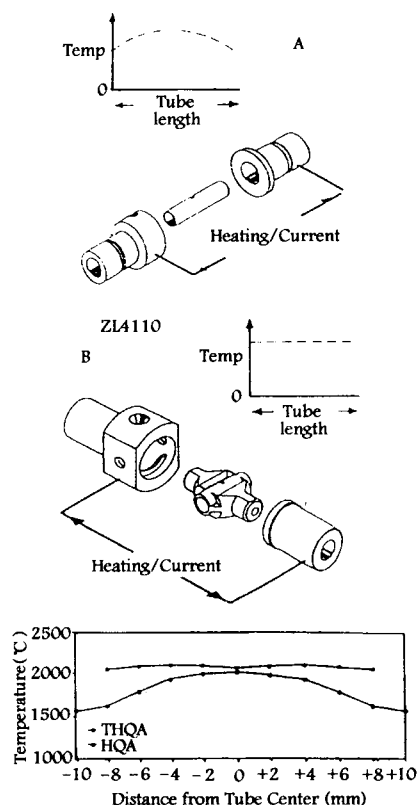


图1 PE公司 Massmann 型炉(A)和 THGF(B)结构图和温度分布曲线图

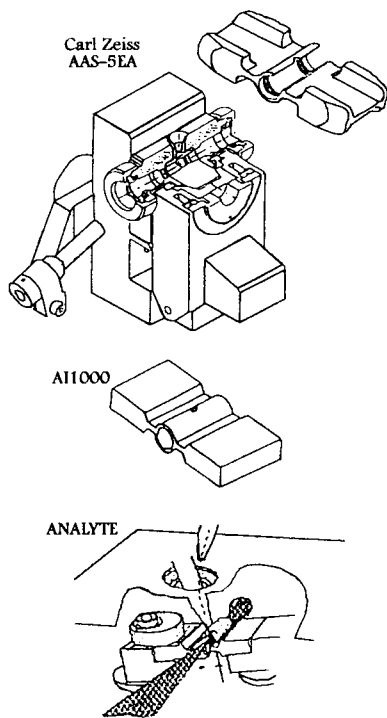


图2 Aurora公司 AH1000 型、Carl Zeiss 公司和 Leeman Labs 公司的 THGF 结构示意图

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碳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 兆氩气气氛中,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。

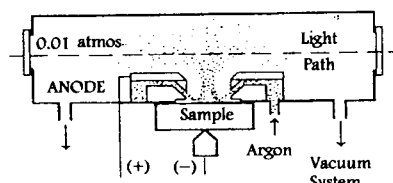


图3 阴极溅射辉光放电原子化器示意图

## 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。

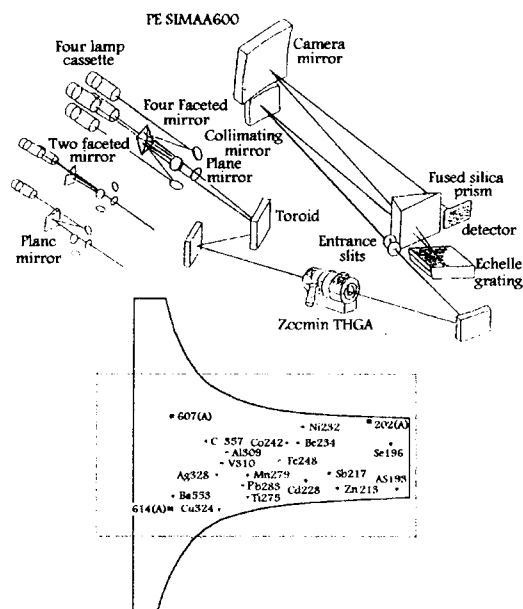


图4 SIMAA6000型多元素同时测定GFAAS仪器的光路图及固体检测器受光面示意图

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Gilmudnov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Gilmudnov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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# 原子吸收光谱分析技术在环境、医学卫生和食品分析方面的应用

邓 勃

(清华大学 化学系, 北京 100084)

**摘 要:** 回顾了原子吸收光谱分析在我国环境、医学卫生和食品分析方面的应用概况。

**关键词:** 原子吸收光谱; 环境监测; 食品分析; 药物分析; 临床诊断

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

Deng Bo(Department of Chemistry, Qinghua University, Beijing 100084)

**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 引言

1955年,原子吸收光谱作为一种仪器分析手段问世,当今,它已成为测定痕量和超痕量元素的最有效方法之一。由于A. Walsh和B. B. ЛЕБОВ对发展原子吸收光谱的杰出贡献,分别于1991年和1997年在挪威和澳大利亚召开的第27届和第30届国际光谱学大会(CSI)上被授予第一届和第二届CSI奖。1961年美国Perkin-Elmer公司推出了世界上首台原子吸收光谱商品仪器,1970年,当时的北京科学仪器厂生产了我国第一台单光束火焰原子吸收分光光度计商品仪器。今年,正值原子吸收光谱分析法面世45周年和我国原子吸收光谱商品仪器生产30周年。国产原子吸收光谱仪器的发展,为在我国大范围地推广和普及这一新的分析技术提供了物质基础,原子吸收光谱基础理论研究、分析技术发展以及应用领域的开拓,又为原子吸收光谱仪器进一步发展奠定了技术基础和提供了广阔的发展空间。《现代科学仪器》将在2000年出版专期,以纪念我国原子吸收光谱商品仪器生产30周年。本文仅就30年来原子吸收光谱分析在我国环境、医学卫生和食品分析方面的应用做一简要的回顾。

