

A COMPARISON BETWEEN ZEEMAN AND SMITH-HIEFTJE
BACKGROUND CORRECTION SYSTEMS FOR GRAPHITE
FURNACE ATOMIC ABSORPTION SPECTROSCOPY

by

Gale A. Graves

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Dary W. Minzey Aug. 1, 1985
Adviser Date

Sally M. Hotchkiss August 29, 1985
Dean of the Graduate School Date

YOUNGSTOWN STATE UNIVERSITY

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ABSTRACT

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Background correction in furnace atomic absorption spectroscopy is essential. Several interferences encountered while using this technique require the use of an efficient background correction system. Interferences commonly encountered include chemical, physical, background, and spectral.

There are three types of background correction systems commercially available today. These are the Deuterium Arc, Smith-Hieftje, and Zeeman background correction systems, each having its own advantages and drawbacks. The most recent development in background correction is the Smith-Hieftje system, coming out in 1982.

There is much debate over which background correction system is better. Comparisons have been made between the Deuterium arc system and the Smith-Hieftje system. There have also been comparisons made between the Deuterium arc system and the Zeeman system. However, there has yet to be a comparison made between Smith-Hieftje and

Zeeman background correction systems. This project compares these two systems for the determination of cadmium in a sodium chloride matrix,

The Smith-Hieftje system was located at Youngstown State University and the Zeeman system was located at the Food and Drug Administration in Cincinnati. Because of this, several variables were identified and held constant in an attempt to isolate just the background correction systems. Three experiments were then conducted. The first of these was a loss in sensitivity study due to the background correction system. After losses in sensitivity were determined, a precision study was done in order to determine which system was more accurate and reliable. A final experiment was performed to look at the distortion in signal caused by each background correction system.

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LIST OF SYMBOLS

SYMBOL	DEFINITION
N	Number of scattering particles per unit volume
λ	Wavelength
V	Square of the particle volume
uv	Ultra-Violet light
τ	Scattering coefficient
I_{-}	Pi
$\langle \rangle, \%$	Components of a Zeeman split atomic line

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CHAPTER I

Introduction

Since atomic absorption spectroscopy is a relative method, i.e., quantitative determinations can only be carried out by comparison to reference substances, any behavior of the sample which is different from the reference substance implies an interference. Many methods and procedures are available today to correct for interferences in atomic absorption spectroscopy. Two of these methods, namely Zeeman and Smith-Hieftje background correction systems, are compared in this research project.

Depending upon their cause, interferences are referred to as chemical, physical, background, ionization, and spectral (1). While background and spectral interferences are based on the measurement of non-specific signals, chemical and physical interferences have an influence (positive or negative) on the total number of atoms N formed per unit volume.

Chemical interferences are the most common, and are caused by the presence of a thermally stable material in the sample which is not removed by the

flame or graphite furnace. Strictly defined, a chemical interference is any formation of a compound that prevents quantitative atomization of the element being determined. This absolute definition, used especially when different methods of atomization are compared, can be replaced by a relative definition. For comparing different samples when the same means of atomization is being used - for example a graphite furnace - a chemical interference is understood as an alteration of the total number of free atoms formed per unit volume owing to the formation of chemical compounds. With this definition of chemical interference, it is possible that the effect can be positive or negative relative to the standard. With the absolute definition of chemical interference, the effect can only be negative, i.e., every interference is recognized as a decrease in the total number of atoms that can be formed.

There are two causes for the occurrence of chemical interferences. Either the conversion of the sample into atoms is not quantitative, possibly because a difficultly melted or vaporized salt is formed or the molecules formed are not completely dissociated, or the free atoms react spontaneously with other atoms or radicals in the environment so that they are not long enough available for absorption. With flameless atomization procedures, chemically inert or reducing atmospheres are

used so that various interferences caused by the properties of the flame are excluded. A characteristic of graphite tube furnaces is the fact that although the atomization is a thermal dissociation of molecules into atoms, it is not an equilibrium reaction. This is due to the fact that the small amount of element under study is atomized in a chemically inert environment which is considerably cooler than the tube surface. Since the atomization of a sample in a graphite tube furnace can only take place from the graphite surface, the sample must remain in good contact with the hot surface for as long as possible to become as completely atomized as possible. This means that the sensitivity of a determination can be increased if the sample is converted into a difficultly melted or vaporized form. In contrast to flame atomic absorption, the formation of sulphates, phosphates, or oxides in the graphite tube is often advantageous. However, good contact with the graphite surface is only desirable as long as the compound of interest can be dissociated into atoms rapidly enough at temperatures below 2500 degrees celsius. If this does not occur, the formation of compounds can be a hindrance with a resultant loss in signal height. The best known interference of this type is probably carbide formation from reaction with the graphite or decomposition products from the sample, for example carbon produced from ashing of biological materials. To avoid the latter interference,

the matrix must be destroyed in many cases prior to the introduction of sample into the graphite furnace. It stands to reason that the forming of a compound of the element of interest which withstands high decomposition temperatures, but which can quantitatively dissociate at the atomization temperature, eliminates the majority of interferences.

Physical interferences are understood as those caused by differing physical properties of the sample and reference substance such as different viscosities, surface tensions, or specific gravities of the solutions. This type of interference in the past has been known only to flame applications since the sample is nebulized into the flame. In contrast to this, samples are introduced into the graphite furnace by pipetting. However, because of the new sample introduction devices on the market today, e.g., the I.L. Fastac (2) which sprays the sample into the furnace, and automatic samplers, the same types of physical interferences that influence flame analysis also affect furnace analysis. Most often, physical interferences can be avoided by matching the physical properties of the sample and standard solutions. This can be achieved by diluting the sample solution, making up standards with the same matrix as the sample solutions, or by the method of standard additions (3).

Background absorption occurs from two sources: light scattering particles in the flame or furnace producing a broad band effect, and true molecular

absorption caused by undissociated molecules in the light path. This type of interference is due to a non-specific (not caused by a specific element) light loss which leads to a signal that is too high. This high signal consists of the true absorption of the element under study, and the non-specific absorption of the background. The absorption bands from molecules are usually broad, both in comparison to the hollow cathode emission line and the monochromator bandpass (4). It is typical for all types of non-specific light losses to have a broad band absorption. It does not alter measurably over several nanometers while atomic absorption is restricted to a very narrow wavelength, λ , range (approximately .002 nm).

The first effect, scattering of light from the hollow cathode lamp on solid particles in the flame or furnace, obeys Rayleigh's stray light law in the first approximation, in which the scattering coefficient τ is given by $\tau = 24 \pi^3 \frac{N \cdot \nu^2}{\lambda^4}$. This scattering effect will thus occur quite strongly with increasing particle size and for decreasing wavelength. The two important characteristics of background absorption are that background absorption is much higher with furnace atomization as opposed to flame, and background absorption is much greater in the UV range of the spectrum than in the visible range. There are several methods available to correct for this type of interference and these will be discussed later.

Spectral interferences in atomic absorption analysis are very much related to background interferences. Spectral interferences are due to scattering of radiation, broadband absorption, non-analyte absorbing lines within the spectral bandwidth, and direct absorption overlap. These types of interferences can be virtually eliminated with good instrumental design.

As stated previously, it is typical for interferences due to non-specific light losses to be broad band in nature. Almost all attempts to eliminate interferences are based on this fact. One of the fundamental rules for all procedures and methods used to correct for background interferences is that the correction should take place as near as possible to the actual absorption line. Slavin (6) recommended that the non-specific light losses should be corrected by measuring the effect at a non-absorbable line and then subtracting the results from the measurable signal.

One of the first instrumental designs developed to correct for background was developed by Koirtyohann and co-workers (?). They used a dual channel system in which light from the hollow cathode lamp and light from a continuous source was passed through the atomized sample. The continuous source that was used was a deuterium arc lamp. The emission spectrum of a deuterium arc, shown in figure 1, is quite intense up to 400 nm

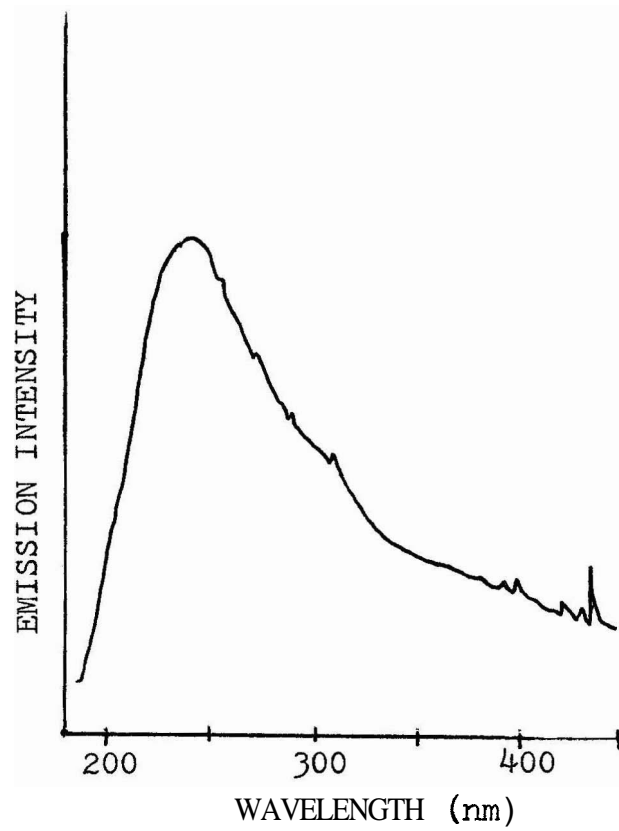


Fig. 1. Spectrum of a Deuterium *Arc*

but declines to almost zero in the visible wavelength range.

