The Zeeman Effect: A Unique Approach to Atomic Absorption

Sample preparation for atomic absorption spectrometry can be greatly simplified and the accuracy of measurement substantially improved with a new technique known as Zeeman-effect atomic absorption (ZAA) spectrometry. The technique eliminates the need for the complicated double-beam optics previously required for sensitive atomic absorption measurements. In the process, ZAA spectrometry provides a fivefold improvement in the amount of background interference that can be tolerated and a tenfold increase in the precision with which background correction can be made. The net effect is that less sample preparation is required to reduce the concentration of extraneous materials that might obscure the elements being analyzed.

There are two types of ZAA spectrophotometer. In the first, which might be called type 1, the magnetic field is applied to the sample chamber. In the second, or type 2, the magnetic field is applied to the light source. Type 1 ZAA spectrophotometers were introduced commercially in this country earlier this year and deliveries to laboratories are just beginning. The type 2 spectrophotometer is about a year behind the type 1 in development, but several prototype instruments are in use here and abroad.

The ZAA spectrophotometer was originally conceived by Tetsuo Hadeishi of the Lawrence Berkeley Laboratory, who was searching for a simple instrument that could be used by the crew members of small fishing boats to determine the mercury contamination in catches of fresh fish. With that initial instrument, which could measure only mercury, a piece of flesh was simply cut off the fish, weighed, placed in a furnace, and vaporized. The mercury content could then be read off the instrument. The current spectrophotometers are more sophisticated versions of that original instrument, which is still used by Japanese fishermen, the Environmental Protection Agency, and the U.S. Army Corps of Engineers. The development of the commercial type 1 instrument was accomplished primarily by Hideaki Koisumi of Japan's Hitachi Limited. Hitachi markets the spectrophotometer (for $16,500) through its U.S. subsidiary, Nissei Sangyo Instruments Inc. (NSI), of Sunnyvale, California.

The Zeeman effect occurs when a radiation source (or a substance that absorbs light) is placed in a magnetic field. In the simplest case (elements such as mercury, zinc, and cadmium), each spectral line is split into three lines. The so-called π line, with half the original intensity, remains at the original wavelength (Fig. 1). Two σ lines, which together also have half the original intensity, are displaced by equal wavelengths on each side of the π line. For more complicated systems (most other elements), each σ line and each π line is split into as many as 11 additional lines.

In addition to being split by the magnetic field, the spectral lines are also polarized. The π line or lines are polarized in a plane parallel to the magnetic field and the σ lines are polarized in a plane perpendicular to the magnetic field. The net effect is that, when only one light beam and appropriate polarization filters are used, the change in light intensity caused by the absorption of the element under analysis can be separated from that caused by scattering and absorption by smoke and vapors. In a conventional instrument, this can be accomplished—but not nearly as well—only with a complicated system involving two light beams having precisely the same geometry, intensity, and wavelength.

In the type 2 ZAA spectrophotometer, a magnetic field around the light source splits the light and polarizes it. A rotating polarizer allows the π and σ components to pass alternately through the vaporized sample. The π beam is diminished by absorption by the sample and by light scattering and broadband molecular absorption. The σ beam is diminished only by scattering and broadband absorption. By comparing the two beams electronically, it is thus possible to quantify the amount of the element present.

In the type 1 instrument, the magnetic field is placed around the sample chamber. In this case, the element under analysis can absorb only light that has been polarized in a plane parallel to the magnetic field. The monochromatic light is then passed through a rotating linear polarizer before it reaches the sample. Again, comparison of the two polarized beams makes it possible to quantify the amount of the element present.

In both instruments, the continual comparison of the sample and reference beams permits quantification of elements even in the presence of either smoke (from extraneous materials in the sample) or other interference that absorbs as much as 95 percent of the incident light. The continuous comparison also means that it is not necessary to wait for the light source to become fully warmed up to obtain a stable background correction. Furthermore, background correction can be achieved over the entire spectrum covered by the light source; conventional atomic absorption spectrometers provide correction only at wavelengths above 350 nanometers.

The differences between the types 1 and 2 ZAA spectrophotometers are actually quite small. In the type 1 instrument, the requirement to maintain both a high temperature in the graphite cuvette that holds the sample and a high magnetic field around the sample limits

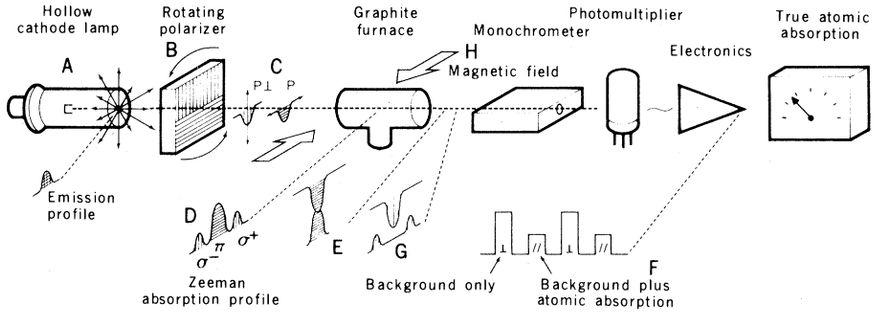

Fig. 1. Mechanical and optical function diagram for type 1 ZAA spectrophotometer. The lamp (*A*) emits light at a wavelength that is characteristic of the element being analyzed. This light is alternately polarized (*B*) into planes parallel and perpendicular to the plane of the magnetic field (*H*). Application of the magnetic field to the sample produces the Zeeman absorption profile (*D*) for the element being analyzed. Light polarized in a plane parallel to the magnetic field is absorbed by the π component of the element's profile (*E*), but light polarized into the perpendicular plane is not absorbed by the σ components (*G*). Comparison of the two beams (*F*) then produces the true atomic absorption.

the size of the sample to about 1 or 2 milligrams. But placing the magnetic field around the sample means that conventional, well-developed light sources can be used. One of the most difficult problems with the type 2 instrument has been the development of a light source that can operate reliably within a high magnetic field (on the order of 15 kilogauss).

