



Improvement and application of nonflame atomic absorption instrumentation
by Douglas Edmund Shrader

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
DOCTOR OF PHILOSOPHY in Chemistry
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Abstract:

An optical system applicable to single beam instruments is presented to correct for background absorption found in atomic absorption spectroscopy. The optical system involves two Glan-Taylor air-spaced calcite polarizers.

The hollow cathode light is polarized perpendicular to the reference beam. The polarizers are used to combine and finally separate the two beams after passage through the furnace atomization device and a Beckman DU. Individual photomultipliers are used for the two beams, whose outputs are recorded individually and compared. An improved furnace design is presented. Representative signals for the two channels are presented. Calibration curves for Ag, Au, and Hg were obtained and sensitivities are given.

The design, construction, specifications, and operation of a new dual-wavelength spectrophotometer is presented. The instrument utilizes only one fixed grating and mobile exit slits with photomultiplier light sensors. Two wavelengths can be monitored simultaneously and both channels may be scanned independently. The spectrophotometer has been integrated into an atomic absorption system which includes a Woodruff furnace and Ithaco dual-channel lock-in amplifier. The two channels may be used separately (A and B) or may be ratioed (A/B). Taking the ratio of the intensity of a resonance line of interest and the intensity of a nearby nonresonant line allows background absorption corrections to be made. In the separate channel mode, two elements may be simultaneously determined in a single sample. Results are given for the determination of Ag and Pb in various sample types requiring background correction using the ratio (A/B) mode. Results are also given for the simultaneous determination of Ag and Pb in synthetic samples using the separate channel (A and B) mode. Calibration curves were obtained for the two most sensitive lines of both Ag and Pb.

Applications of furnace atomic absorption are presented. Trace element concentrations of different elements were determined in Various types of samples and the results are given and discussed. The average relative standard deviations of the results ranged from 3.1% to 15.4% for amounts of metals in the nanogram and sub-nanogram region. . Sensitivities for Ag, Pb, Au, Cd, Cu, Hg, and Mn are presented.

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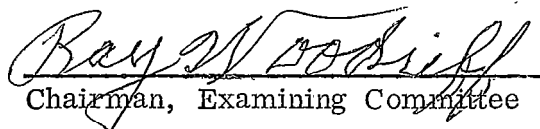
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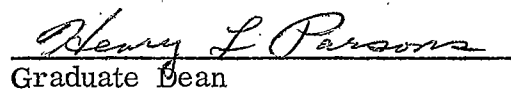
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ABSTRACT

An optical system applicable to single beam instruments is presented to correct for background absorption found in atomic absorption spectroscopy. The optical system involves two Glan-Taylor air-spaced calcite polarizers. The hollow cathode light is polarized perpendicular to the reference beam. The polarizers are used to combine and finally separate the two beams after passage through the furnace atomization device and a Beckman DU. Individual photomultipliers are used for the two beams, whose outputs are recorded individually and compared. An improved furnace design is presented. Representative signals for the two channels are presented. Calibration curves for Ag, Au, and Hg were obtained and sensitivities are given.

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INTRODUCTION

Since its introduction in 1955 ⁽¹⁾, atomic absorption spectroscopy has become a very useful analytical technique and is a part of almost every modern analytical lab. Atomic absorption theory, its application to numerous fields, and the problems involved in its use have been the subject of many publications and texts in the past.

Inherent in flame atomic absorption is a high noise level caused by turbulence in the flame and nebulized sample introduction. This imposes a limit on sensitivity and detection limit, thus relatively large samples are needed. Also, the samples need to be in relatively pure liquid form for aspiration into the burner head. These facts put the analyst at a disadvantage in many fields such as clinical, forensic, and environmental chemistry where the available sample is or should be very small, or in a solid or a complex, viscous form.

The recent concern over the environment and its quality has made necessary the development of new instrumentation in order to improve sensitivities and detection limits. Several nonflame atomization devices for atomic absorption have been introduced during the last few years ^(2, 3, 4, 5, 6, 7, 8, 9). These devices have the advantage of much greater sensitivity, allowing a smaller sample to be analyzed. Also, in some cases, solids, complex liquids,

and gases may be analyzed directly or with a minimum of sample preparation. This is extremely valuable if the sample size is or should be small, or in some form other than a relatively pure liquid. Even though many of the problems involved in the use of flame atomic absorption have been eliminated by the nonflame devices, more work needs to be done to perfect them.

