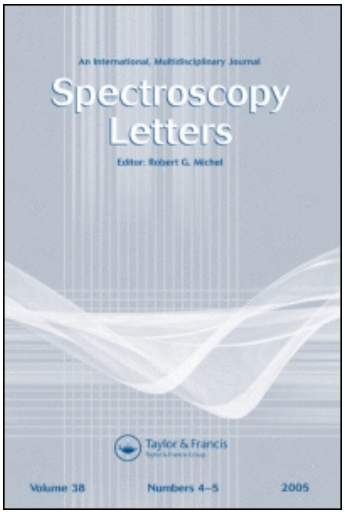

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AN IMPROVED DOUBLE STAGE FURNACE FOR SPECIATION AND QUANTITATIVE ATOMIC ABSORPTION SPECTROMETRY

Key words: furnace atomic absorption spectrometry, double stage furnace

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ABSTRACT

Atomic absorption using furnace atomization suffers from three major problems. First, the matrix causes a change in absorption signal, second, the decomposition products cause a very high, variable background, and third, volatile elements are often lost during the evaporation and ashing steps. These problems are significantly reduced using the double stage system described below.

It consists of a separately heated atomization section, and vaporization section; and a light path which does not pass through the atomization section. This reduces background. The system operates in three modes. With the atomization section hot and the sample placed in the vaporization section, the latter is heated rapidly. This gives a fast quantitative signal with reduced background. With the atomization section cold, the sample is heated leisurely. The metal

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atoms liberated are trapped in the atomization section which is subsequently heated and a quantitative signal obtained. Thirdly with the atomization section hot, the vaporization is heated slowly and speciation data may be obtained.

INTRODUCTION

In 1980, Robinson and Rhodes (1) introduced a double stage furnace, designed for speciation studies. The double stage furnace consisted of two, separately controlled, heating chambers, one contained the atomization chamber and the light path. The other contained the vaporization section. The sample was inserted into the vaporization chamber and heated. Each vaporized compound passed through the hot atomization section, where it was atomized, and then into the light path where the atomic absorption measurement was made. Molecular species were broken down in the atomization chamber to carbon monoxide and hydrogen, which do not absorb strongly in the UV. Since this process took place in the atomization section, before the sample vapor reached the light path, the molecular background problem was greatly reduced. Sample loss was greatly reduced because the entire vaporized sample was forced through the hot atomization section and into the light path.

Designs by other workers followed (2, 3). They were used for quantitative analysis rather than speciation but lost some versatility. A third design, described here, enabled the device to be used for quantitative analysis, while retaining the desirable speciation capabilities.