To correct for background interferences, light from the deuterium arc and from a hollow cathode lamp is alternated rapidly (ten or more times per second) through the sample cell. A simplified optical design is shown in figure 2. The light from the hollow cathode is absorbed by both the element being determined and the background. The light from the deuterium arc is essentially unabsorbed by the element but absorbed by the background. The difference between the hollow cathode absorbance and arc absorbance is the legitimate or element absorbance. In most cases, deuterium arcs produce very good background correction; however, there are some drawbacks. The deuterium arc will yield incorrect results in the presence of structured background. This effect occurs when broad band molecular absorption possesses narrow band fine structure, due commonly to rotational or vibrational transitions within the molecule. This effect is shown in figure 3. Since the deuterium arc averages the background across the monochromator bandpass, it may differ from the actual background absorbance at the analytical line, resulting in an over or under correction of background absorbance. Also, exact alignment of the two optical beams is essential. A last disadvantage of the deuterium arc system is that the presence of two light sources doubles the likelihood of baseline drift.

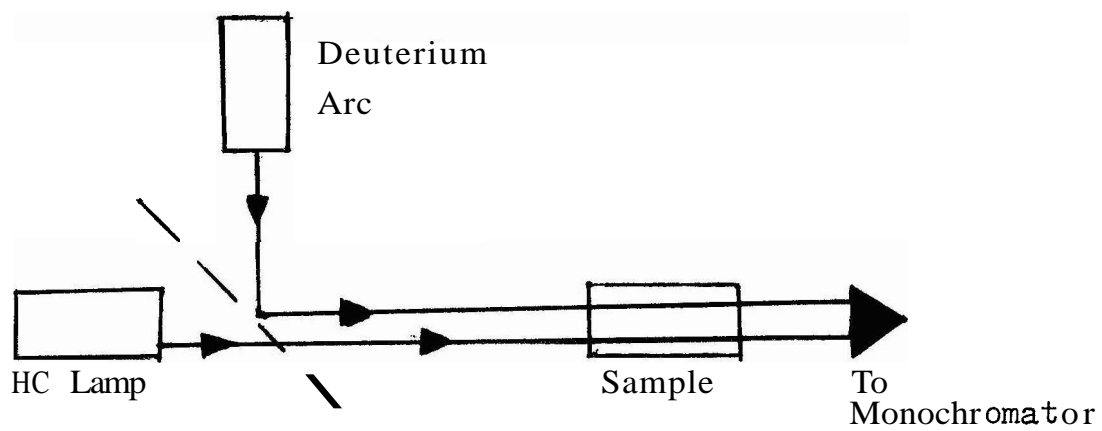


Fig. 2. AA Optical System with Deuterium *Arc*

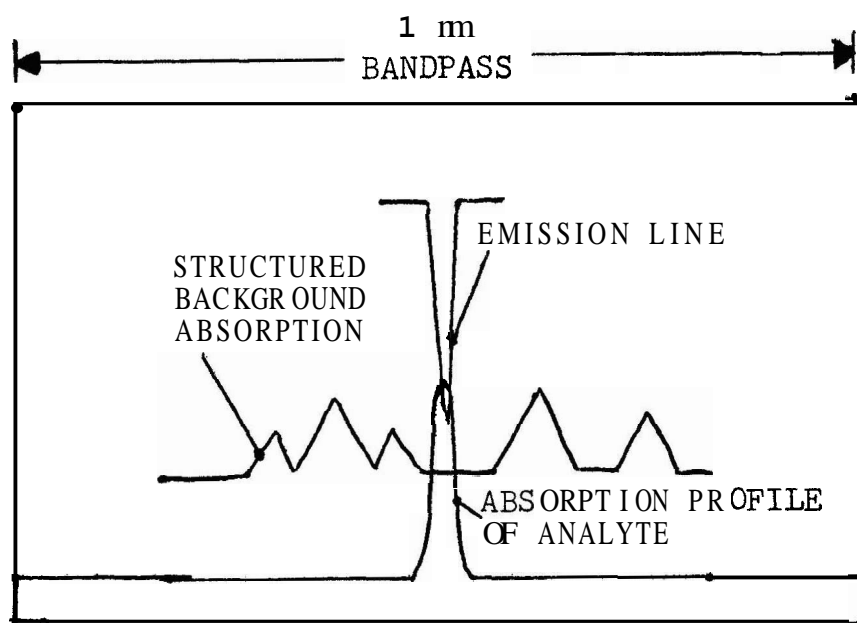


Fig. 3. Interference from Structured Background

In the late 1970's, a new background correction system based on the Zeeman effect became available(8). When the atomizer is placed between the poles of a strong magnet, the spectral lines absorbed by the atoms of interest are split into at least three components: a central component which is less intense yet maintains the original wavelength, and two sigma components that are shifted in wavelength. The Zeeman effect is shown in figure 4. These components are symmetrical and the sum of the π component, and the sigma components ($+\sigma$ and $-\sigma$) is always equal to the intensity of the unaffected spectral line. The number and intensity of Zeeman shifted spectral lines will depend strongly upon the spectral transition, as well as the strength of the applied magnetic field. The magnetic field also polarizes these components. The π component is polarized in a plane which is parallel to the magnetic field, and the σ components are polarized in a plane which is perpendicular to the magnetic field. The splitting of spectral lines by the magnetic field, as well as the polarization of those lines, forms the basis of background correction by the Zeeman effect.

In general, normal Zeeman-shifted lines form a triplet of intensity ratio 1:2:1 that is symmetric about the magnetic field-free line. However, some elements do not undergo normal Zeeman splitting but instead yield complex anomalous splitting patterns.

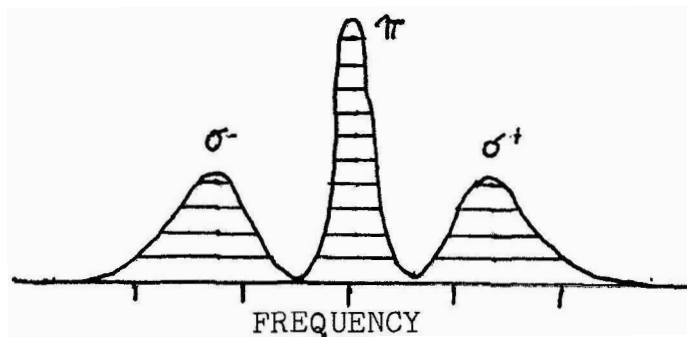


Fig. 4. Illustration of the Zeeman Effect

An example of this is the sodium 589.00 spectral line shown in figure 5. For elements that undergo anomalous splitting patterns, sensitivity is typically reduced 10% to 50%.

There are several factors that can affect a Zeeman-shifted line. Doppler broadening (due to motion of the atom relative to the detector) and collision broadening (due to collisions with like or foreign atoms or molecules) will contribute to the overall line width. In a hollow cathode lamp, Doppler effects dominate because of low pressure, but in a furnace, where both temperatures and pressures are higher, both Doppler and collision broadening are important in determining linewidths (9). These effects shift further all of the π and $\pm\sigma$ components of a Zeeman shifted line and must be taken into account when using a Zeeman background correction system.