## 2 在环境监测方面的应用

环境直接关系每一个人的生活,保护环境是经济持续发展的必要条件,近年来受到世界各

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作者简介: 邓勃(1934-),男,湖南祁阳人,教授,硕士,主要从事原子光谱与化学计量学的教学和研究工作。

国的高度重视。环境监测数据是进行环境科学研究和制定环境战略、政策和规范的基础资料与依据。环境研究中感兴趣的一些元素正是原子吸收光谱分析法所擅长测定的元素。因此,它在环境监测方面获得了相当广泛的应用。

### 2.1 水环境监测

原子吸收光谱法广泛用于水环境中重金属的监测。侯贤灯等<sup>[1]</sup>用 FIA-FAAS 单标准连续稀释校正法测定了水样中的镁,免除了标准系列的配制,提高了分析速度。吴福全等<sup>[2]</sup>测定了环境水中的 Cu、Cd、Pb 和 Zn。魏复盛等<sup>[3]</sup>利用  $\text{SO}_4^{2-}$  和  $\text{BaCrO}_4$  置换反应释放出  $\text{CrO}_4^{2-}$  测定铬,间接定量水中可溶性硫酸盐。陈泽民等<sup>[4]</sup>以巯基苯骈噻唑为萃取剂,用活性硅胶柱萃取色谱富集环境水样中的 Zn、Cu、Pb、Cd、Fe、Ni、Mn 等,富集稀释达到 200,方法快速,富集完全,柱寿命长,至少可使用 50 次。何海诚等<sup>[5]</sup>利用吸附有双硫脲的微晶萘萃取色层富集,甲基二甲胺洗脱,FAAS 测定了天然水中的铜。

液膜富集是一种新技术,能有效地富集水中的微量元素。王宗孝等<sup>[6]</sup>用 N205 煤油溶液、P204 和液体石蜡、硫酸搅拌制乳液,在  $\text{pH}=9$  富集水中痕量镍,取有机相破乳,分层后取水相 FAAS 测定镍。富集系数 250。郭伊苻等<sup>[7]</sup>在 3 000 r/min 搅拌下,往 P204 或 P507+ 液体石蜡+煤油体系中加入内相水溶液,制成油包水(W/O)型乳化液,富集钴和镍,分析了松花江半拉山水样,分离系数达 180。顾景贤等<sup>[8]</sup>以二(2-乙基己基)磷酸酯(P204)为流动载体,双丁酰亚胺为表面活性剂,液体石蜡为膜增强剂,煤油为膜溶剂的液膜体系,富集水中的铅,使富集系数达到 100,方法选择性好,分析了长春南湖和第二松花江水中的铅。

在线富集是未来的发展热点。张素纯等<sup>[9]</sup>用在线离子交换预富集,冷原子吸收光谱法测定了多种水样中的汞,富集率为 40 倍,测得的检出限达到  $0.002 \mu\text{g/L}$ 。刘劲松等<sup>[10]</sup>用阴离子交换树脂为填料,8-羟基喹啉-5-磺酸为螯合剂,流动注射在线微柱富集天然水中的铜,富集倍数达到 23,FAAS 测定铜的检出限为  $0.2 \text{ ng/L}$ 。周蕾等<sup>[11]</sup>采用双柱交替正相富集和反相洗脱在线离子交换流路系统,使用 60~100 目 732 阳离子交换树脂富集环境水样中的镍 90 min,用  $2 \text{ mol/L}$  硝酸洗脱,FAAS 测定,检出限为  $0.5 \mu\text{g/L}$ ,灵敏度提高 12 倍,采样频率 30 次/h。苏淑娟<sup>[12]</sup>建立了流动注射在线富集与电热原子化器全自动联用系统,将水中的铅与 DDTc 络合后,通过  $9 \mu\text{m}$  C18 键合硅胶微柱吸附预富集,富集倍数为 64,再用  $80 \mu\text{L}$  甲醇洗脱,自动进样到横向加热的一体化的平台上进行测定,检出限为  $4.5 \text{ ng/L}$ ,没有基体干扰。金劲草等<sup>[13]</sup>用 DDTc-Zn 作载体,在高酸度下流动注射在线共沉淀富集铅,收集在编结反应器内,用 MIBK 溶解沉淀后直接引入 FAAS 测定,经 40 s 富集,检出限为  $2.7 \mu\text{g/L}$ ,用此法测定了人发、水和废水中的铅。