EQUIPMENT

A schematic diagram is shown in Figure 1

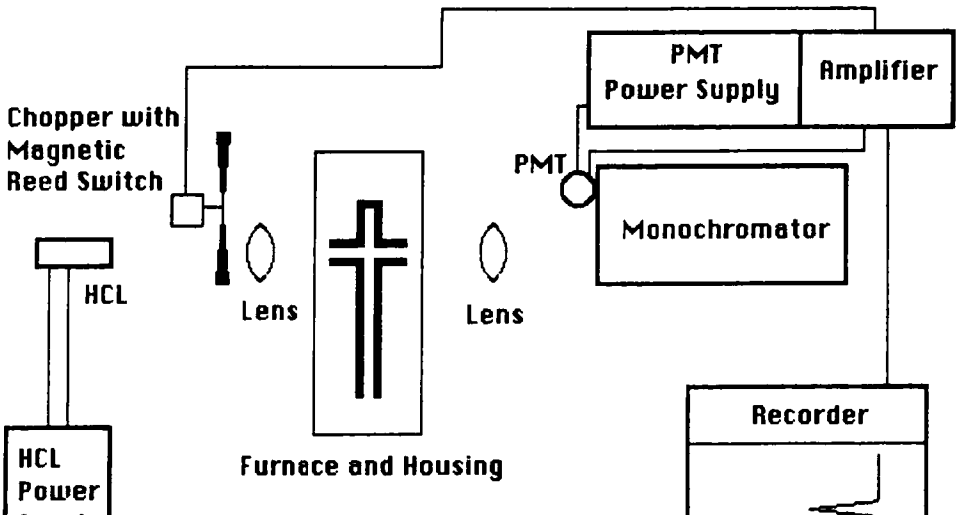


Figure 1

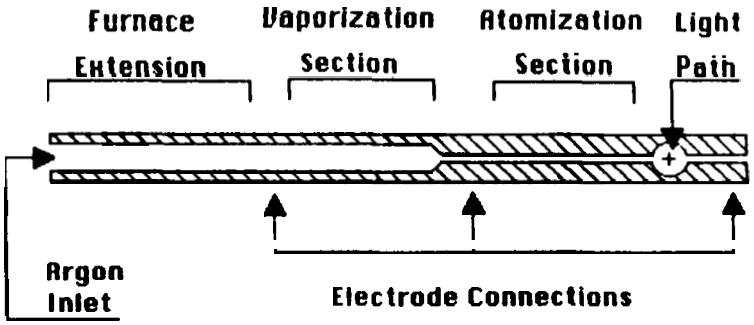
Optical and Electronic Components of the Double Stage Furnace

FURNACE COMPONENTS

1 Modified Electrodes

The front and back electrodes, as well as the tube itself, were redesigned to eliminate the need for the carbon supports. A single tube was used for both the vaporizer and the atomizer in the new furnace design. Thus, it was possible to divide the center carbon electrode into two parts. These carbon supports were positioned above and below the tube to connect the tube with the top and bottom brass, water-cooled electrodes.

Collets were used to clamp the tube directly to the electrode in the new design. The collet design allowed the use of one long carbon furnace rather than two short tubes, as had been used previously. A hose clamp was placed around the collet to tightened the



SIDE VIEW OF THE SINGLE TUBLE USED FOR THE VAPORIZATION, AND ATOMIZATION SECTIONS.

Figure 2

New Furnace Design

grip of the collet on the tube. This provided a better and less complicated electrical connection between the electrode and the tube than provided by carbon supports.

2. Carbon Furnace

A cross-sectional diagram of the furnace is shown in Figure 2. The furnace was machined from a length of 0.615 cm (0.242 in.) diameter carbon rod.

Initially, a mixture of furfuryl alcohol and concentrated HCl was used to cement a cross piece onto the furnace, to extend the light piece. It was determined that no loss of sensitivity occurred if the cross piece was allowed to simply rest on the furnace, without being cemented into place. This method was used throughout most of

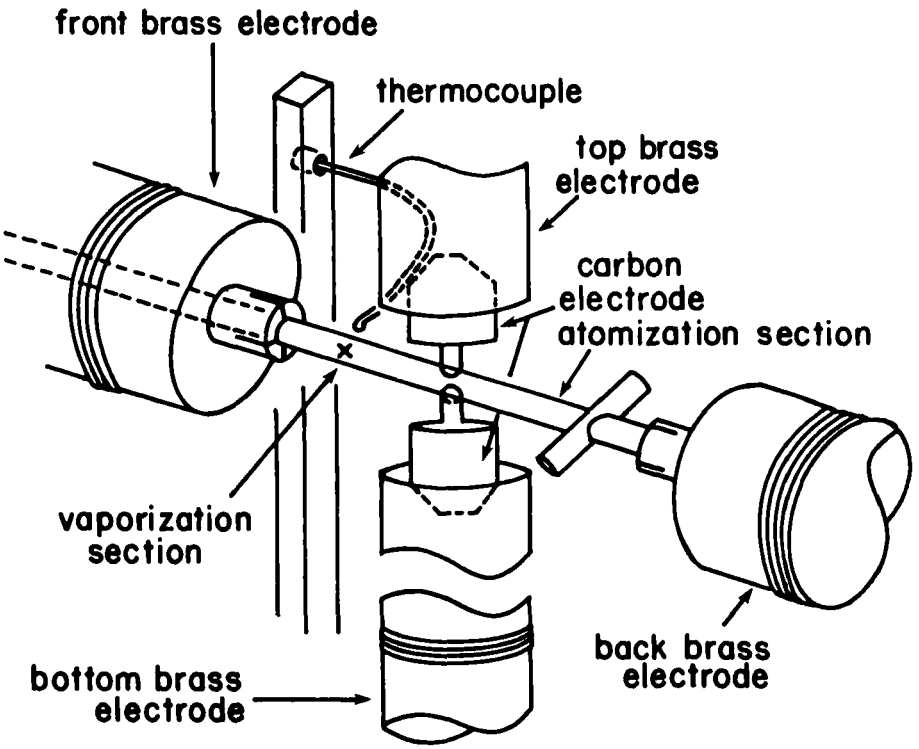


Figure 3

SCHEMATIC DIAGRAM OF TWO STAGE ATOMIZER.

this work. The furnace with cross piece and electrode connections are illustrated in Figure 3.