Today, there are two instrumental designs available using Zeeman effect shifts to accomplish background correction. These are source-shifted Zeeman background correction and analyte-shifted Zeeman background correction which is the newer of the two. In source-shifted correction, a magnet is placed around the hollow cathode lamp. Lines emitted from the lamp are split into π and $\pm\sigma$ components, and these new lines are passed through the atomized sample. The π component is absorbed by both the element and the background, but the Zeeman-

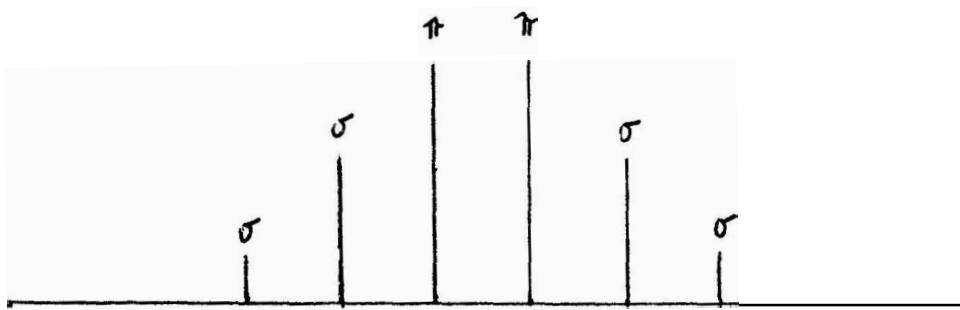


Fig. 5. Anomalous Zeeman Effect in Sodium

shifted σ components are only absorbed by the background. Conversion of the π and σ signals to logarithms, and finally subtraction of the two signals, yields the true sample or element absorbance.

Because of stability problems encountered when a strong magnet is placed around the source, another instrumental design was developed and is widely used today. This instrumental design places the magnet around the furnace atomizer to produce analyte-shifted Zeeman background correction. In an instrument equipped with a permanent magnet surrounding the atomizer, to separate the π and σ components, a rotating polarizer can be placed between the light source and the sample, alternating the passage of parallel and perpendicular polarized light. This type of instrumental configuration is shown in figure 6. When the parallel component is being transmitted, it will be absorbed by the central unshifted π component as well as the background that is present. In the next quarter cycle, only the perpendicular source light is transmitted. This perpendicular light will not be absorbed by the central π component of the analyte (although it is at exactly the same wavelength) because its polarization is different. In the ideal case, the perpendicularly polarized sidebands are split far enough from each other so that they too do not absorb any perpendicular radiation. Therefore, only background absorbs in this case. Subtraction of

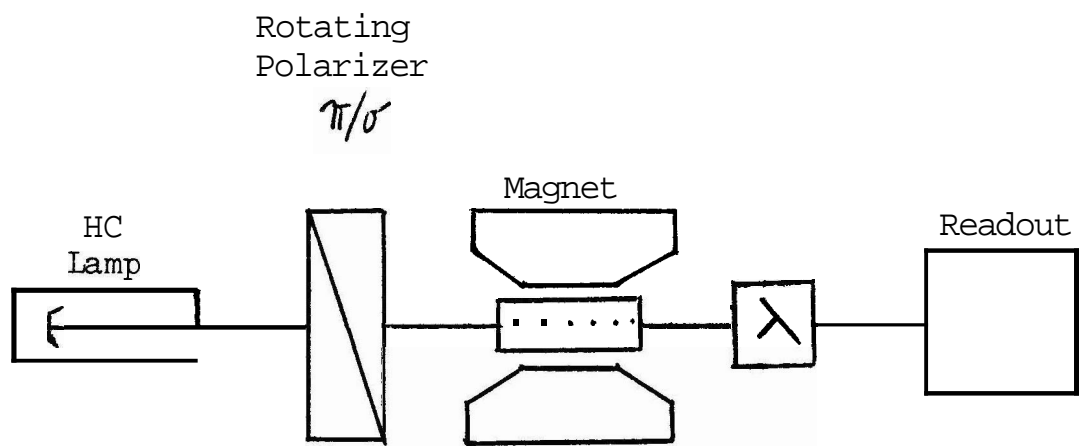


Fig. 6. Optical Design for Analyte-Shifted Zeeman AA.

the σ signal from the π signal produces background correction. A similar design employs an alternating current magnet with a fixed polarizing filter.

There are many advantages as well as disadvantages to Zeeman-shifted techniques. Some of the advantages are that the techniques can be applied to a wide range of wavelengths unlike deuterium arc correction methods and are considerably more sensitive with most elements. Because both source-shifted and analyte-shifted techniques generate correction within the atom, they are not subject to limitations of spectral range. One important advantage is that a Zeeman background corrector often remains unaffected by structured background absorption because correction occurs at the same wavelength at which the element is being determined.

However, as mentioned earlier, there also are some drawbacks. Analytical curves can be double valued, which means that two widely different concentrations produce the same absorbance readings. As the concentration of the analyte increases, the σ sidebands broaden and begin to absorb more and more of the perpendicular component of the source. This absorbance is construed as background and is subtracted, causing the working curve to bend over and actually reverse direction. This effect is known as rollover. Another restriction of Zeeman techniques is that the element must possess a resonance line that shows a suitable Zeeman effect,

either normal or anomalous, in a 10 - 15 kilogauss magnetic field. This requirement is the most severe disadvantage, since many of the stronger resonance lines show strong anomalous Zeeman effects and spread the π envelope to such a large extent that a weaker resonance line showing a more tightly grouped π envelope gives greater sensitivity. Lastly, Zeeman techniques are very difficult to apply to flame methods and are very expensive.

A new and exciting concept in background correction, the Smith-Hieftje system, was described for the first time at the 1982 Pittsburgh Conference (10). This type of background correction is achieved through a manipulation of the hollow cathode lamp. It has been known for several years that when an excessive current is passed through a hollow cathode lamp, its emission line is broadened and atomic absorption from the analyte is greatly reduced. This effect is known as self-reversal, because unexcited atoms in the lamp absorb the radiation at the atomic spectral line, so that the output resembles that shown in figure 7. Figure 7 shows that when a hollow cathode lamp is operated at high currents, a broadening of the atomic line occurs, while operation at lower currents produces a much sharper emission line. The effect on atomic absorbance while the lamp is operated at high currents is shown dramatically in figure 8. In figure 8, the apparent absorbance of a constant

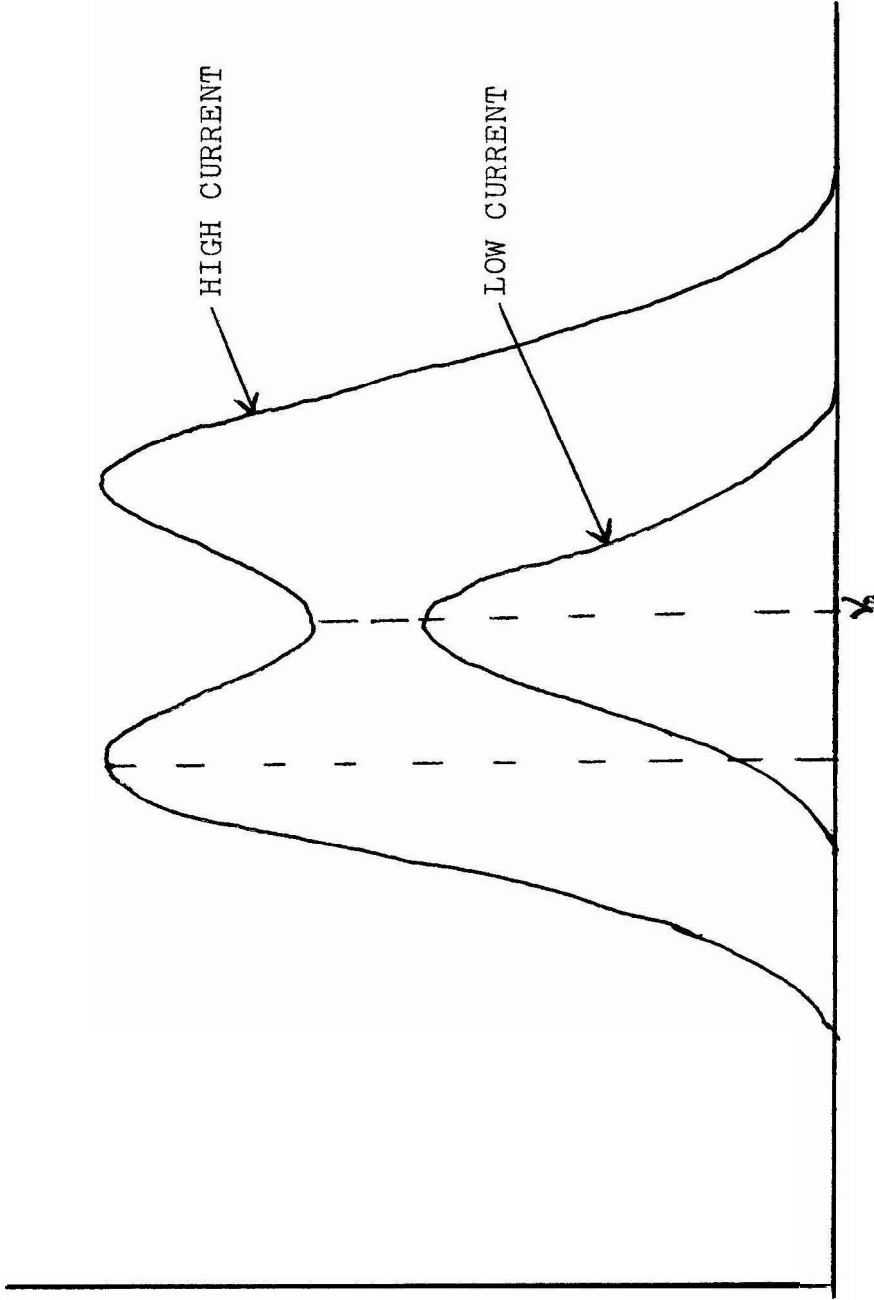


Fig. 7. Emission Line Profiles of a Hollow Cathode Lamp Showing Effect of Self Reversal at High Currents.

concentration of cadmium atoms in an air-acetylene flame is shown to decrease progressively as the hollow cathode primary source is operated at higher currents.

