



Development of techniques for non-flame spectroscopic determination of trace metals
by Darryl Duane Siemer

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:

A mercury analysis system is presented which is adaptable to the determination of mercury in any type of sample. Mercury vapor in air or other gases is captured by filtration through gold plated, porous graphite carbon rod atomizer tubes. Mercury in solid samples is converted to the metal vapor by burning the sample in pure oxygen. Mercury in aqueous samples is reduced to the vapor with stannous chloride. The gold plated porous tubes are placed between the rods of a carbon rod atomizer and the mercury atomized and measured with an atomic absorption spectrometer. Substances which normally interfere in the atomic absorption determination of mercury pass through the walls of the porous graphite tubes and are not a problem. Operating parameters and some applications are discussed. Detecting limits in the ppm to the ppb level with relative standard deviations of 4% to 10% range are achieved.

Porous graphite tubes are used as air filters. Particulate matter filtered from the air is analyzed for a wide range of metallic elements by atomizing the material on the tubes directly into the light path of an atomic absorption spectrometer with a carbon rod atomizer. The filtration characteristic of the tubes, standardization, and the applications are discussed. The detection capabilities of the technique for most elements are better than those of most other methods published to date.

A process for coating graphite objects with an impervious coating of pyrolytic carbon is described. The method consists of passing natural gas over the object to be plated inside a wire-wound tubular quartz furnace. The coating process and the properties of the pyrolytic carbon coating are discussed. The pyrolytic carbon coatings are demonstrated to significantly improve flameless atomic absorption atomizers. The process also allows construction of graphite objects useful for other purposes.

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DETERMINATION OF TRACE METALS

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemistry

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August, 1974

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ACKNOWLEDGEMENT

I would like to thank my wife, Judy, for her support and for her patience during my years in graduate school.

Dr. Ray Woodruff deserves special credit for supplying inspiration and advice, and for providing a good environment for research.

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ABSTRACT

A mercury analysis system is presented which is adaptable to the determination of mercury in any type of sample. Mercury vapor in air or other gases is captured by filtration through gold plated, porous graphite carbon rod atomizer tubes. Mercury in solid samples is converted to the metal vapor by burning the sample in pure oxygen. Mercury in aqueous samples is reduced to the vapor with stannous chloride. The gold plated porous tubes are placed between the rods of a carbon rod atomizer and the mercury atomized and measured with an atomic absorption spectrometer. Substances which normally interfere in the atomic absorption determination of mercury pass through the walls of the porous graphite tubes and are not a problem. Operating parameters and some applications are discussed. Detecting limits in the ppm to the ppb level with relative standard deviations of 4% to 10% range are achieved.

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GENERAL INTRODUCTION

The use of atomic absorption spectroscopy as a routine analytical tool began in the nineteen forties, when it was applied to the determination of mercury in air (1). In 1954 a paper (2) was published concerning the use of atomic absorption for the analyses of gases. Up to 1955, the use of atomic absorption spectroscopy for analysis work was confined to the applications discussed in these references.

The primary reason for this dearth of progress in the light of the burgeoning application of various atomic emission techniques was that none of the methods in which atomic absorption measurements had been made by experimental physicists satisfied the practical requirements of an analytical tool from the standpoints of the range of elements embraced, sensitivity, and simplicity. Perhaps even more important was the fact that the potential advantages of absorption methods of analyses with respect to emission methods had not been clarified to the extent to promote research in the field.

In 1955 Walsh (3) and, independently, Alkmade and Milatz (4) published papers indicating substantial advantages of absorption methods over emission techniques for quantitative spectrochemical analysis. During the ensuing years several thousand works have been published on atomic absorption. They were concerned both with research on the mechanisms inherent to the absorption measurements and on the extension of the field to an ever increasing range of substances. The method is now widely used in many countries and has become the most pop-

ular technique of elemental analysis for a wide range of sample types.