将化学富集与缝管富集相结合,可以获得更高的测定灵敏度。刘志民等<sup>[14]</sup>将黄原酯棉富集与石英缝管技术结合,FAAS 测定了环境水中的铅,灵敏度总共提高了 35 倍,方法可用于野外作业。刘立行等<sup>[15,16]</sup>联合使用离子交换和原子捕集技术 FAAS 测定水中的镉和镍,离子交换富集倍数为 40,原子捕集提高灵敏度近 81 倍。马学良等<sup>[17]</sup>使用离子交换和喷涂铝盐的石英捕集管(管壁上形成  $\text{Al}_2\text{O}_3$  层),FAAS 测定水中的铜,使捕集效率提高了 192 倍,总灵敏度提高了 7 463 倍。

海水是一个复杂体系,测定其中的微量元素有相当的难度。文献[18—20]用柠檬酸做基体改进剂,成功地测定了海水中的锌和土壤中的汞。张展霞等<sup>[21]</sup>详细地研究了有机基体改进剂

酒石酸、柠檬酸和抗坏血酸等对测定海水中 Cd、Pb、Cu、Co、Ni、V、Se、As、Mn、Cr 的基体改进作用, 将其作用归结为(1)助熔作用; (2)与分析元素析出热稳定的络合物, 避免分析元素与 Cl<sup>-</sup> 形成共挥发物质; (3)降低分析元素的挥发性; (4)和有机物燃烧时产生大量的 H<sub>2</sub>、CO、C 形成强还原性气氛, 有利于氧化物的还原。作者还采用 Б. М. Седых 等的公式来评价有机基体改进剂的效力, 酒石酸效果最好, 柠檬酸次之, 与实验结果一致<sup>[21-23]</sup>。邵秘华等<sup>[24]</sup>用 STPF 技术分析了海洋悬浮物 Cu、Pb、Cd 的化学状态, 测定了它们在可交换态、碳酸盐结合态、铁锰氧化物态、有机硫化物态和残渣态中的含量。周永国等<sup>[25]</sup>由 D-氨基葡萄糖以 β-1, 4, 苷式长链结合而成的天然高分子化合物壳巨糖, 以其中的 -NH<sub>2</sub> 与金属离子配位形成螯合物, 在 pH = 8 时吸附 Cd<sup>2+</sup>, 1 mol/L 硫酸洗脱, FAAS 测定海水和河水中的 Cd<sup>2+</sup>。

谢素原等<sup>[26]</sup>用正交设计优化了硫化物沉淀分离富集 AAS 测定钢铁废水中铋的条件。

元素的不同形态的生物和环境效应差别很大, 决定了它们在生态环境中和生物体内的行为和归宿。联用技术, 特别是色谱—原子吸收光谱联用, 综合了色谱的高分离效率与原子吸收光谱检测的专一性的优点, 是分析元素化学形态的有效手段。陈甫华等<sup>[27]</sup>建立了氢化物发生—冷阱捕集—色谱分离—原子吸收测定天然水中的 4 种主要砷形态的方法, 检出限分别为 As(V) 0.51 ng, As(III) 0.43 ng, MMA 0.38 ng 和 DMA 0.67 ng。并分析了天津港海水、海河水等, 表层河水、湖水和海水中以 As(V) 为主, 地下水中 As(III) 含量增高, 有机砷含量降低。刘志红等<sup>[28]</sup>利用离子交换分离, 建立了分析 4 种主要砷形态的流程, GFAAS 测定了珠江水中的砷形态, 检出限分别为 As(V) 0.89 μg/L, As(III) 0.94 μg/L, MMA 0.94 μg/L 和 DMA 0.26 μg/L, 测定总砷的检出限为 0.90 μg/L。邓勃等<sup>[29]</sup>将探针技术与化学修饰电极富集技术巧妙地结合起来, 用化学修饰石墨探针预富集—石墨炉原子吸收法测定 Cr(VI) 和 Cr(III)。黄淦泉等<sup>[30]</sup>以二本卡巴肼(DPCI)与 Cr(VI) 生成红色配合物, 后者与十二烷基硫酸钠生成离子缔合物, 实现浮选富集 Cr(VI), 再用 0.6% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 氧化 Cr(III) 为 Cr(VI), 测定总铬, 用这种方法测定了水中 Cr(III) 和 Cr(VI)。

## 2.2 大气环境质量分析

蒋守规<sup>[31,32]</sup>用超低温捕获阱采集大气样品, 首次在生态环境中追踪到了硒的甲基化合物, 从而发现在生态环境中存在硒的甲基化过程。并测定了大气中的烷基硒, 使用氩气流中加氢的方法克服了远紫外区基体和杂质的严重干扰, 检出限为 0.2 ng/m<sup>3</sup>。作者还研究了二甲基二硒的热稳定性<sup>[33]</sup>。白文敏等<sup>[34-37]</sup>建立了多种联用系统, 用石英管原子化器测定了大气和汽油中的烷基铅, 分析了 (CH<sub>3</sub>)<sub>4</sub>Pb、(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb、(CH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Pb、(CH<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)Pb、(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)Pb 5 种化学形态, 得到了很好的分离, 最小检出量达到 30 pg。张必成等<sup>[38,39]</sup>用一定气孔性石墨探针收集大气中的微粒物质, GFAAS 直接测定样品中的铈和镉, 方法简便、灵敏, 检出限分别为 21.5 pg 和 1.86 pg。