It occurred to Smith and Hieftje that the self-reversal effect could be applied to background correction. The system that they designed functions by operating the hollow cathode lamp in a double pulsed mode (11-13). An initial low current pulse produces an emission line from the hollow cathode which is similar to that ordinarily employed in atomic spectrometry and provides a combined measure of atomic and background absorption. The lamp is then pulsed at a high current and this produces a broadened spectral line which is somewhat self-reversed. Absorbance measured during the high current pulse consists primarily of that produced by background absorbers. Subtraction of absorbance values measured during the two pulses then provides a background corrected signal,

It is clear that for this new approach to be effective, it is necessary to broaden appreciably the emission line of each element under investigation, The degree of broadening is different for each element and depends upon the peak current at which the hollow cathode lamp is driven. The selection of these peak currents and the current waveforms used for each element must be made judiciously to maintain hollow cathode lamp reliability and longevity. The current waveform shown in figure 9 is the one used in the Smith-Hieftje

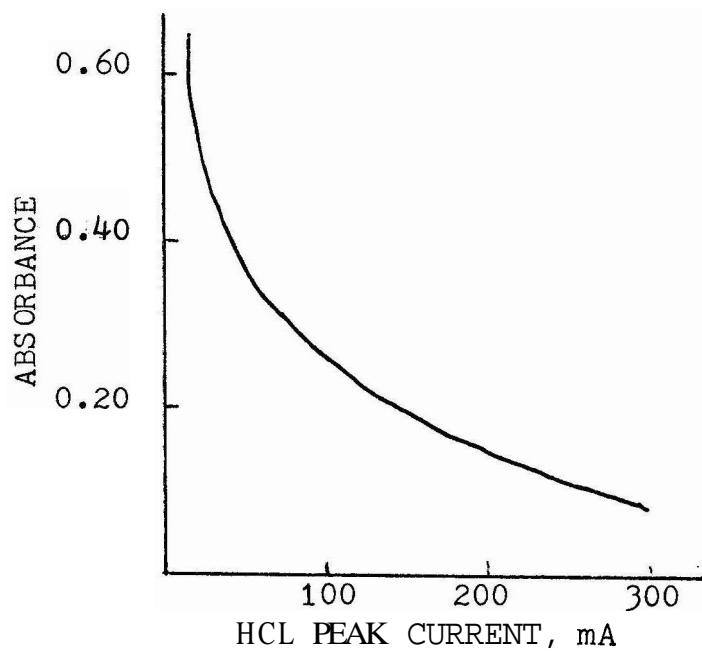


Fig. 8. Effect of Lamp Current on Absorbance of Cd (1 ppm) Aspirated into an Air-Acetylene Flame.

system. The lamp is pulsed repetitively within a period of 50 milliseconds. The time between low current and high current pulses is only 4.5 milliseconds. After the high current pulse, the lamp remains idle, operating at 1 milliamp(mA) for 40 milliseconds, before the next current cycle.

In comparison to conventional deuterium background correction, Smith-Hieftje has all the advantages of Zeeman. It works in the visible as well as the ultraviolet portion of the spectrum. It isn't thrown off by structured background caused by vibrational or rotational transitions. It is able to eliminate most spectral interferences, and a single source is used both for atomic absorption and background.

The Smith-Hieftje system also has some advantages over the Zeeman system. With new software, there are no double valued working curves caused by rollover. There are no restrictions placed on either the source or sample areas. Smith-Hieftje can easily be applied to both flame and furnace analysis. And finally, the Smith-Hieftje system is, by nature, less expensive than a deuterium arc system and much less expensive than a Zeeman system.

Both the Zeeman and the Smith-Hieftje system have been compared to the deuterium arc system. However, a direct comparison between Smith-Hieftje and Zeeman has yet to be reported. Most Zeeman and Smith-Hieftje

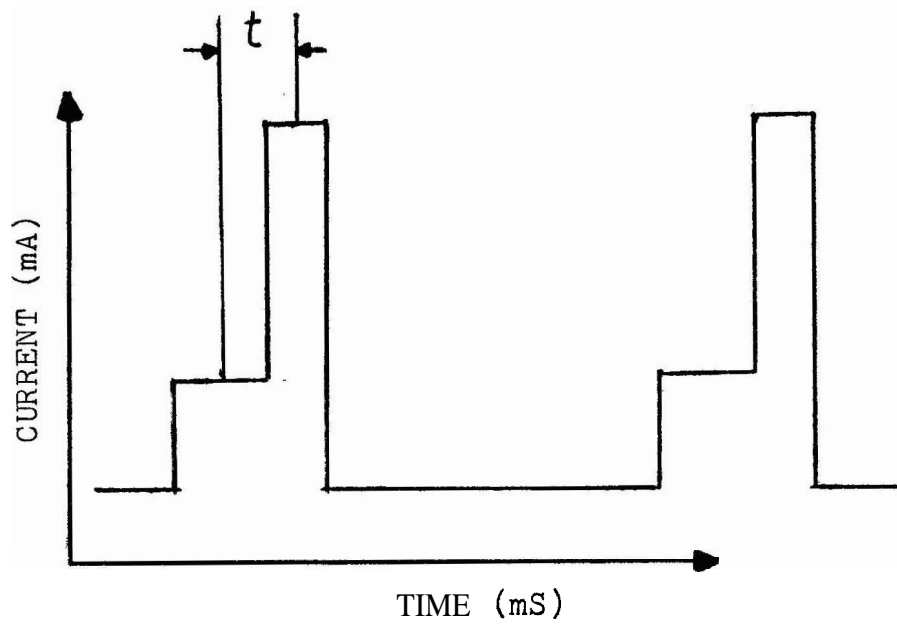


Fig. 9. Current Waveform Used to Drive Hollow-Cathode Lamp in the Smith-Hieftje System. The Difference Between High Current and Low Current Pulses (t) is only 4.5 mS.

systems also have deuterium arcs incorporated within them. However, no instrument is available today that has both Zeeman and Smith-Hieftje background correction systems. This makes a comparison between the two much more difficult.

This research project, done in conjunction with the Food and Drug Administration in Cincinnati, focuses upon the determination of cadmium, comparing Smith-Hieftje and Zeeman background correction systems.

Cadmium has caught the attention of many investigators in recent years because of its toxicity. The accumulation of cadmium in the body has been linked with respiratory ailments, hypertension, and damage to bones, kidney, and liver (14). Cadmium ranks close to lead and mercury as a metal of current toxicologic concern. Estimated lethal doses in man range from 350 to 8,900 mg. The minimum acute toxic dose is probably less than 10 mg (15).

Because of its adverse affects on humans and other living organisms, cadmium determinations are done on a wide variety of biological fluids and tissues. Several electrothermal atomic absorption methods have been published for cadmium (16). However, the presence of major organic and inorganic species causes spectral, chemical, and background interferences. To overcome these interferences, several approaches have been used: (i) separation of the analyte from the bulk matrix by

solvent extraction (17); (ii) selective volatilization of the analyte or matrix (18); (iii) matrix modification in which the atomization rate of the analyte is slowed sufficiently to resolve the atomic absorption signal of the analyte from the nonatomic absorption signal of the matrix (19-20).

Often, none of these measures are sufficient, and an effective background correction system is essential. A comparison between Smith-Hieftje and Zeeman background correction for the determination of cadmium is described. The loss in sensitivity as well as the precision of each system with a background absorber present is also discussed.

CHAPTER II

Experimental

The instruments used in this study were at two different locations. The Zeeman system was at the Food and Drug Administration in Cincinnati and the Smith-Hieftje system was at Youngstown State University. The Zeeman system consisted of a Perkin-Elmer model 5000 spectrophotometer, a Perkin-Elmer model 500 furnace power supply, and a Perkin-Elmer AS-40 autosampler, all of which were interfaced to a Perkin-Elmer model 3600 data station. The Smith-Hieftje system was manufactured by Instrumentation Laboratory. It consisted of an IL Video 11 AA/AE spectrophotometer with an IL model 655 furnace attachment,

Because of the location of the two instruments and the fact that the instruments were manufactured by two different companies, all efforts were made to isolate just the background correction systems, minimizing as many variables as possible. I was not interested in comparing the two instruments, but instead was interested in comparing the background correction systems incorporated within them,

Sodium chloride was chosen to act as a background absorber in this study, Sodium chloride was chosen as the matrix for several reasons. It turns out that sodium

chloride is widespread in nature and is a classical example of a background absorber. Sodium chloride volatilizes in the form of a white smoke at about 1800 degrees celsius. This so-called smoke blocks a certain amount of the hollow cathode source light and an abnormally high signal is the result. The chloride matrix is frequently encountered in furnace atomic absorption analysis. Biological samples are rich in chlorides and other salts and are frequently analyzed for trace metals. Any sample rich in chlorides and salts requires an efficient background correction system.