3. Carbon Rod Sampling Device (CRSD)

The carbon rod sampling device (CRSD), illustrated in Figure 4, was a carbon rod approximately 12.7 cm long and slightly less than 0.38 cm in diameter. Each CRSD was machined from a carbon rod of 0.242 inch (0.615 cm) diameter.

One end, called the sample head, was slightly larger in diameter and had a flat face. A small depression carved into the sample head held 2 - 5 μL of sample. These carbon rods were designed to be slid into the vaporization section from the furnace inlet.

4. Furnace Housing

The furnace housing has been described previously (1, 4).

Electriconic and Optical Components

The major optical and electronic components of the instrument are depicted in Figure 1. Components have been previously described (1, 4).

Temperature Measuring Equipment

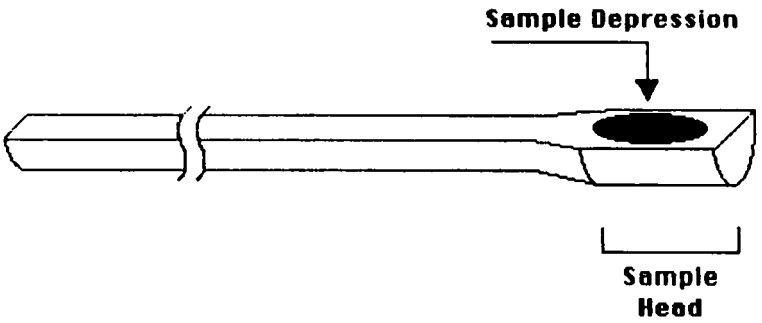
An iron-constantan thermocouple, positioned about 5 mm over the center of the vaporization section was used to measure the temperature of the vaporization section. It was calibrated and related to the furnace temperature with an optical pyrometer (Leeds and Northrup Co., model 8632-0).

Gas Handling Equipment

A diagram of the gas handling system is shown in Figure 5.

Argon was used to purge the furnace housing and as a flow gas through the furnace. In order to minimize gas phase reactions and deterioration of the carbon furnace, the argon was scrubbed with activated charcoal, silica gel and hot copper turnings.

Methane was occasionally mixed with argon. It was obtained from in-house gas lines and passed through activated charcoal and silica gel scrubbers.



THE SAMPLE IS PLACED IN THE SAMPLE DEPRESSION WHICH IS THEN PUT INTO THE VAPORIZATION SECTION.

Figure 4

Carbon Rod Sampling Device

The gases were metered using needle valves and rotometers.

A three-way stopcock was installed between the rotometers and the furnace inlet. In one valve position, the gas flowed through the valve to the furnace. The other position allowed the gas to be vented to the atmosphere. This enabled the flow gas to the furnace to be stopped without adjusting the needle valves at the rotometers.

Sample Dispensing Device

A microliter syringe (Hamilton model 701 - RN) with a 10 cm removable needle was used to place sample directly on the furnace wall.

Chemicals

1. Water

Water was distilled and Deionized (DDW).