## 2.3 土壤和固体物分析

张素纯等<sup>[40]</sup>用 FIA—AAS 测定土壤和植物中的 Cu、Zn、Fe、Mn、K、Na、Ca、Mg, 测定速度最高可达 514 次/h, RSD 为 1%; 用气体扩散流动注射冷原子吸收光谱法测定土壤和粮食中的痕量汞时, 让 Hg<sup>0</sup> 渗透衬有 100 目尼龙网的聚四氟乙烯微孔气体扩散膜进入吸收池进行测定, 检出限低到 0.06 μg/L, 分析速度为 200 样次/h<sup>[41]</sup>。朱秋滨等<sup>[42]</sup>用 GC—GFAAS 测定了湖水、尿液、土壤和硒酵母中的二甲基硒和二乙基硒, 检出限分别为 0.14 ng 和 0.28 ng。淦五

二等<sup>[43]</sup>以草酸铵为稳定剂,  $\text{PdCl}_2$  为基体改进剂, 测定土壤中的镉, 检出限为  $1.5 \times 10^{-13} \text{ g}$ 。邓勃等<sup>[44]</sup>应用信息容量综合评价了用管壁和探针原子化法测定土壤中铅和镍的效果。

马怡载等<sup>[45-47]</sup>使用钨钼石墨管结合快速升温获得恒温原子化条件, 测定了水系沉积物和煤飞灰中的镉和铅, 用氨水为基体改进剂消除高氯酸干扰, 热解涂层石墨管结合快速升温测定了生物样品、水系沉积物和土壤中的铬, 并计算了铬在不同温度下的特征量。陈洪等<sup>[48]</sup>用微量进样技术测定了沉积物中的  $\text{Cu}$ 、 $\text{Ni}$ 、 $\text{Cr}$ 。韩恒斌等<sup>[49, 50]</sup>结合平台和最大功率升温技术克服了氯化物、硫酸盐、磷酸盐的干扰, 加入硝酸铵消除高氯酸盐的干扰, 测定了沉积物、土壤和果叶中的镓。用涂铑和钽平台结合最大功率升温测定了含卤化物废水和人发中的铈, 灵敏度是管壁法的 24 倍。何铭兹<sup>[51]</sup>用  $\text{Ir}$ 、 $\text{Te}$  为基体改进剂, 用平台原子化技术测定了水系沉积物中的  $\text{Ag}$ , 检出限为  $0.051 \mu\text{g/g}$ 。袁智能等<sup>[52]</sup>用铈和维生素 C 混合基体改进剂和以硫酸铵为基体改进剂, 悬浮液进样分别测定了环境样品中的铈和镉。

陈亚蕾等<sup>[53]</sup>用硝酸镁和柠檬酸铵混合基体改进剂直接测定了固体废弃物浸取液中的铍。王秀等<sup>[54]</sup>用  $\text{HGAAS-FIA}$  测定了大米土壤污水和五味子酒中的砷, 检出限为  $4.0 \times 10^{-11} \text{ g}$ 。韩恒斌等<sup>[55]</sup>用自行设计的带预原子化的电热石英炉, 氢化物发生法测定了环境标准参考物质中的砷和硒。文献<sup>[56]</sup>用涂铑石墨管测定了煤飞灰中的铈, 并将这种氢化物原位富集技术制成自动进样器, 能自动定时完成氢化物发生、输送等程序<sup>[57]</sup>。殷学锋等<sup>[58]</sup>用流动注射发生氢化物, 采用因子分析法分析了砷的 4 种形态  $\text{As(V)}$ 、 $\text{As(III)}$ 、 $\text{DMA}$  和  $\text{MMA}$ 。

### 3 医学卫生方面的应用

无机微量元素在人体内参与生命活动过程和其它营养素如蛋白质、碳水化合物、某些维生素的合成与代谢, 一定浓度水平的微量元素是维持生物体正常功能所必须的, 缺乏或过量都会引起不良的生理后果。因此, 微量元素的监测结果是辅助医疗诊断的重要资料。

#### 3.1 毛发分析

原子吸收光谱法广泛用于人发中微量元素的测定, 用此法测定了人发中的镉<sup>[59]</sup>、 $\text{Mg}$ 、 $\text{Cu}$ 、 $\text{Fe}$ 、 $\text{Mn}$ 、 $\text{Ca}$ 、 $\text{Zn}$ 、 $\text{Se}$ <sup>[60, 61]</sup>、 $\text{Hg}$ <sup>[62]</sup>、 $\text{Zn}$ 、 $\text{Cu}$ 、 $\text{Fe}$ 、 $\text{Ca}$ 、 $\text{Mg}$ 、 $\text{Mn}$ <sup>[63]</sup>、 $\text{Ni}$ <sup>[64]</sup>、 $\text{Co}$ <sup>[65]</sup>、铜<sup>[66]</sup>等。蔡火操等<sup>[67]</sup>、周立群等<sup>[68]</sup>用石墨探针测定了人发中的痕量钨和锰, 检出限分别为  $21.5 \text{ pg}$  和  $11.69 \text{ pg}$ 。方肇伦等<sup>[69]</sup>在溴化四丁基胺( $\text{TBABr}$ )的存在下, 溴化四丁基胺阳离子  $\text{TBA}^+$  与荷负电的钴—亚硝基 R 盐络合物形成离子对, 流动注射在线吸附预富集, 火焰原子吸收光谱法测定人发中的钴。原子捕集是一种在火焰中浓缩被测原子的预富集技术, 是提高火焰原子吸收法测定某些元素灵敏度的有效方法。张志恒等<sup>[70]</sup>用这一方法测定了人发中的痕量铜。方法的灵敏度为  $2.17 \times 10^{-4} \mu\text{g/L}$ , 灵敏度比常规火焰原子吸收法高 7.7 倍。何滨等<sup>[71]</sup>用石英毛细管色谱柱—不锈钢原子化器联用技术测定了水貂皮和毛发中的有机汞, 测定了氯化甲基汞、氯化乙基汞和氯化苯基汞。