The same furnace program was used at each site for this study. The program that was used, showing the time and temperature of each stage, is shown in table 1. It must be pointed out that the program used is not necessarily the optimum program prescribed by the manufacturers in each case. In some cases, the furnace program can be manipulated in such a way so that the matrix volatilizes off before the element of interest, or so that the element volatilizes off before the matrix. This may eliminate the need for a background correction system. We designed our program so that the element, cadmium in this case, volatilized at essentially the same time as the sodium chloride interference. This allowed us to see how effectively

TABLE 1

CADMIUM FURNACE PROGRAM

Stage	Temperature (°C)	Time (Seconds)
Dry	70	5
	110	45
Ash	370	25
Atomize	1800	0 (step)
	1800	5

each background correction system was working. Because cadmium is more volatile than sodium chloride, a step atomization was used so that they both atomized simultaneously. Each instrument was operated in the peak area mode with an integration time of 2 to 3 seconds.

As was stated in the introduction, the use of any background correction system introduces a loss in sensitivity. This phenomenon was investigated on both systems. To study this effect, two cadmium calibration curves were set up on each system - one with and one without the background correction system on. This was done by varying the injection volumes of a 1 part per billion cadmium standard. The standards used during this part of the experiment contained no sodium chloride. Two plots relating absorbance to picograms of cadmium were obtained on each system. The slope of each plot was calculated and from the slopes, the loss in sensitivity due to each background corrector was determined.

After losses in sensitivity were calculated, a precision study was done on each system. The precision study was done using two different cadmium concentrations at two different levels of sodium chloride. To start this portion of the study, a sodium chloride plot was set up with no cadmium present. This was done by varying injection volumes of a .1% sodium chloride solution so

that a plot relating absorbance to micrograms of sodium chloride was obtained. The same sodium chloride and distilled - deionized water was used at each site. The amount of sodium chloride necessary to produce an absorbance unit of 1 and .1 was then determined from these plots. Both instruments were operated in the peak height mode for the sodium chloride plots. The amount of cadmium required to produce .005 and .020 absorbance units was then determined from plots constructed in the loss in sensitivity study. The precision study was then done by doing 20 separate determinations on 4 different solutions. The first solution contained enough sodium chloride to produce an absorbance unit of 1.0 in peak height and enough cadmium to produce .005 absorbance units in peak area. The second solution contained the same amount of sodium chloride but this time had enough cadmium to produce .020 absorbance units. The third and fourth solutions contained enough sodium chloride to produce .1 absorbance units in peak height with the same amounts of cadmium as before. Both instruments were operated with the background correction systems on. The standard deviation and relative standard deviation was then determined for each solution on both systems.

It is known that a fast moving background causes considerable distortion in the signal when a background correction system is used. It is very difficult, however,

to measure the speed in which a given background is moving. In order to study this effect, a screen was mounted on a jig saw which was plugged into a variac. The screen that was used produced an absorbance unit of .4 when placed in the light path of the atomic absorption unit. By using a jig saw, we were able to move the screen in and out of the light path at different speeds, creating an artificial moving background. In this way, the distortion due to a background moving at different speeds could be studied on both systems.

CHAPTER III

Results and Discussion

Each instrument was tuned to the 228.8 resonance line of cadmium throughout the study. The loss in sensitivity due to background correction on both systems was nearly identical. As can be seen in table 2, the loss in sensitivity due to Smith-Hieftje correction was slightly less than that due to Zeeman correction.

TABLE 2

% LOSS IN SENSITIVITY WITH BACKGROUND CORRECTION

Smith-Hieftje System	16.7
Zeeman System	17.0

Calibration curves on each system are illustrated in figure 10 and figure 11. From the calibration curves, it appears that the Smith-Hieftje is about twice as sensitive as Zeeman. However, this may be due to the geometry of the graphite cuvettes and not an effect of the background correction system.

Both systems gave identical sodium chloride calibration curves. The sodium chloride curve that was generated is illustrated in figure 12. It was interesting that the sodium chloride curve was linear

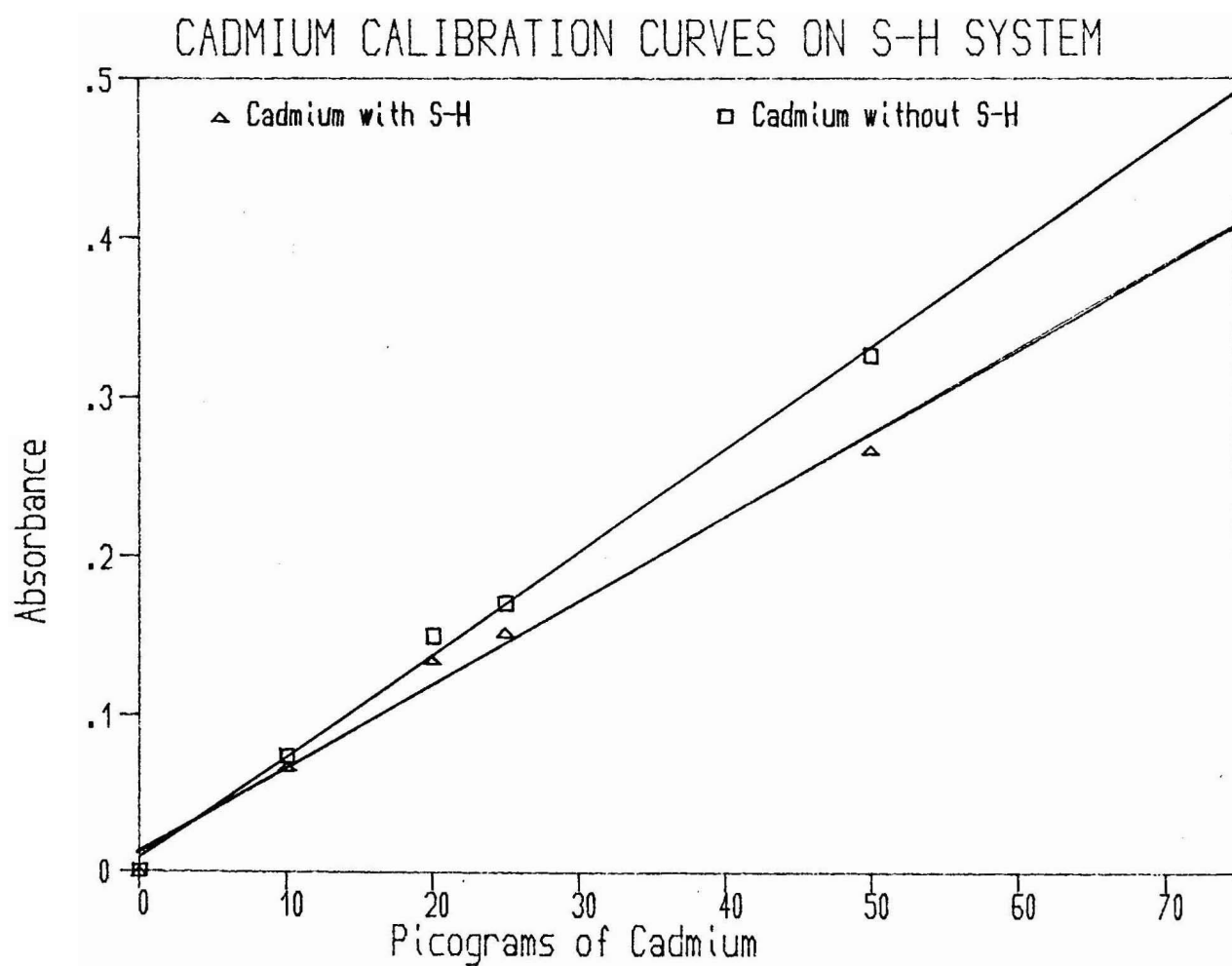
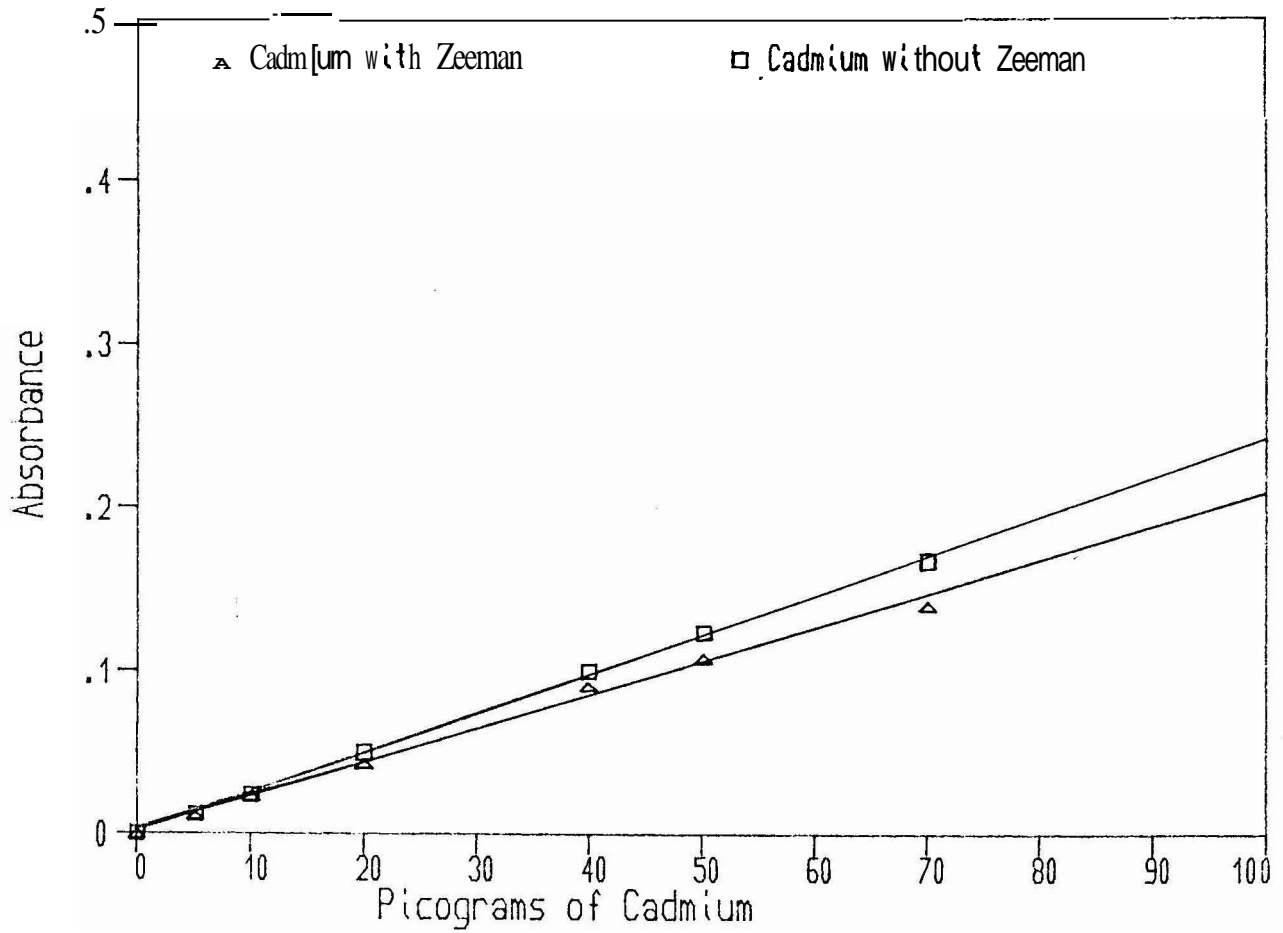