Hadeishi and his colleague Ralph McLaughlin have recently developed a new light source, called the magnetically confined lamp, that seems to have solved this problem. And because the magnetic field is around the light source, the type 2 instrument can accommodate much larger samples, even larger than those that can be accommodated in conventional atomic absorption spectrometers. Because detection is proportional to the absolute amount of an element in the sample, the type 2 instrument can often detect smaller concentrations than either the type 1 or the conventional instrument.

The chief advantage of ZAA spectrometry—a direct result of the ability to monitor an element in the presence of high background absorptions—is that sample preparation is greatly simplified. In conventional atomic absorption spectrometry, the sample frequently must be put into solution or otherwise manipulated to increase the concentration of the element being monitored or to decrease the concentration of extraneous smoke-producing materials. With ZAA spectrometry, according to McLaughlin, this is generally not necessary. Most of the time, he says, an untreated sample can simply be put into the graphite cuvette and vaporized. This simple procedure greatly reduces the possibility that the sample might be contaminated during preparation, that the element to be analyzed might not be completely dissolved, or that it might be absorbed onto the walls of the glassware.

ZAA spectrometry thus has a large number of potential applications where the ability to detect an element in the presence of a high background absorption makes it clearly superior to conventional atomic absorption spectrometry. One good example is the analysis of trace elements in seawater. Extensive treatment of seawater samples prior to analysis is generally required for atomic absorption spectrometry because the sodium chloride in a sample generates too much smoke for accurate analysis. ZAA spectrometry, however, is able to compensate for the background interference produced by the sodium chloride, so that almost all analyses can be performed directly.

In a similar fashion, analyses can be performed directly on blood and urine samples. The technique can also be used, for example, to analyze trace elements in steel. This generally cannot be accomplished with conventional atomic absorption spectrometers because the numerous spectral lines of iron generally produce too high a background absorbance. Among the other substances that Hadeishi's group and NSI have been able to analyze without prior treatment are cow's liver and other tissue samples, coal, ash, ceramic pots, geological samples, sediments, and oil shale.

Hadeishi and McLaughlin and the investigators at Hitachi have done most of the initial work demonstrating the utility of both types of ZAA spectrometry. One other investigator in this country who is familiar with the instrument's potential is James Westhoff of the Corps of Engineers' Waterways Experiment Station in Vicksburg, Mississippi. Westhoff has a prototype type 2 ZAA spectrophotometer built by NSI specifically for the measurement of mercury, selenium, arsenic, and cadmium. The instrument is used at the station to detect these metals in industrial wastes, urban waste treatment products, and solid wastes. It is also used to measure trace concentrations of these elements in river waters and sediments and to determine the uptake of metals by plant tissue.

Westhoff says that many of the samples studied at the station require much more extensive prior treatment when analyzed by conventional atomic absorption spectrometry than when analyzed by ZAA spectrometry. All of his experiences, Westhoff says, point to the great utility of ZAA spectrometry and to the advantages of its superior background correction capabilities relative to conventional instruments.

ZAA spectrometry does not solve one of the major problems that is inherent in atomic absorption spectrometry, the extraneous formation in the cuvette of molecular products that interfere with measurement of the desired element. It does, however, partially solve a second problem, the inability of atomic absorption techniques to assay more than one element at a time. The great speed of measurement achievable with ZAA makes it possible to assay a large number of elements sequentially in about the same time that would be required for other techniques that assay them simultaneously, such as nuclear activation analysis or x-ray fluorescence. In any case, the greater sensitivity of ZAA spectrometry compared to these other techniques may still make it desirable in many cases even if sequential analysis should take longer. It thus seems safe to say that ZAA spectrometry will find its own niche in the instrument world and will prove to be a valuable analytical tool.—THOMAS H. MAUGH II

Bacterial Genetics: Action at a Distance on DNA

Conventional views of the structure and function of DNA molecules are being extended by some recent studies of bacterial DNA. Researchers have now found evidence of "action at a distance" on these molecules. That is, a protein will bind to the DNA at one spot and will affect gene expression at a position some distance away. How this can occur is a matter of some speculation, but the existence of the phenomenon indicates that DNA is far from the "inert" molecule assumed by many models in molecular biology.

In many cases, expression of bacterial genes is controlled by regulatory proteins that bind to the DNA molecule near the gene. (A gene is expressed when the protein it codes for is actually produced by the processes of transcription and translation.) According to Robert Wells of the University of Wisconsin at Madison, the notion of action at a distance comes down to the question of the role of DNA in the control of gene expression. Wells asks, "Is DNA an inert molecule on which interesting [regulatory] proteins act, or does the DNA itself play an active role?" Wells's long-held belief that DNA plays an active role was not only considered a maverick idea but was also found to be very difficult to demonstrate.

The problem is that naturally occurring DNA is such a large molecule that it is hard to search for long-range effects. For several years, Wells, John Burd of Miles Laboratories, Inc., in Elkhart, Indiana, and their associates have used short strands of synthetic DNA molecules to demonstrate, as Wells puts it, that "one end of the molecule knows