唐军等<sup>[72]</sup>测定了 316 对母儿头发中的铁、锌、铜和镁, 并探讨了其相关关系, 新生婴儿头发中的铁、锌、镁含量高于母发值, 铜含量低于母发值。新生婴儿头发中的铁含量与其体重呈负相关, 在孕期应适当给孕妇补充铁剂以满足胎儿发育的需要。沙玉成等<sup>[73]</sup>用  $\text{GFAAS}$  测定了葡萄胎患者血清和头发中的  $\text{Cu}$ 、 $\text{Zn}$ 、 $\text{Fe}$ 、 $\text{Mn}$ 、 $\text{Ca}$  和  $\text{Mg}$  及  $\text{Cu/Zn}$  比, 并与中期妊娠健康孕妇正常组进行了比较, 统计检验表明, 在显著性水平  $0.01 < \alpha < 0.05$  时, 葡萄胎患者锌、镁、钙含

量显著地低于正常组。

### 3.2 血和体液分析

血液是医院临床诊断常规化验项目,用原子吸收光谱法检验微量元素简便快速,已用来测定铬<sup>[74]</sup>、铬与锰<sup>[75]</sup>、锌和铜<sup>[76-78]</sup>、铜、铁和锌<sup>[79]</sup>、锌<sup>[80,81]</sup>、铜、锌、铁、钙<sup>[82]</sup>等。血液基体复杂,使用基体改进剂能更有效地进行测定。单孝全<sup>[83-85]</sup>首先提出钨基体改进剂,用于环境和生物样品中汞、铅、砷、硒、碲和铋等易挥发性元素的测定,现已发展成为通用基体改进剂,获得了广泛的应用。梁琰<sup>[86]</sup>以磷酸二氢铵为基体改进剂,全血基体匹配标准,灰化除去蛋白质,消除高背景吸收,测定了全血中的Cd和Pb,回收率95%~104%。郑衍生等<sup>[87]</sup>用涂钨石墨管和 $\text{NH}_4\text{NO}_3$ 或 $(\text{NH}_4)_2\text{HPO}_4$ 为基体改进剂测定血液中的锂,5000倍的氯化物不干扰测定,特征量达到 $8.3 \times 10^{-11} \text{ g}$ 。陈振玲等<sup>[88]</sup>用0.2% Triton 将全血稀释4倍,以铈和硝酸铵为双基体改进剂,使测定锆的灰化温度提高到1000℃,平台原子化法直接测定了全血中的锆。舒永红等<sup>[89]</sup>以硝酸钡和镍为双基体改进剂,将锆的灰化温度提高到1400℃,测定血浆和尿中的锆,检出限达到28 pg。

黄淦泉等<sup>[90]</sup>采用贫焰捕集、富焰释放测定锌,特征浓度达到 $9.1 \times 10^{-5} \text{ mg} \cdot \text{L}^{-1}/1\%$ ,用10 g/L 铝溶液喷涂石英管,灵敏度提高5倍。用此法成功地测定了血清和水中的锌、铅<sup>[91]</sup>,人发和水中的镉<sup>[92]</sup>。孙书菊等<sup>[93]</sup>用不锈钢缝管原子捕集法测定了血清中的Cu和Zn,灵敏度分别提高了3倍和2倍。方向东等<sup>[94]</sup>用琼脂糖凝胶电泳和GFAAS联用测定了7个血样中的铜,特征量为 $2.0 \times 10^{-11} \text{ g}$ ,血清中 $\alpha_2$ 蛋白区带和白蛋白区带中的铜含量分别为 $(0.93 \pm 0.27) \mu\text{g}$ 和 $(0.22 \pm 0.06) \mu\text{g}$ 。刘忠英等<sup>[95]</sup>用氯仿—正己烷—甲醇萃取血浆中的游离脂肪酸,再与铜溶液作用形成铜皂加入有机相,未反应的铜进入水相,测定有机相中的铜,间接定量游离脂肪酸。