The need for more sensitive analytical equipment spurred research in nonflame, pulsed atomizers for atomic absorption (5, 6, 7, 8). These atomizers are much more sensitive and, in some cases, allow chemical analysis of samples with no preconcentration or separation steps. Several versions of these atomizers have been made commercially available by major scientific instrumentation companies within the last three years. The purpose of the work described in this thesis is to extend the analytical capability of these atomizers in the area of environmental analysis by improving both the atomizers themselves and the analytical techniques for which they are used. A widely distributed atomizer, the Varian Techtron Model 63, was chosen as the model to be used for this research both because of its availability to analytical chemists and its potential versatility for different atomization chamber modification.

THE DETERMINATION OF MERCURY IN AIR, WATER, AND SOLID SAMPLES
WITH THE CARBON ROD ATOMIZER

Introduction

The analysis of samples for fractional part per million levels of mercury is a common problem in analytical laboratories. Several excellent reviews have been published recently which discuss the extent of the contamination problem as well as the analytical methodology presently used. (9, 10, 11) There are three basic approaches used for the analysis. The first and oldest technique involves a controlled pH dithizone extraction of mercury from a solution with subsequent spectrometric analysis. This analysis is neither as specific nor as sensitive as are the other two approaches.

The second approach is neutron activation analysis. The absolute detection limits achievable, on the order of 10^{-8} gram absolute (12), are very good; however, it suffers from poor reproducibility, very high cost, and generally involves sending samples off to central facilities equipped with high neutron flux sources. This feature usually necessitates fairly long waits for analytical results.

Atomic absorption, on the other hand, is relatively inexpensive and can be accomplished with readily available equipment. A. A. analysis for mercury is usually accomplished by adding a reducing agent (usually stannous chloride) to a digestate and sweeping the evolved elemental mercury out of the solution into a cold vapor absorption tube in which the absorption of the Hg 2537 Å resonance line is measured. The analytical sensitivity reported varies but is usually on the order of 1 - 2

ng Hg for 1% absorption.

The flameless technique is feasible because mercury possesses the properties of having an appreciable vapor pressure at room temperature and of not being readily oxidized by air. These properties were first exploited by Woodson (13) who described in 1939 a simple instrument for measuring mercury vapor in air. Ballard et al (14 -16) extended the method to solution analysis. They ran the solutions through asbestos pads soaked in cadmium sulfide. Mercury displaced the cadmium and was effectively filtered from the solutions. It was subsequently driven off into the absorption cell by the application of heat. Pappas and Rosenberg (17, 18) employed a modification of the technique for the analysis of solid foodstuffs. The samples were oxidized in a combustion flask, and the gaseous combustion products were absorbed in 1.2 N HCl. The pH was adjusted to 6 - 7 and the solution passed through CdS impregnated pads as previously described.

Poluektov, Bitkun, and Zelyukova (19) were the first to utilize direct reduction of mercury to the elemental state by stannous chloride for cold vapor A. A. determination of mercury. Hatch and Ott (20) applied the technique to acid digested soil and cobalt and nickel metal samples. The most commonly used technique today for mercury determination in a wide range of organic samples was described by Lindstedt (21) who analyzed urine by combining the potassium permanganate-sulfuric acid digestion method of Jacobs and Singerman (22) followed by stannous

chloride reduction of the mercury. The evolved mercury is swept from the solution with a gas stream which carries the mercury into a quartz-windowed flow-through cell mounted in an A. A. spectrometer. The peak absorption of the 2537 Å mercury resonance line is measured.

The reduction-aeration technique is fairly rapid, adaptable to a wide range of samples, and inexpensive, but it suffers from two major weaknesses. As the analysis is commonly performed, the final measurement is subject to the vagaries of kinetics. The rate of flushing gas flow and the rate of mercury reduction by stannous ion, which in turn is affected by the temperature, volume, and chemical nature of the solution, both affect the peak atomic absorption. The second problem concerns other materials present in the sample which volatilize and subsequently absorb radiation at the mercury 2537 Å line. Among these are cyclic organic compounds, sulfides, acetone, and water vapor.

There are several basic approaches to solving these problems. The most obvious way to solve the problems associated with the kinetics of the reduction process is to integrate the atomic absorption peak and use a peak area instead of peak height as the measure of mercury. However, most atomic absorption instruments are not capable of this.