Fig. 10. Cadmium Calibration Curves on the Smith-Hieftje System.

CADMIUM CALIBRATION CURVES ON ZEEMAN SYSTEM



Fig, 11. Cadmium Calibration Curves on the Zeeman System.

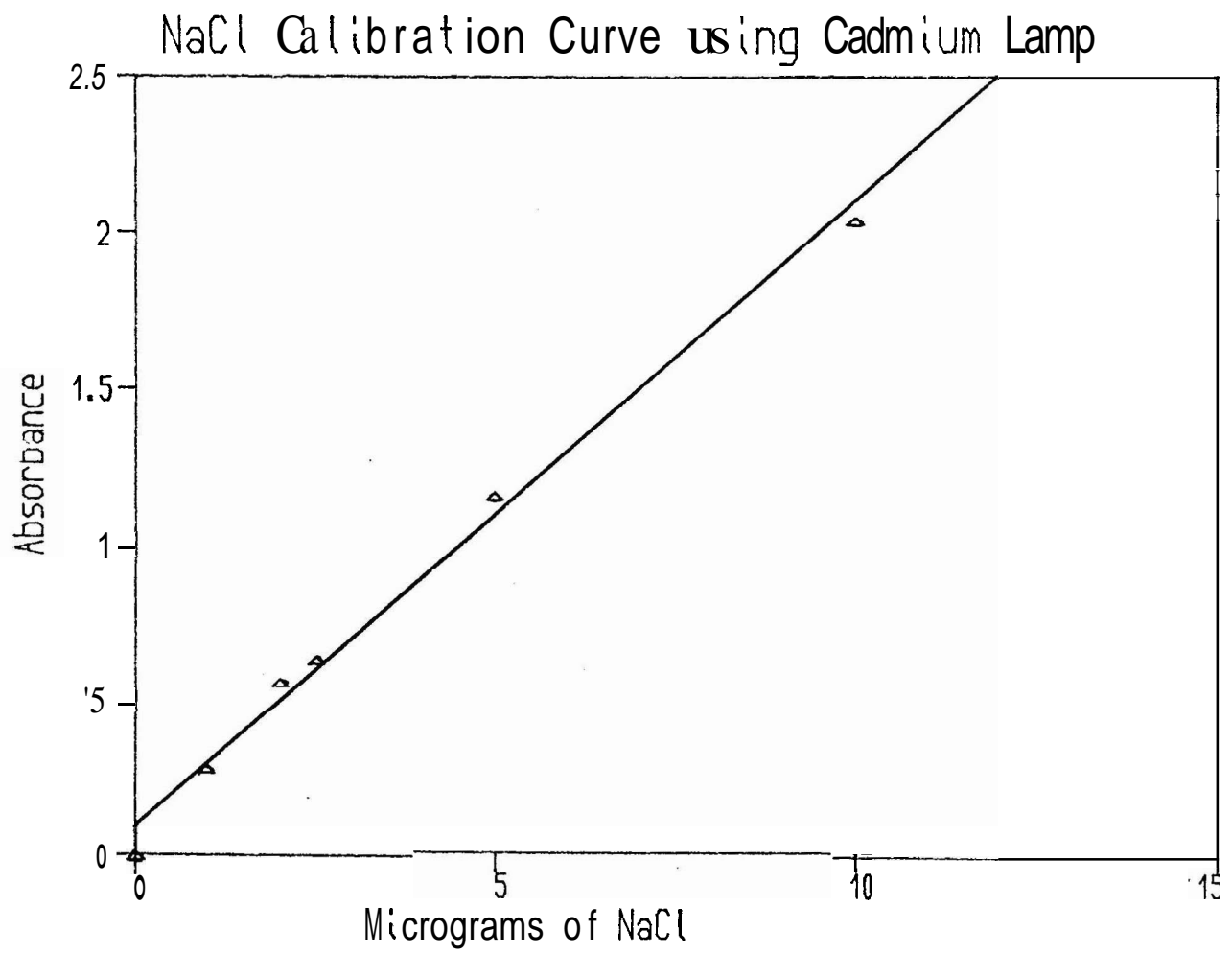


Fig. 12. Sodium Chloride Calibration Curve.

to about 3.5 absorbance units in each case. The sodium chloride curve was generated with the instruments in the peak height mode with the background correction systems off.

Tables 3 and 4 show results of the precision study. The levels of cadmium and sodium chloride that were used were determined from the calibration plots that were previously obtained. It required about twice as much cadmium to generate the same signal on the Zeeman system. The lower level of cadmium produced a higher relative standard deviation in both cases. However, the Zeeman system consistently gave better precision values throughout the study. As can be seen in tables 3 and 4, the Smith-Hieftje system seemed to have a little more trouble correcting at higher levels of sodium chloride. The important thing to note is that both systems corrected for the sodium chloride interference fairly well. Since an autosampler was used on the Zeeman system, slightly better precision values were expected.