Another problem found in atomic absorption spectroscopy is that of background absorption^(10, 11). The cause of this background absorption is molecular absorption and/or scattering of light due to particles. This non-atomic absorption can cause erroneously high results if not compensated for. Several methods of correction for background absorption have been described^(12, 13, 14, 15, 16). These all involve the use of a hydrogen or deuterium continuum in various instrumental arrangements to measure the background absorption at the wavelength of interest and allow for correction. Also, the use of a nonabsorbing wavelength near the resonance line of interest for the purpose of background correction or reference has been reported in several publications^(10, 17, 18, 19, 20).

An additional problem, or rather disadvantage, of atomic absorption spectroscopy is that in practice it is generally only useful for single-element determinations. Several instrumental arrangements for the determination of more than one element have been published^(21, 22, 23). Very recently Fisher

Scientific Co. and Instrumentation Laboratory, Inc. have introduced spectrophotometers which can be used to determine two elements simultaneously by atomic absorption. These instruments can monitor two wavelengths. Perkin-Elmer, American Instrument Co., and Phoenix Precision Instrument Co. also have instruments with dual-wavelength capabilities but have not applied these to atomic absorption but rather to UV-Visible spectroscopy. In all but one case the instruments are composed of two grating monochromators. The Instrumentation Laboratory instrument utilizes one grating monochromator and an interference filter for the second channel.

This thesis deals with the improvement of instrumentation available for use in atomic absorption spectroscopy. Complete instrumental systems have been developed as well as improvements in the atomization device, the Woodriff furnace. The instrumental systems have been developed in order to provide a method of background correction to compensate for nonatomic absorption. The second instrumental system may also be used for the simultaneous determination of two elements. Applications of furnace atomic absorption have been developed and are part of this thesis. They show that the Woodriff furnace can be utilized to determine trace element concentrations in real samples, taken in connection with problems or projects of current interest, and that reproducible results in the nanogram and sub-nanogram region can be obtained.

STATEMENT OF PROBLEM

Briefly, the problem was to look into the improvement of instrumentation (complete systems as well as the furnace atomization device) available for use in atomic absorption spectroscopy. This improvement involves applications and evaluation of results with real samples.

As was stated previously, there are several problems which one encounters in atomic absorption spectroscopy. A major breakthrough in solving some of the problems associated with flame atomic absorption came about with the introduction of various nonflame atomization devices. The Woodriff furnace is such a device. Since its introduction to the public in 1966⁽²⁴⁾, various publications have presented sensitivities, detection limits, and some of the problems encountered in its use. Heater tubes had a very short life (15 hours)⁽⁴⁾. Blanks were many times irreproducible⁽²⁵⁾. A large portion of this was thought to be caused by furnace design and materials. The construction of a second generation furnace with enclosed ends and improved chucks for end cooling and electrical conduction seemed to increase the life of the heater tubes⁽¹⁴⁾. On this basis it was decided that the furnace design needed additional improvement, not only with the goal of increased life of heater tubes and other graphite parts, but also with the goals of increasing reproducibility of results and the development of a design which would promote

safety, simplicity, and efficiency. A third generation furnace and an improvement of it were constructed and are discussed.

The problem of background absorption caused by the scattering of light by particles in the optical path and/or molecular absorption needed to be confronted. The instrumental arrangements previously used to correct for background absorption are in some cases very complicated and either give only the net absorbance or individual absorbances at different times or on different samples. It was thought that a system of background correction involving plane polarized light could be useful. By using two polarizing beam splitters, reference and sample radiation, polarized perpendicularly to each other, could be combined into a single beam and, after passage through the furnace, could be separated and monitored. The use of DC electronics would allow a continuous and simultaneous record of both hollow cathode and hydrogen lamp radiation to be obtained.

Along the same lines but more versatile was an idea for a dual-wavelength monochromator. It would have one fixed grating and two mobile exit slit and photomultiplier tube assemblies. Being able to monitor two wavelengths would allow one to use a nonresonant line, close to the resonant line of interest, as a reference and thus be able to compensate for background absorption. A simultaneous record of both reference and sample beams could

be obtained or the outputs from the two channels could be ratioed, giving the net absorbance. Also, it would have the capability of simultaneously determining two elements by atomic absorption. The versatility would be greater and the construction would be simpler than commercially available dual-wavelength spectrophotometers.

Both instrumental arrangements were developed and incorporated into atomic absorption systems involving a Woodriff furnace. The instruments are presented and discussed.

Finally there arises the problem of applications. Techniques for determining very small amounts of metals are in great demand due to the current emphasis on the environment and its quality. A technique such as furnace atomic absorption can fulfill the requirement of being very sensitive. It is in fact 3 or 4 orders of magnitude more sensitive than conventional flame atomic absorption. However, with this technique, as well as any other technique, real samples need to be analyzed in order to determine its applicability to routine analysis. Applications of nonflame devices available from different instrument companies have been the subject of various publications^(26,27,28,29,30). The Montana State University group has published only two applications to real samples^(31,32). The opportunity to become involved in the analysis of samples from various

research projects presented itself and was accepted. The methods used and the results obtained in these projects are presented.