Several ingenious techniques have been developed to circumvent the problem of non-atomic background absorption by compounds. Ballard (16) took readings of the cell containing the mercury vapor on two separate instruments, the first being a unit containing a mercury lamp and the

second a standard spectrophotometer having a wide bandpass (32 Å) and a continuum source. The difference between the two readings is due only to mercury.

Barringer (23) and Ling (24, 25) compensated for non atomic absorbers by using the wings of the broadened 2537 Å line, the center of which has been completely absorbed by passing through an intermediate absorption cell saturated with mercury vapor. This source is insensitive to mercury but is sensitive to other substances which absorb in that region. By comparing this signal with that obtained using the emission line of the mercury lamp with no intermediate mercury filter, a measure of mercury vapor alone is made.

The background method described by Koirttyohann and Pickett (26) and applied by Kahn (27) in which light from a continuous source and a mercury lamp are alternatively beamed through the absorption cell is also useful. Lech, Siemer, and Woodriff (28) ratioed the absorption of a nearby non-resonance mercury line to the 2537 Å line as a means of background correction.

These expedients, with the exception of peak integration, do not eliminate the kinetics difficulties. In order to solve this problem and to eliminate the bulk of the non-atomic absorption interferences, several means of separating and concentrating the mercury alone in a solution or stream of gas have been used. With these techniques, the mercury is collected over a period of time and released and measured

under carefully controlled conditions in a short period of time.

Moffit and Kupel (29) collected mercury in gas streams with specially impregnated charcoal filters. The graphite was then placed into a sampling boat which was swung over a flame in a standard A. A. spectrometer. The sampling boat A. A. measurement did not fully realize the potential of the system.

Another method for the determination of mercury is deposition from solution onto a silver wire or screen, either by chemical deposition (Hinkle and Learned, 30, 31) or electrolysis (Brandenberger and Bader, 32, 33). The collected mercury was driven off the wire by rapid heating and the mercury introduced into and measured in an absorption cell just as in the aeration method.

Vaughn and McCarthy (34), Ulfvarson (35), Lidduns and Ulfvarson (36), and Anderson et al. (37) concentrated mercury in streams of gas onto finely divided gold by amalgamation. All interfering substances passed through the system and were vented, after which the mercury was driven off the gold by heating to 400 - 500 °C into the absorption cell. Lech, Siemer, and Woodriff (28, 42) used gold plated graphite to collect mercury in air or to retain the mercury from solutions dried in plated cups. The cups were then inserted into a Woodriff furnace atomizer for the mercury determination.

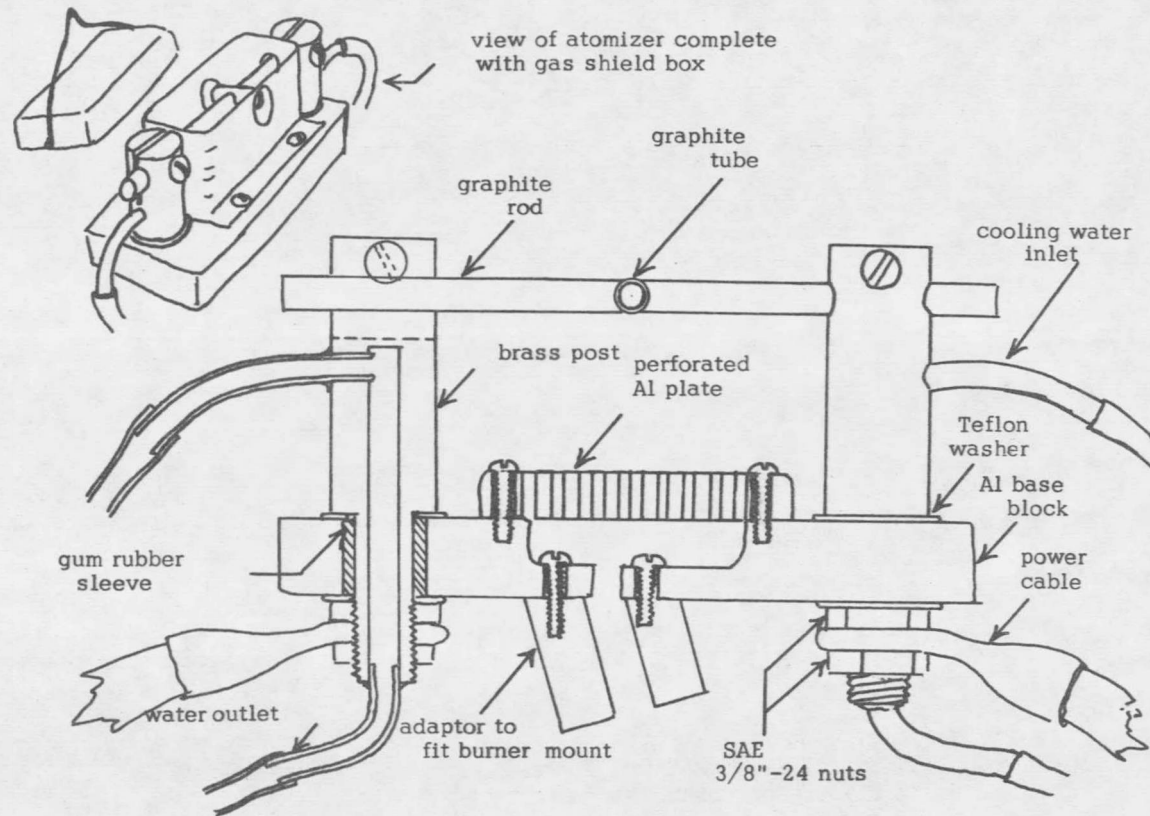
The sensitivity of the furnace technique of Lech, Siemer, and Woodriff was better by a factor of two or three than that of any other A. A.

