Constant temperature electrothermal atomizers as a solution to matrix interferences in atomic absorption spectroscopy
by Lynn Robert Hageman

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:
The application of electrothermal atomization techniques for atomic absorption spectroscopy has increased many fold in recent years. Along with this widespread application, matrix interferences in pulsed-type electrothermal atomizers have been observed. Until recently, few interference studies have involved constant temperature electrothermal atomizers. In this thesis a comparison is made of interferences in pulsed-type versus constant temperature atomizers for various metals.

During the one to three seconds necessary to heat commercial electrothermal atomizers to the desired atomization temperature, many reactions take place and analyte compounds may be lost from the rapidly heating furnace at varying temperatures with varying matrices—often at sub-optimal temperatures with inadequate atomization, since residence times are short. Thus, matrix interferences are common in these pulsed-type atomizers. However, the same solutions, when atomized in a constant temperature furnace (CTP), show no significant matrix interferences. Lack of ruggedness of analytical procedures using pulsed-type atomizers seems to be an inherent limitation, whereas equipment ruggedness limitations of the GTF are amenable to elimination by appropriate attention to engineering aspects of fabrication. Difficult samples representing common matrices reveal the ease of obtaining interference free results directly with the CTF--and the difficulty, even with pretreatments, of correcting for interferences on a routine basis in pulsed-type atomizers.

CONSTANT TEMPERATURE ELECTROTHERMAL ATOMIZERS AS A SOLUTION TO MATRIX INTERFERENCES IN ATOMIC ABSORPTION SPECTROSCOPY

by

LYNN ROBERT HAGEMAN

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Approved:

Ray W. Woodriff
Chairperson, Graduate Committee

Edwin H. Abbott
Head, Major Department

Henry L. Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

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ABSTRACT

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INTRODUCTION

HISTORY

Atomic absorption (AA) has developed into the most widely used technique for analysis of metals and many metalloids [1] since its introduction as an analytical technique about 20 years ago [2]. The widespread use is justified by its versatility, low cost, and high sensitivity. In addition, the high degree of selectivity and relative freedom from interferences are obvious advantages over conventional emission spectrometry. Although considerable research has been aimed at higher sensitivities and lower detection limits, the most ubiquitous and most pressing problem in using the technique is one of matrix interferences - in many cases the response to an analyte in distilled water is simply not the same as the response in a more complex matrix. If all analyte atoms were desolvated, dehydrated, decomposed, and atomized at the same rate regardless of matrix components few interferences would exist [3]. This of course has not been the case for flame [3-5] and most electrothermal atomizers [6-10].

Theoretically, electrothermal (ET) atomization is an absolute method of quantitative analysis by AA spectra involving complete vaporization and atomization of a known amount of substance in a graphite cell. In a 1959 publication by L'vov [11] dealing with ET technique of sample atomization, it is concluded that matrix effects

on the results of the quantitative analysis are eliminated, providing considerable advantage over flame version of atomic absorption as well as over the emission methods of spectral analysis. The conclusion was supported by manganese analyses in the presence of NaCl $Pb(NO_3)_2$, and $Sr(NO_3)_2$. Subsequent publications [12, 13] also indicated absence of matrix effects. But since that early work, numerous publications have appeared in the literature [14-18] dealing with significant and varied interference problems associated with ET atomization for AA spectroscopy. If L'vov's early findings with electrothermal atomizers are correct, interference problems are now present in a technique which theoretically should not have interference problems.

The history of electrothermal atomization use with atomic absorption spectroscopy can be divided into two periods. The boundary between the two periods is sometime in the late 1960's. The first period witnessed the emergence of electrothermal atomization, development, and use by research teams on laboratory designed equipment. The second period, involved the rapid spread of ET atomization methods in analytical laboratories as a promising method of microanalyses due to the advent of commercially available equipment.

Excellent work was done during the first historical period by L'vov in Russia. L'vov developed a graphite atomizer which involves

a graphite tube (40 mm by 2.5 mm) held constantly at a high temperature in the optical path of the AA instrument (see Figure 1,a). The graphite tube is heated to the desired temperature and maintained at this temperature by an electric current and resistance heating. The samples contained in a small carbon cup, are brought to an opening in the side of this tube and heated to attain vaporization and atomization by a separate power supply. The entire atomizer is enclosed in a chamber pressurized with argon. This chamber must be depressurized and the carbon tube must be cooled before the next group of samples can be introduced to the chamber. Extensive work has been done with this type of atomizer attaining very good absolute sensitivities and as has been stated previously with very few matrix effects.