冀正堂等<sup>[96]</sup>用石墨炉原子吸收光谱法测定西安地区116例成年人血清铜,平均值为 $(18.88 \pm 3.30) \mu\text{mol/L}$ 。师长宏等<sup>[97]</sup>用脉冲进样技术火焰原子吸收光谱法测定了血清中的结合态与非结合态锌。测定30例正常人血清的结果表明,血清中总锌为 $0.769 \sim 1.247 \text{ mg/L}$ ,其中与蛋白结合的锌占 $(81.95 \pm 9.55)\%$ 。冠心病血清总锌量基本上不变,而结合锌明显升高,在胃癌病人血清中,总锌和结合锌量都降低。张晓光等<sup>[98]</sup>测定了视网膜脱离伴高度近视病人血清中锌、铜含量,测定结果表明,视网膜脱离伴高度近视病人血清中锌含量显著地高于正常人的血锌含量,而血清铜含量无显著性变化。

陈震阳等<sup>[99]</sup>用APDC络合萃取和涂钨石墨管测定了尿样中的钒。倪哲明等<sup>[100]</sup>用石墨管涂钨和锆之后进行原位富集后再原子化,测定人尿、海水中的硒、锡,灵敏度远高于文献报道的方法。

贝源等<sup>[101]</sup>比较了多种基体改进剂和石墨管后,选定Pt-维生素C为基体改进剂,在涂锆热解石墨管中原子化,测定了脑脊液中的钴,检出限为 $2.23 \mu\text{g/L}$ 。

### 3.3 生物脏器和组织分析

高双斌等<sup>[102]</sup>将硝酸稀释后用GFAAS直接测定眼玻璃体和房水中的铜和铁,避免了化学处理引起的沾污和损失,消除了基体干扰,回收率为98%~104%。杨根原等<sup>[103]</sup>采集静脉血,分离红细胞。用含 $0.15 \text{ mol/L}$ 氯化钠的 $50 \text{ mmol/L}$  Tris-HCl的等渗缓冲溶液( $\text{pH} = 7.4$ )洗涤红细胞3次,按高速冷冻离心法分离制备红细胞膜。用FAAS测定了34例正常人和30例肺癌患者细胞膜结合铁。结果表明,肺癌患者红细胞膜结合铁显著高于正常人。许亚辉等<sup>[104]</sup>测定

了 70 例喉癌病人喉鳞状细胞癌组织、头发和血样中的 Ni、Zn、Cu、Fe、Cr、Mn、Cd 和 Mg, 并和正常人做了对比。癌组织样品取自手术后切除的喉鳞状细胞癌组织, 对照组样品取自死犯人的正常喉内软组织。样品用湿法消解。用 FAAS 测定消解液中的 Zn、Cu、Fe 和 Mg, 用 GFAAS 测定 Mn、Ni、Cr 和 Cd。曾得国<sup>[105]</sup>以 BaF<sub>2</sub> 为基体改进剂, 用 GFAAS 测定肝组织中的钼, 不仅使钼灰化温度提高到 1 800 ℃, 消除了基体干扰, 也避免了碳化钼的形成, 回收率为 94.7% ~ 104%。

罗淑梅等<sup>[106]</sup>使用硝酸镁和硝酸钡双基体改进剂, 在平台上原子化, 使铬和锰的灰化温度由 1 200 ℃ 提高到 1 600 ℃, 消除了大量的 K、Na、Ca、Mg 的干扰, 直接测定了人眼视网膜下液中的铬和锰。

张勇等<sup>[107]</sup>用邻菲罗啉为金属螯合剂, 高氯酸钠为配体, 用 1, 2-二氯乙烷萃取富集, FAAS 测定了动物骨骼中的微量 Cu、Zn、Cd 和 Fe。杨海燕等<sup>[108]</sup>用涂 Al<sub>2</sub>O<sub>3</sub> 的开缝石英管原子捕集法测定钴, 间接定量腺苷辅酶维生素 B<sub>12</sub>, 灵敏度比常规火焰法提高 8 倍。徐通敏等<sup>[109]</sup>用 Nafion 化学修饰钨丝圆盘预富集牛血超氧化物歧化酶(SOD)中的 Cu<sup>2+</sup> 和 Zn<sup>2+</sup>, GFAAS 测定铜和锌, 铜和锌的检出限分别为 2.2 μg/L 和 0.2 μg/L。证实 SOD 中金属辅基铜锌原子数之比为 1: 1, 计算了 SOD 中 Cu<sup>2+</sup> 和 Zn<sup>2+</sup> 的表观平衡常数分别为  $2.02 \times 10^{-7}$  和  $2.02 \times 10^{-7}$ 。