While doing the precision study, we noticed that there was considerable distortion in the signal at higher levels of sodium chloride on both systems. This effect is shown dramatically on the Zeeman system in figure 13. The dotted line in figure 13 represents an uncorrected signal due to 2.5 picograms of cadmium and 8 micrograms of sodium chloride. The solid line

TABLE 3

PRECISION STUDY ON ZEEMAN SYSTEM

Amount of Cd and NaCl	Average Absorbance Value	% RSD
2.5 pg Cd	.0056	13.3
2.5 pg Cd ; 0.8 ug NaCl	.0055	11.0
2.5 pg Cd ; 8.0 ug NaCl	.0059	12.0
10 pg Cd	.0249	2.5
10 pg Cd ; 0.8 ug NaCl	.0244	1.6
10 pg Cd ; 8.0 ug NaCl	.0237	3.9

TABLE 4

PRECISION STUDY ON SMITH-HIEFTJE SYSTEM

Amount of Cd and NaCl	Average Absorbance Value	% RSD
1.25 pg Cd	.0090	17.4
1.25 pg Cd ; 0.8 ug NaCl	.0086	23.2
1.25 pg Cd ; 8.0 ug NaCl	.0115	14.4
5.0 pg Cd	.0277	5.4
5.0 pg Cd ; 0.8 ug NaCl	.0289	7.0
5.0 pg Cd ; 8.0 ug NaCl	.0293	8.5

Cadmium in NaCl Matrix

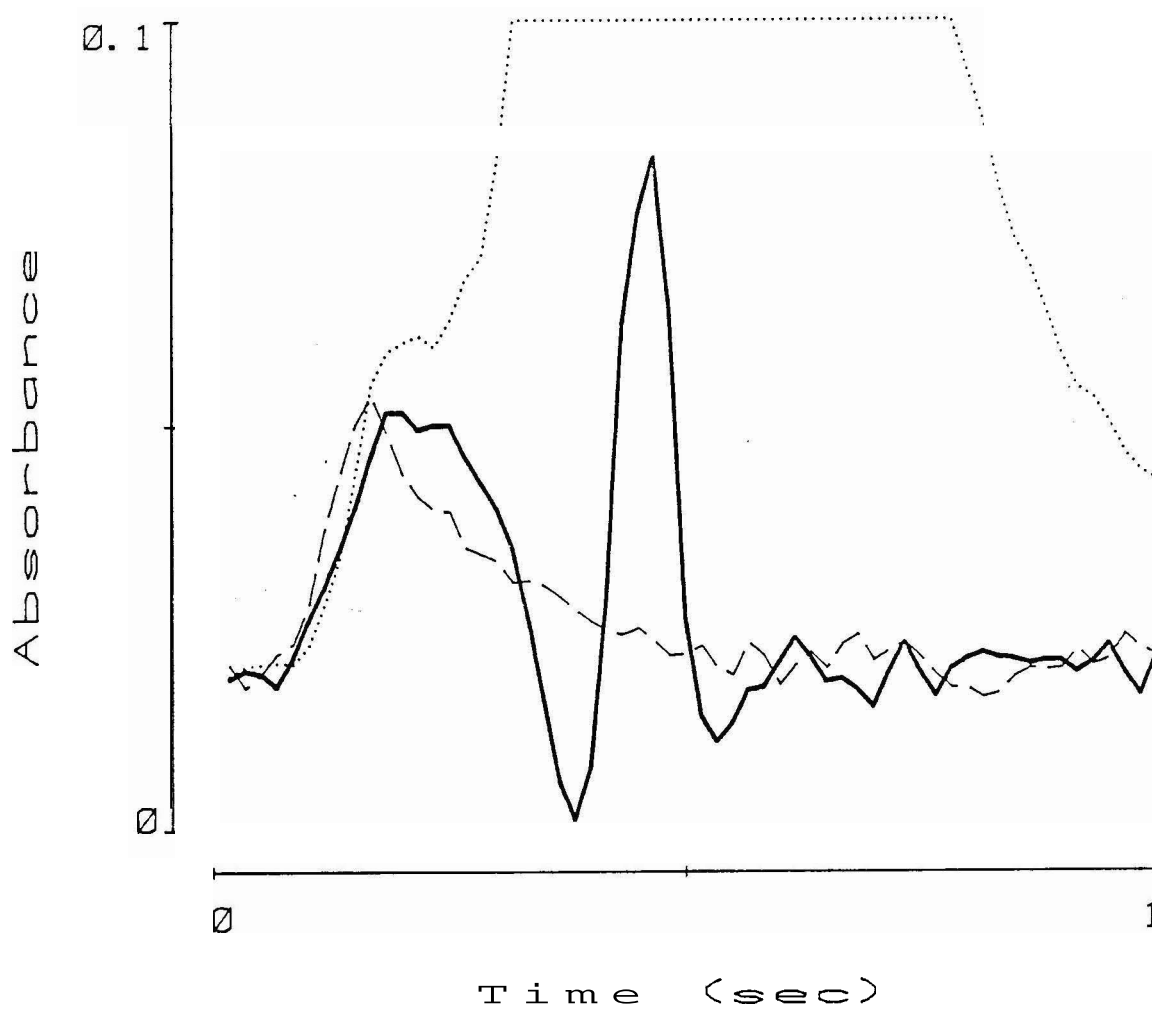


Fig. 13. Illustration of distortion in the Zeeman signal during the determination of cadmium in a sodium chloride matrix. The solid line is the Zeeman corrected signal.

shows the corrected signal with positive and negative distortion. The dashed line represents the atomic signal from 2.5 picograms of cadmium only. It is interesting that the absorbance of the dashed and solid lines are nearly identical even though they look drastically different. This indicates that the positive and negative distortion in the solid line cancel each other so that the net signal is the same.

To study the distortion effect more thoroughly, a .4 absorbance screen was mounted on a jig saw and placed in the light path of each atomic absorption unit. The jig saw was hooked up to a variac so that we were able to vary the speed in which the screen moved in and out of the light path. It was noticed that increased speeds caused much more distortion on both the Zeeman and Smith-Hieftje system. Figures 14 and 15 show this effect on the Smith-Hieftje system and figures 16 and 17 show this effect on the Zeeman system. By using a screen we were able to mimic a fast moving background signal. The point at which the background correction system failed was nearly identical in both cases.

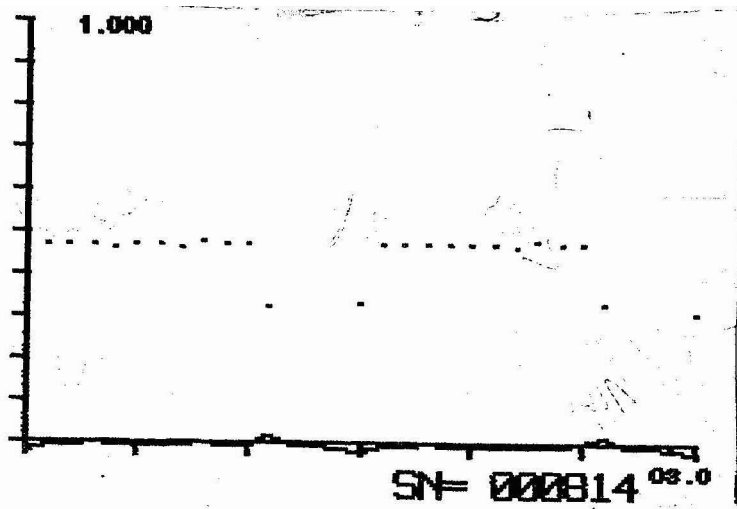


Fig. 14. Distortion in signal on Smith-Hieftje system caused by a slow moving screen. The dotted line is the uncorrected signal and the solid line is the corrected signal.

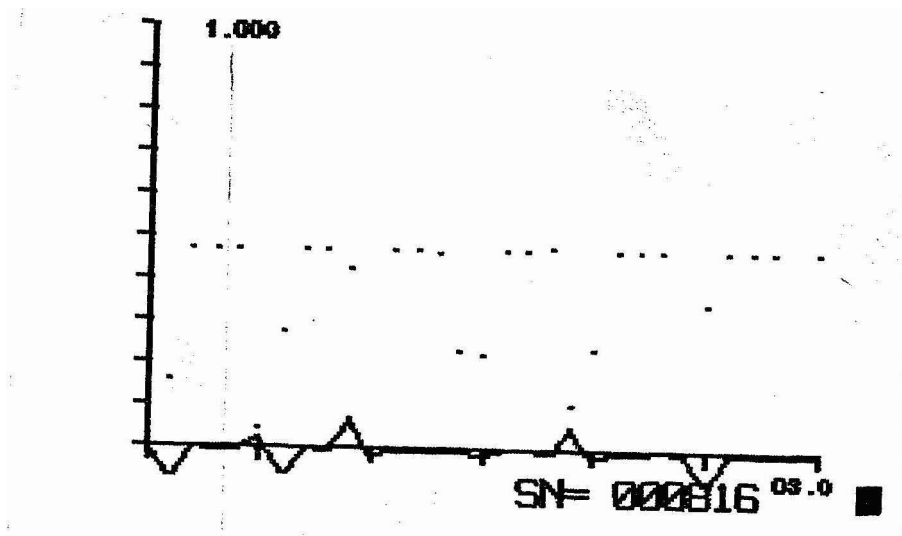


Fig. 15. Distortion in signal on Smith-Hieftje system caused by a fast moving screen. The dotted line is the uncorrected signal and the solid line is the corrected signal.