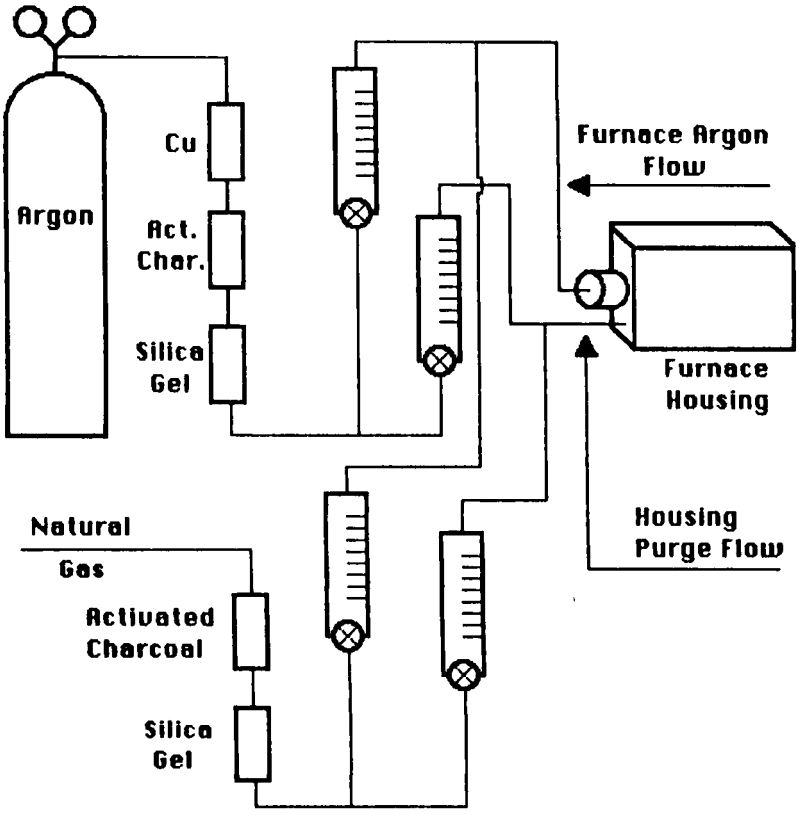


Figure 5

Gas Handling System

2. Standards

Stock standards of 1000 μg/mL were prepared by dissolving the appropriate mass of the element or its salt in DDW or an appropriate acid. Stock standards were stored in polyethylene bottles. Dilute standards were made up daily for quantitative work.

Chemicals used for stock standards were of reagent grade or better.

EXPERIMENTAL

Pyrolysis

To reduce the porosity of the furnace, the exterior was continuously pyrolyzed (5, 6) with a mixture of argon containing 3% natural gas at a rate of 200 - 250 mL/min.

Experimental Paramenters for Quantitative Analysis with the Double Stage Furnace

1. Furnace Temperature

The maximum temperature attainable for the double stage furnace was about 2500°C.

2. Flow Rate of Furnace Housing Purge Gas

The argon flow rate through the furnace housing was usually 200-250 mL/min. The methane flow rate was usually about 4mL/min.

3. Flow Rate of Gas Through the Furnace

The flow rate of gas through the furnace was an important variable since it controlled the time the sample vapor was inside the furnace.

There were at least four factors to be considered. First, the longer the analyte was in contact with the hot carbon, the more efficient the atomization process became. Second, gas phase interactions may decrease the free atom population. The third factor was sample diffusion and loss through the furnace walls. A fourth factor to be considered was the instrument response time, which must be fast enough to follow the signal.

The results from typical flow studies are illustrated in Figures 6 and 7.

4. Atomization Section Warm-up Time

The atomization section usually required about 30 s to reach its maximum temperature.

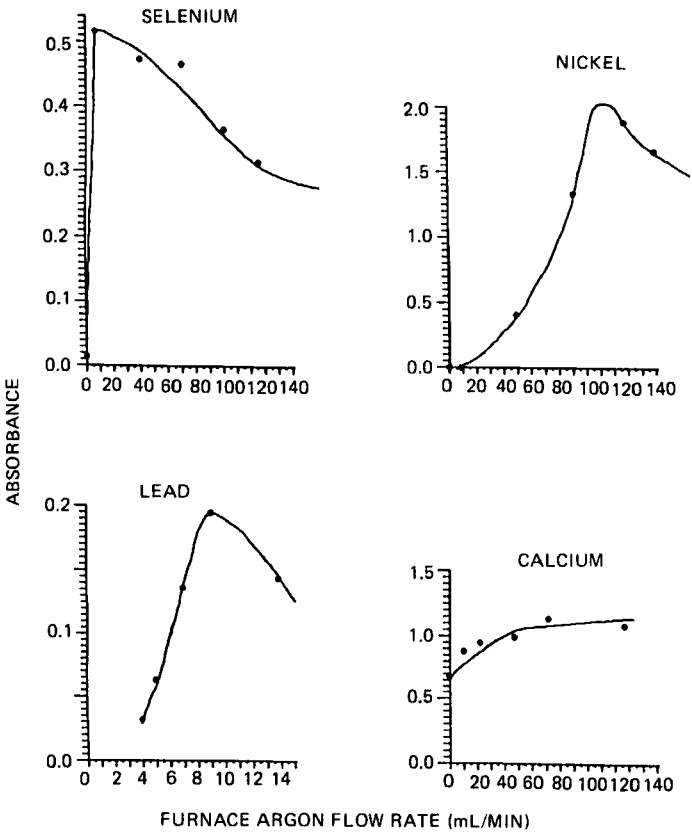


Figure 6

EFFECT OF FLOW RATE ON RESPONSE FOR VARIOUS ELEMENTS

Experimental Modes of Procedure Using the Double Stage Furnace

1. Hot Atomizer, Cold Vaporizer Method

The sample was injected into the cold vaporization section. The atomization section was then heated, followed by heating of the vaporization section, as follows.