At about the same time that L'vov was developing his graphite atomizer, a similar type was developed by Woodriff and associates at Montana State University [19-21]. It is similar to that of L'vov's in that the graphite tube is maintained at constant temperature in the optical path by resistance heating (Figure 1,b). The sample, introduction, on the other hand, is at atmospheric pressure against a stream of argon. The Woodriff Constant Temperature Furnace (300 mm by 7 mm) is also larger than that developed by L'vov. No auxillary power supply is necessary for the volatilization of

sample. A stream of argon is also used to flush the graphite tube as a means of preventing oxidation.

During this period, Massmann in Germany[22], also developed an electrothermal atomizer. This atomizer consisted of a graphite tube 55 mm long with an inside diameter of 8 mm supported at the ends by water cooled electrodes (Figure 1, e). It employs a different mode of operation than the two ET atomizers discussed previously. The sample is placed in the tube at room temperature. A three step program is then employed - drying the sample near 370 K, ashing the sample from 370 to 1800 K depending on the matrix and finally, atomizing at temperatures as high as 3300 K. A sheath of Ar or N_2 is used to reduce reaction with O_2 in the air.

At the onset of the second historical period, when electrothermal atomizers became readily available through commercial production, the companies involved opted to use the most simple equipment and technique, which is the Massmann design. The Massmann design was adopted essentially without change by Perkin-Elmer Instrument Company, and a mini-Massmann ET atomizer was developed by Amos and Matousek[23] and adopted by Varian Techtron Instrument (Figure 1, d). The mini-Massmann or carbon rod atomizer (CRA) is operated with the same type of three step program as the Massmann, but is much smaller in size (9 mm long with an inside diameter of

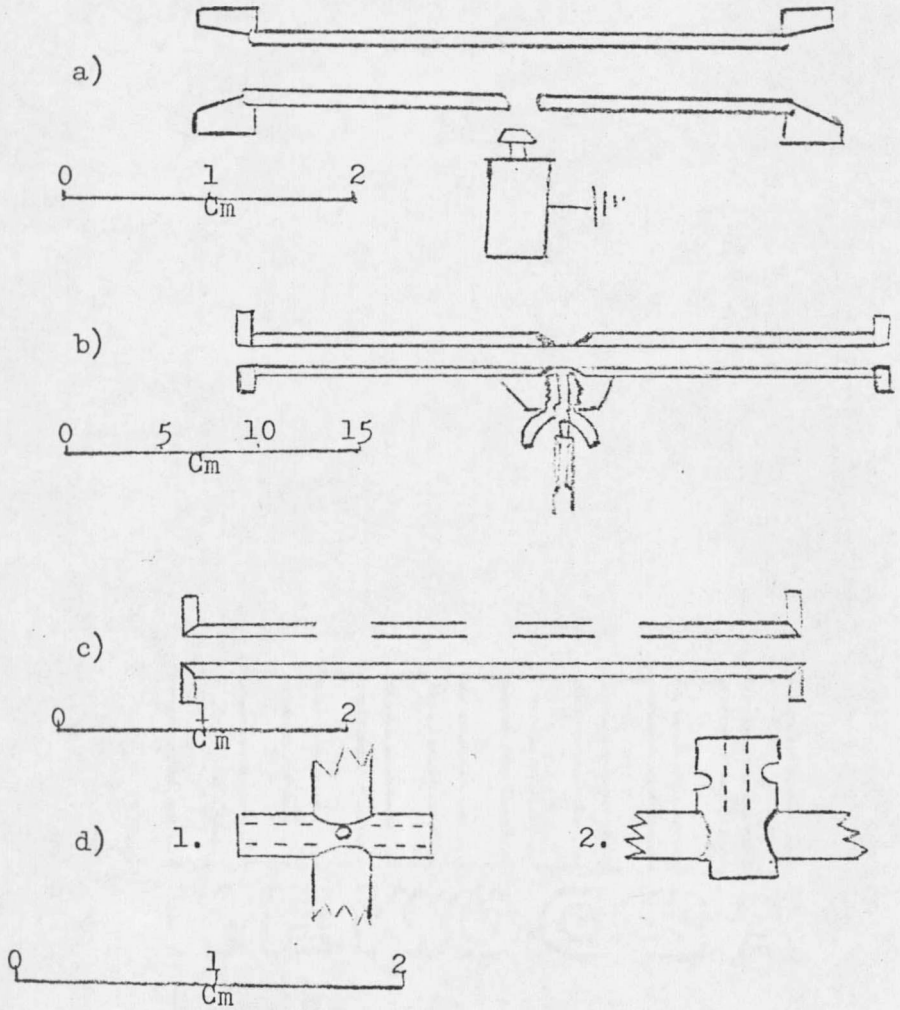

Figure 1. Electrothermal atomizers

a) L'vov Constant Temperature Furnace

b) Woodriff Constant Temperature Furnace

c) Massmann Pulsed-Type Atomizer

d) Varian Mini-Massmann Atomizer
   1. Carbon Rod Atomizer
   2. Carbon Cup Atomizer