method reported to date. The only disadvantage of the system as far as the average analytical chemist is concerned is that the Woodriff furnace atomizer is not widely distributed. The purpose of the research to be discussed here was to develop a complete mercury analysis system applicable to a commercially available non-flame atomizer--specifically the carbon rod atomizer.

An outline of the method is as follows. The mercury in the sample is converted to the free metal vapor by stannous chloride reduction or by combustion in oxygen. Then the mercury is carried by a stream of gas into a filter adaptor containing a gold-plated cylindrical tube of porous graphite. The mercury is retained on the gold while potentially interfering gases pass through the tube. The tube is then placed between the rods of a carbon rod atomizer similar to that marketed by Varian Techtron and heated to atomize the mercury. The atomic absorption spike is then recorded.

General Outline of Experimental Technique

The carbon rod atomizer (CRA) was constructed at this laboratory and is depicted in Figure 1. It is designed to fit into a Techtron burner-spray chamber assembly in the same manner that a Varian Techtron Model 63 CRA does. The main functional points of difference between the Techtron CRA and our homemade version is that our model is somewhat larger (to accommodate standard spectrographic $\frac{1}{4}$ " rods and tubes) and features flexible mounting of both rod support posts and a superi-



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Figure 1. Carbon Rod Atomizer

or gas shield system. Nitrogen gas is used to flush the air from around the hot carbon when a sample is atomized.

The CRA is powered with a 5 KVA G. E. transformer (9t21B1037G2) controlled with a type 242, 4.2 KVA Powerstat autotransformer. This power supply provides from 0 to 13 rms volts and can furnish in excess of 400 amps. The temperature of the atomization tube is measured with a Pyro optical pyrometer. Temperatures in excess of 3000 °C are readily obtainable with this system.

The porous graphite tubes are made by drilling a 4.5 mm hole (No. 13 drill) in 15 mm lengths of 6.2 mm diameter National AGKSP or AGKS spectroscopic graphite rods. Each tube is plated on the inside with about 1.5 mg of gold in the following manner: One end is sealed off with a rubber tube sealed with a glass bead; 0.3 ml of an acidified gold chloride solution is placed into the tube; a platinum wire anode is inserted; and the plating current is applied between the tube and the anode for 4 - 5 minutes with a 12 V automobile battery in series with a 75 ohm resistor. The gold solution contains about 5 mg/ml Au. Figure 2 schematically depicts the process.

Figure 3 illustrates the filtration adaptor used to support the gold plated tubes. It is essentially similar to the one described by Woodriff and Lech (38) except that the soft elastomer gaskets seal both ends of the tube with the exception of the air inlet. The body of the filter adaptor is machined from acrylic plastic. The gasket material