EXPERIMENTAL

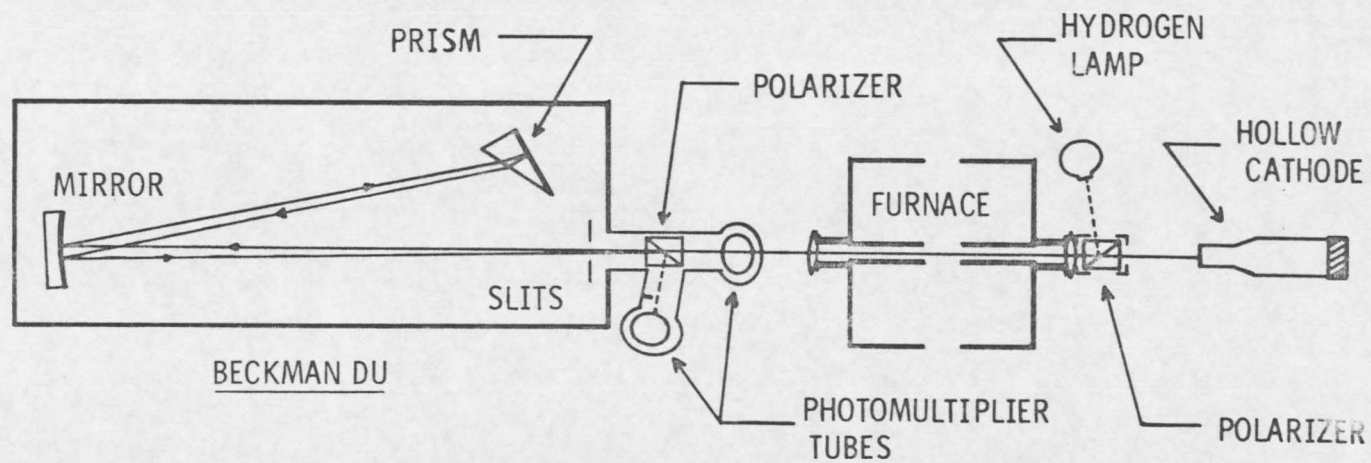
Furnace Atomic Absorption with Reference Channel

Systems mentioned earlier to compensate for background absorption employ alternating sample-reference observation and give only the difference between the two signals or measure the sample signal and reference signal at two times relatively far apart or on two samples. The system described here gives a continuous, simultaneous record of both signals.

Optical System and Readout

Figure 1 shows the optical system which was used. The hollow cathode light enters the primary Glan-Taylor polarizer and is polarized parallel to the optical axis of the polarizer. The polarized hollow cathode light then passes down the optical path of the furnace. The hydrogen lamp light enters the primary polarizer through the side window and is divided into two perpendicularly polarized beams which are reflected in such a manner that the portion which is polarized perpendicular to the optical axis of the polarizer follows the same optical path as the beam from the hollow cathode. The other portion of the hydrogen lamp beam leaves the optical path and is absorbed. Before passage through the furnace, the two beams of interest are collimated by means of a quartz lens placed between the polarizer and the furnace.

Both beams, the hollow cathode beam polarized horizontally and the



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Figure 1. Optical System Diagram.

hydrogen lamp beam polarized vertically, after passing through the furnace are focused on the slit of the Beckman DU with a second lens placed on the end of the furnace. After passing through the monochromator, the combined beams pass through the second slit and fall on the secondary Glan-Taylor polarizer. The polarizer separates the two perpendicularly polarized portions of the beam. The hollow cathode portion is transmitted straight through the polarizer and falls on a photomultiplier tube. The hydrogen lamp portion is reflected through the side window of the polarizer and falls on a second photomultiplier tube.

Enlarged diagrams of both the primary and secondary polarizers are shown in Figure 2. The polarization of the hollow cathode and hydrogen lamp beams is indicated. A horizontally polarized portion is reflected through the side window of the secondary polarizer at a slightly different angle than the vertically polarized hydrogen lamp beam of interest. This portion is kept from striking the reference photomultiplier tube by placing a baffle between the polarizer and photomultiplier tube (see Figure 1). A drawing of the optical bench and accessories which were constructed is shown in the Appendix, page 90.

After the hollow cathode light and hydrogen lamp light fall on their respective photomultiplier tubes (RCA IP28's), the signals are recorded