ARTIFICIAL BACKGROUND

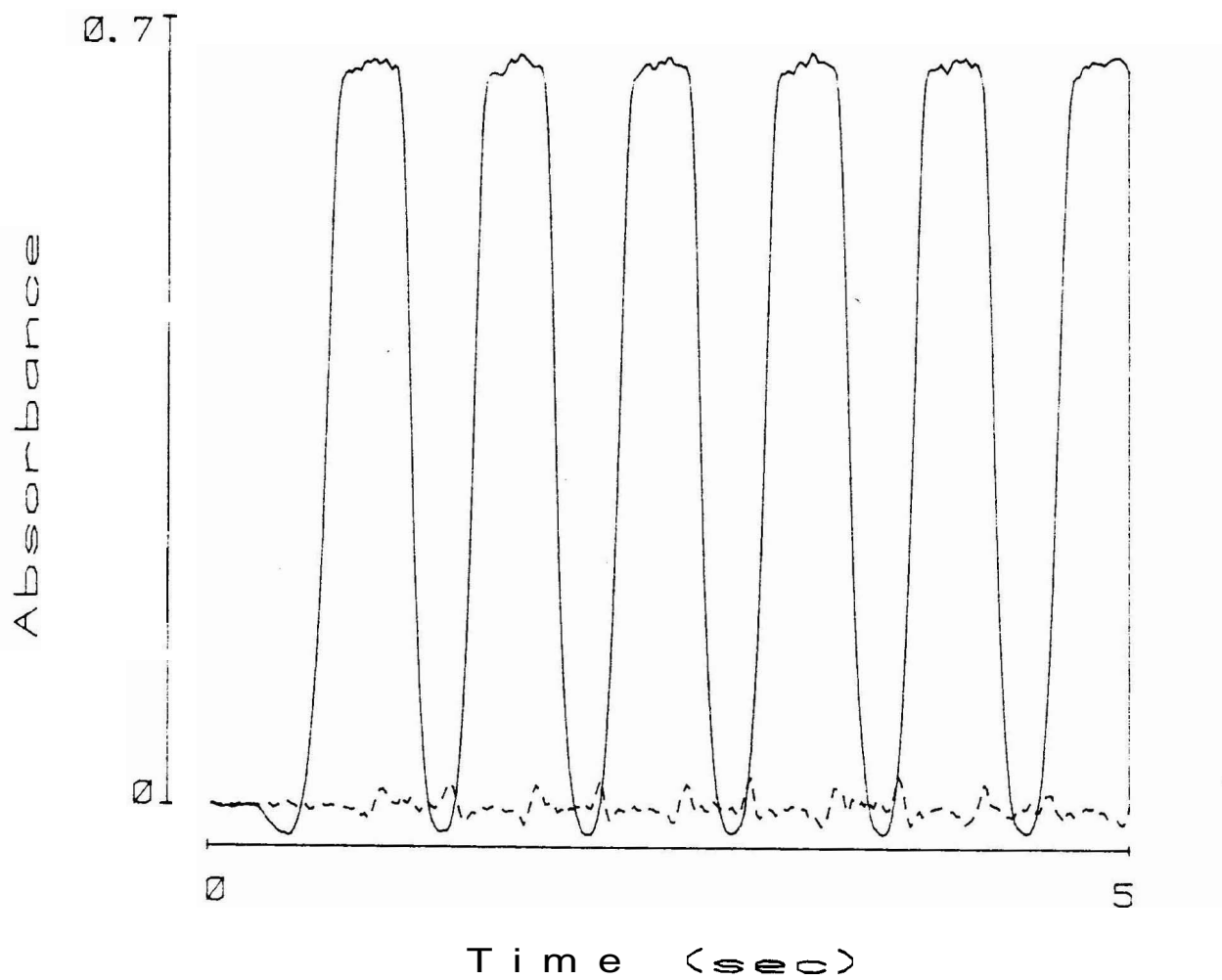


Fig. 16. Distortion in signal on Zeeman system caused by a slow moving screen. The solid line is the uncorrected signal and the dashed line is the corrected signal.

ZEEMAN ARTIFICIAL BACKGROUND

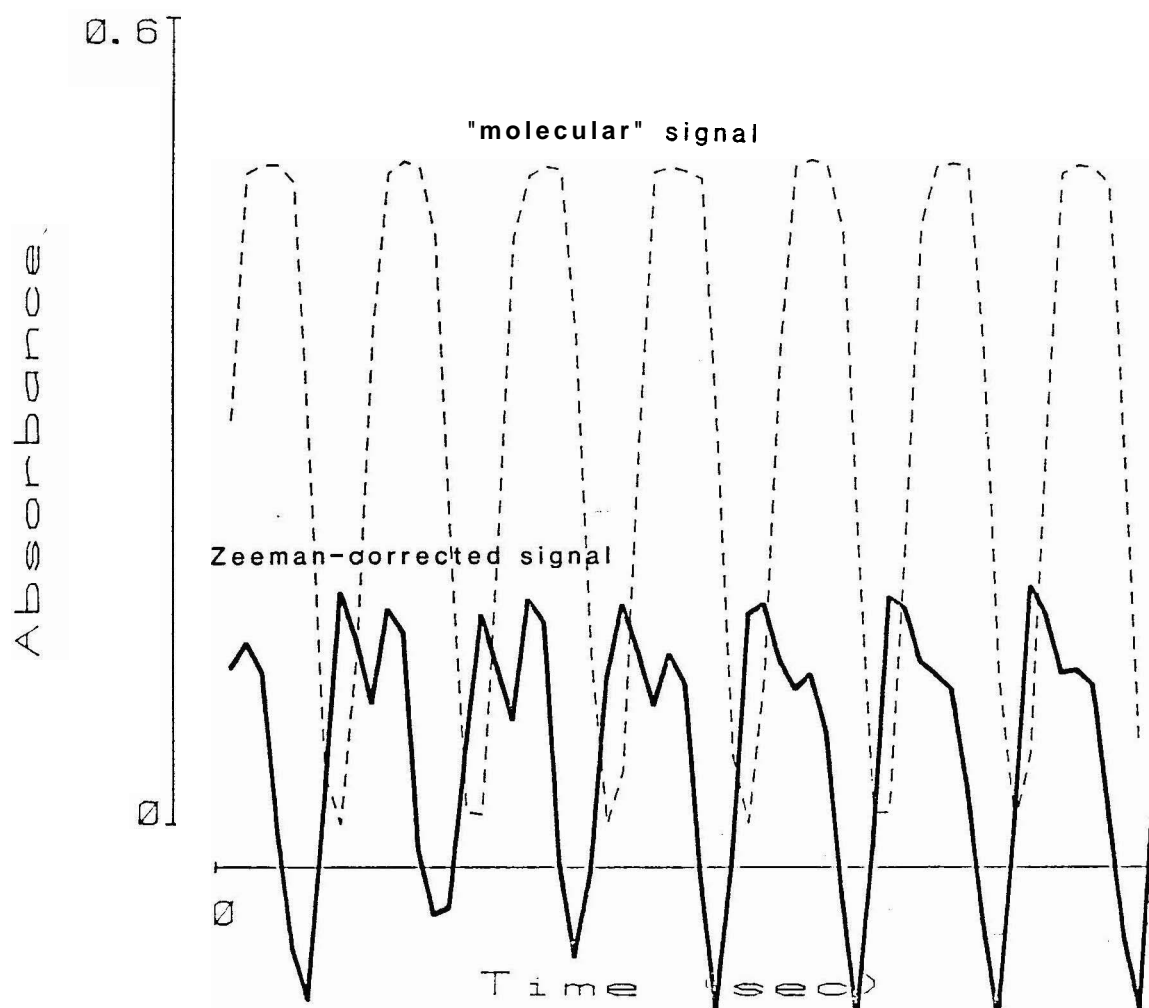


Fig. 17. Distortion in signal on Zeeman system caused by a fast moving screen. The dashed line represents the uncorrected signal and the solid line represents the corrected signal.

CONCLUSION

Background correction in furnace atomic absorption spectroscopy is not only useful, but essential when determining metals in complex matrices. This study indicates that the Smith-Hieftje background correction system is more sensitive than a Zeeman background correction system. However, the Zeeman system gave better precision values at high background levels. The use of either system results in roughly the same loss in sensitivity for the determination of cadmium, and they both show distortion with a fast moving background. Overall, both systems work very well and provide adequate background correction.

To further compare the two systems, other metals should be investigated. Chromium would be an interesting metal to study because of its anomalous Zeeman splitting pattern. Other metals such as lead should also be studied because of its toxicologic concern.

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