### 3.4 药物分析

倪木春等<sup>[110]</sup>在乙酸介质中, 亚硝酸钴钠与苯酚、邻甲酚、间甲酚、对甲酚邻氯苯酚等加热生成邻亚硝基酚类, 再与三价钴离子生成有色钴螯合物, BIBK 萃取, 测定钴定量酚。朱铿等<sup>[111]</sup>利用 I<sup>-</sup> 与硫脲-铜(I<sup>+</sup>)形成离子对, MIBK 萃取, 通过测定铜间接定量碘。方法用于甲状腺肿和机能亢进药物及海产品中碘的测定。张继伦等<sup>[112]</sup>用硫氰化锡与 Triton X-100 形成离子对缔合物, 萃入二甲苯内, 测定锡间接定量 Triton X-100。邓世林等<sup>[113]</sup>用盐酸小檗碱与 [Co(SCN)<sub>4</sub>]<sup>2-</sup> 络阴离子形成 2: 1 离子对缔合物, 在 pH = 2.0 被二氯乙烷萃取, 转为水溶液后测定钴, 间接定量黄连素片剂中的盐酸小檗碱。杨光等<sup>[114]</sup>在 N,N-二甲胺存在下, 用二氯乙烷萃取盐酸布比卡因与硫氢酸钴络阴离子生成的离子对缔合物, 用水反萃取后 FAAS 测定钴, 间接定量盐酸布比卡因。杨成隆等<sup>[115]</sup>用氯化钡+硝酸镁双基体改进剂, 使锡的灰化温度由 800 ℃ 提高到 1 200 ℃, 测定六味地黄丸中的锡, 检出限为 0.3 μg/L。并发现加入基体的方式有重要影响, 加入基体后先在 900 ℃ 预处理再加入样品, 比同时加入基体改进剂和样品的灵敏度提高 1.5 倍, 作者认为其原因是氯化钡在 900 ℃ 预处理后转化为钡, 钡对 Sn、SnCl<sub>2</sub> 和 SnO<sub>2</sub> 具有更强的吸附能力, 形成 Pd-Sn 固溶体。

## 4 食品分析方面的应用

### 4.1 农产品分析

在农产品分析方面测定了大米中的铜<sup>[116]</sup>, 玉米粉中的钴<sup>[117]</sup>, 镁<sup>[118]</sup>和镉<sup>[119]</sup>, 大米、茶叶和蒜头中的硒, 灵敏度提高了 4 倍<sup>[120]</sup>。龙斯华等<sup>[121]</sup>将 BO<sub>3</sub><sup>-</sup> 转化为 BF<sub>4</sub><sup>-</sup> 和 IO<sub>3</sub><sup>-</sup> 转化为 I<sup>-</sup>, 再与 1, 10-邻二氮菲锡络合物形成离子缔合物, 被硝基苯萃取, 测定锡间接定量稻米中的硼和碘, 特征浓度达到 0.016 mg · L<sup>-1</sup>/1% 和 0.028 mg · L<sup>-1</sup>/1%。邹明强等<sup>[122]</sup>以镀金铜丝为载体循环富集。冷原子吸收法测定甲鱼神力源、红小豆等多种食品中的汞, 检出限为 0.4 pg/g。田笠



卿等<sup>[123,124]</sup>将油菜籽中的硫代葡萄糖苷经自酶解产生等摩尔的  $\text{HSO}_4^-$ , 用  $\text{Ba}^{2+}$  沉淀  $\text{HSO}_4^-$ , 通过测定过量的钡, 间接定量油菜籽和籽饼中的硫代葡萄糖苷。白文敏等<sup>[125]</sup>测定了大蒜油中  $(\text{CH}_3)_2\text{Se}$  和  $(\text{CH}_3)_2\text{Se}_2$ , 最小检出量分别为 0.3 ng 和 0.04 ng。水冷石英管捕集测定了甘蓝中的镉<sup>[126]</sup>。微量进样测定松花蛋中的铅<sup>[127]</sup>。在盐酸介质中, 测定新型蔬菜仙人掌中的微量元素, 钙和铁含量高于粮食、各种蔬菜、水果、鱼和肉, 铜含量与蔬菜相近, 但高于苹果和梨等, 锌含量与苹果、梨相当<sup>[128]</sup>。叶绿素是和镁结合的卟啉环, 其中的镁可以被  $\text{H}^+$  置换为去镁叶绿素。用 95% 乙醇提取叶绿素和盐酸提取镁, 测定镁间接定量叶绿素<sup>[129]</sup>。欧阳津<sup>[130]</sup>利用苦杏仁苷在苦杏仁苷酶作用下水解产生苯甲醛、葡萄糖和氢氰酸, 水解产物流经装有硫化铜柱的流动注射流路时,  $\text{CN}^-$  和  $\text{CuS}$  作用生成  $\text{Cu}(\text{CN})_4^{3-}$  可溶性离子, 载入原子化器, 测定铜间接定量苦杏仁苷。

#### 4.2 肉和奶制品分析

柳志龙等<sup>[131]</sup>用固体进样测定猪肝和牡蛎粉末中的铅。用甘油—硝酸—水(1+0.05+4)制成悬浮液, 以铜和镁为基体改进剂, GFAAS 无标样直接测定了猪肝、小麦和甘蓝中的硒<sup>[132]</sup>。将猪组织样品较碎混匀, 高压密封溶样, 测定了锰、铜、铁和锌<sup>[133]</sup>。饶竹等<sup>[134]</sup>用铍基体改进剂消除磷酸盐基体干扰, 测定了海洋生物样品中的砷, 检出限为 25 pg,  $RSD < 7\%$ , 用滤纸将鲜鱼鱼尾肌肉表面的水分吸干, FAAS 测定铁、铜、锌, 用 GBW-080193 牛肝标准物质进行质控, 分析实际样品时  $RSD$  为 0.32% ~ 0.85%<sup>[135]</sup>。