1) The argon supply hose was removed from the furnace argon inlet.

2) Sample was placed in the vaporization section.

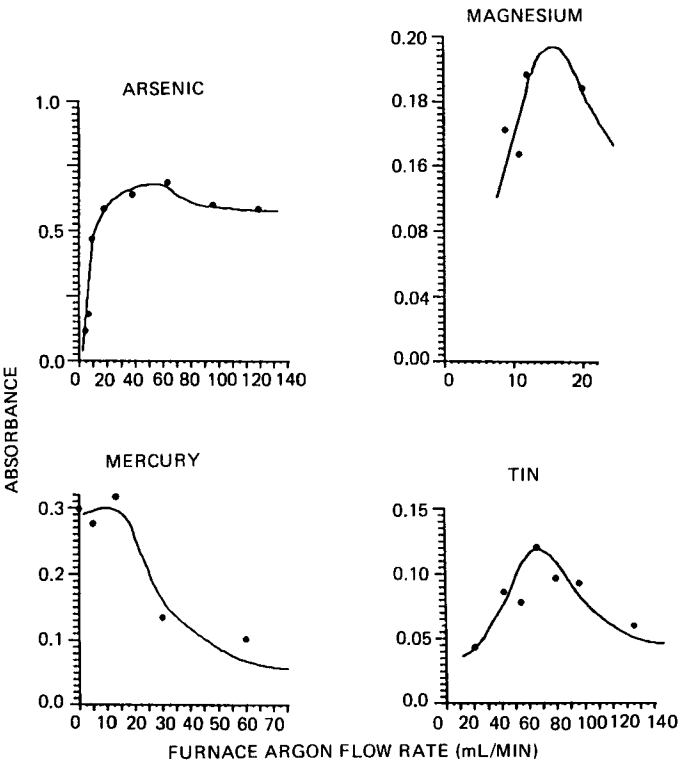


Figure 7

EFFECT OF FLOW RATE ON RESPONSE FOR VARIOUS ELEMENTS.

3) The argon supply hose was reconnected to the furnace argon inlet.

4) The atomization section was heated to its maximum temperature. By conduction, the vaporization section was heated to 100 - 150 °C. This dried the sample. After 25 - 30 s, the atomization section temperature stabilized.

5) The vaporization section was rapidly heated to its maximum temperature. The sample was vaporized, atomized in the atomization section and pushed into the light path.

6) Power to both sections was turned off. The furnace was allowed to cool for 30 - 60 s before the next sample was run.

2. The Cold Trapping Method

The sample was placed inside the vaporization section, which was then heated. Analyte was vaporized and trapped in the cold atomization section. Next, the atomization section was heated to release and atomize the analyte. In the case of mercury, best results were obtained by leaving the atomization section cold throughout, and inserting the sample in the vaporization section and heating.

For other elements the trapping method may be used to trap several aliquots of sample in the unheated atomization section before that section was heated to release the analyte. This allowed the element being determined to be accumulated in the cold atomization section before heating and atomization.

A microliter syringe or pipet was used to load 2 - 5 μL of sample onto the sample head of the CRSD. The sample was dried by heating the CRSD to about 80 °C with a heat lamp. After the sample was dry, another aliquot was added to the CRSD and the procedure was repeated two or three times, as desired. This concentrated the sample by increasing the absolute amount of analyte on the CRSD.

3. Method Modification by the use of the Carbon Rod Sampling Device (CRSD)

The precision associated with some of the above methods was rather poor at times, on the order of 20 - 30 % relative standard deviation (RSD). It was hypothesized that part of the imprecision resulted because the sample was smeared along the furnace wall as the needle was withdrawn. The carbon rod sampling device (CRSD) was designed to overcome this problem.

A microliter syringe or pipet was used to palce 2 - 5 μL of sample onto the CRSD sample head. The CRSD was then slid into the vaporization section and the rest of the steps in the method were carried out with the CRSD inside the vaporization section.

RESULTS

Evaluation of Methods

Table 1 summarizes the sensitivity data for the elements investigated.

1. Hot Atomizer, Cold Vaporizer Method

This method was the most sensitive for five of the nine elements, investigated.

2. Trapping Method

Of the elements examined in this preliminary study the trapping method proved to be the best for magnesium, selenium and mercury. Other elements investigated probably were too volatile to trap or were not released efficiently when the atomization section was heated. Better cooling of the trapping section and other refinements of the procedure should improve the results obtainable.