钱蜀等<sup>[136]</sup>将面粉样品制成悬浮液直接进样, 以钡为基体改进剂, 石墨炉平台原子化法测定了面粉中的铅和镉, 回收率为 91% ~ 104%。刘红望等<sup>[137]</sup>用磷酸二氢铵作悬浮剂和基体改进剂, 直接悬浮液进样测定奶粉中的铅和镉。

#### 4.3 饮料和营养品分析

原子吸收光谱法也常用来测定饮料和营养品中的微量元素。邓平建等<sup>[138]</sup>用基体改进剂获得了广泛的应用, 已知用铍基体改进剂直接测定了饮料中的 As、Pb、Cu。任建成等<sup>[139,140]</sup>使用  $\text{Pd}(\text{NO}_3)_2$ -Triton X-100 作为硒的基体改进剂, 将灰化温度由 40 °C 提高到 1200 °C, 测定了饮料和大青叶合剂中的硒。宋家诤等<sup>[141]</sup>在碱性条件下用氨基酸从磷酸铜沉淀中定量络合铜, 测定铜间接定量氨基酸, 检出限为 0.1 mg。王吉德等<sup>[142,143]</sup>用碳酸钙和磷酸铵镁悬浮液与饮料中的有机酸反应, 分离未反应的碳酸钙和磷酸铵镁, 测定上清液中的钙和镁, 间接定量总酸度, 间接定量桔汁、亚洲汽水、雪菲力汽水、杏汁汽水等饮料中的总酸度。

孙晓娟<sup>[144]</sup>以硝酸-磷酸二氢铵为基体改进剂多步斜坡升温平台原子化测定了 4 个国家的葡萄酒中的铅。姚金玉<sup>[145]</sup>用  $\text{Pd}/\text{Ca}$  双基体改进剂有效地消除了生物样品中无机伴生物的干扰, 测定了茶叶中的磷, 特征量为 8.2 ng。王吉德等<sup>[146,147]</sup>用甲基异丁酮—丁醇混合溶剂萃取茶汤中的杂多酚和分离氨基酸, 加入碱性磷酸铜溶液悬浮液反萃取, 生成的水溶性 Cu-杂多酚配合物转入水相, 离心分离未反应的磷酸铜, 测定铜间接定量氨基酸和杂多酚。回归分析发现, 茶叶品级与杂多酚含量之间有很好的相关性。

钱沙华等<sup>[148]</sup>用石英缝管捕集技术 FAAS 测定了地表水、茶水和人发中的 Pb、Cu 和 Cd 等, 灵敏度比常规 FAAS 分别高 110、39、和 150 倍。高丽娟等<sup>[149]</sup>用液膜富集, 测定了水蜜桃、汽水、啤酒和娃哈哈营养液中的锌, 回收率为 96.3% ~ 102%。蒋桂华等<sup>[150]</sup>用准液膜分离富集, FAAS 测定矿泉、水果、茶、果汁中的镁和铅。

陈树则等<sup>[151]</sup>用热解管和涂钨热解管测定了灵芝提取物、参茸王浆和矿泉水中的锗,灵敏度分别为 8 pg/1% 和 9 ng/1%。吴士定等<sup>[152]</sup>测定了含盐调味品中的铅,特征量为  $2.5 \times 10^{-11}$  g。

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站定时向子站发送指令,数据记录及处理采用计算机处理收集,通过电话线和 modem 的传送方式进行传送。

## 5 维护及管理

- 1) 水质自动监测站投资较大,必须由专人负责维护保养、定期接受培训,包括原理、故障排除及异常情况判断等,同时必须对仪器进行定期清洗和校正,比对数据的可靠性和准确性。
- 2) 由于水质自动监测系统技术要求高、分布较广,往往远离市区,可实行分级管理。省界断面由总站直管,省站做好维护保养工作;市界断面可由省站牵头,日常维护管理以市站为主,当地县级站做好配合工作。

## 6 存在的问题

对水质污染的连续自动监测一般要比对空气污染的连续自动监测困难得多,这是由于污染水质的污染物种类繁多,成分复杂,干扰严重,经常需要前处理操作,而且水质污染物又往往是痕量的,需要建立各种提取方法及各种痕量分析方法,所有这些均为连续自动监测技术带来一系列麻烦。同时,水质污染分析仪器是在实验室里发展起来的,这些分析仪器虽然原则上可用于无人操作的连续监测系统中,但实际上水质连续监测仪器长期运行的可靠性尚差,故障经常出现,在传感器沾污,采样器、样品流路的易堵塞,不能适应恶劣的环境条件,可监测的项目尚有限,测量系统的校准以及经济投资等方面均存在一系列需要解决的问题。

## 7 结语

多年来由于人员、技术和经济水平的限制,水质自动监测系统在我国应用不普遍,我国的环境监测尚处于初级发展阶段,监测频次仅能做到枯、平、丰水期监测2次,这对于水量、水质变化较大的河流来说,远不能满足管理的需要。因此,建立水质自动监测已势在必行,但从技术角度讲,建立水质自动监测系统是一个复杂的系统工程,由于缺乏经验,我们可以先从国外引进少量水质监测系统,经过消化吸收后加以推广,使我国的环境监测水平跃上一个新台阶。

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