3. Multiple Trapping Method and Method Modification by Multiple Sample Drying on the CRSD

The purpose of the method and the method modification was to concentrate the sample element. It was found that by trapping two aliquots consequetively the signal was increased by 80 - 100 %, as expected. Repeated trapping should produce similar results.

4. CRSD Methods

The various CRSD methods somewhat improved the sensitivity values for three of the lements studied. Most importantly, the precision increased significantly when the CRSD was used, for example, the precision for lead, selenium and mercury increased from 22 %, 14 %

TABLE 1

Selected Methods and Sensitivity Values for Elements Investigated

(in pg/0.0044 A)

Method	As	Ca	Hg	Mg	Ni	Se	Sn	Pb
At. Hot, Vap. Cold	260+	300+	-	0.6	300	-	2500+	70
Trapping	1100	-	600	0.3+	600			
Multiple Trapping				0.6				
Methods with the CRSD								
At. Hot, Vap. Cold	350				200+	600		
60+								
Trapping			220+			300+		
Multiple Sample Drying								60
Multiple Trapping						300		

(Conc. in μg/ml decreases with increased number of aliquots trapped).

+ indicates that this is the preferred method for this element.

TABLE 2

COMPARATIVE SENSITIVITY VALUES

(in pg/0.0044 A)

Element	This Research	Reference Value	Reference
As	256	160	(7)
Ca	300	3.1	(7)
Cu	150	45	(7)
Hg	220	15000	(7)
Mg	0.3	0.3	(8)
Ni	300	330	(7)
Se	300	100	(9)
Sn	2500	5500	(7)
Pb	60	23	(7)

and 34 % relative standard deviation to 8.7 %, 5.5 % and 9.9 % relative standard deviation, respectively.

Sensitivity

Sensitivity data are summarized in Table 2. The data presented in the table are from the most sensitive methods investigated in this work.

The sensitivity values obtained were comparable to the reference values. However, the calcium and mercury, the differences in sensitivity were much more significant.

The sensitivity for calcium was poor, probably because calcium forms a stable carbide. Since the carbide was probably only slowly vaporized at the furnace temperatures available, it caused the absorption peak to be broadened excessively. The use of a metal furnace may eliminate carbide formation and increase the calcium sensitivity markedly. Peak area measurement may also eliminate the problem.

For mercury, the sensitivity value was nearly two orders of magnitude better than the reference value. This was because much of the mercury is lost in a commercial instrument during the drying and ashing steps (10).

CONCLUSIONS

The double stage furnace, as reported here, is still in the developmental stage, even so, it has several distinct advantages over commercial models.

1. Many Heating Modes

Three basic heating modes can be used. (1) Atomization section hot, vaporization section cold, quickly heat vaporization section - for quantitation. (2) Atomization section cold, vaporization section

cold, quickly heat vaporization section, quickly heat atomization section - for quantitation with trapping. (3) Atomization section hot, vaporization section cold, slowly heat vaporization section - for speciation. Many variations of these basic heating modes are also possible.

2. No Sample Loss

Volatile elements, such as mercury, are easily lost from commercial carbon furnaces during the drying and/or ashing steps. The design of the double stage furnace eliminates this source of error.

3. Reduction of Molecular Background Absorption

The atomization process took place in the atomization section, outside the light path. The water vapor and organic compounds were broken down to carbon monoxide and hydrogen, which did not absorb very strongly in the ultraviolet region. Since this occurred before the vapor reached the light path, the molecular background absorption was greatly reduced.

4. Speciation

None of the atomic absorption systems in wide use allow speciation by thermal analysis, as does the double stage furnace. If a slow temperature ramp is applied to a conventional carbon furnace, any analyte specie vaporized below the atomization temperature is lost as the molecular vapor and not detected (4). The double stage furnace has been used quite successfully for speciation studies. Results were presented in previous publications (1, 4).

5. Solid Sampling Capability

Solid sampling was not investigated during this research, primarily because of the difficulty in the preparation of solid state standards. However, the possibility of using the CRSD with solid

samples existed. A few milligrams of solid could have been placed on the CRSD and introduced into the furnace.

Conventional instruments are not easily adaptable to the analysis of solid samples. The major problem is the high variable background caused by erratic combustion. This would not be a problem with the double stage furnace since the vaporization and atomization processes take place outside of the light path.

6. Versatility

The double stage furnace is capable of speciation, solid sampling and quantitation using a wide variety of methods. Such versatility is unravaled by commonly used atomic absorption instruments.

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