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A critical study of the cold vapor atomic absorption and fluorescence instrumentation for the analysis of mercury is described. Some of the important modifications involve the reduction vessel, absorption cell, fluorescence cell, and radiation source. The new modified systems have much greater calibration sensitivities and lower detection limits than those of systems previously employed. Chemical and physical problems such as contamination and mercury loss are discussed. Finally, an evaluation of the sources of imprecision in the measurements is presented.

This new cold vapor AA and AF system has a capability of analyzing 30 samples per hour, has a detection limit of 1 ppt Hg(II) for AA, and has a detection limit of 7 ppt Hg(II) for AF. The relative precision is 3% above 0.05 ppb Hg(II) for AA and AF, and for AA the relative precision is better than 10% down to 5 ppt. This system is

the first capable of directly analyzing Hg(II) solutions below 0.02 ppb, which makes it highly advantageous for the analysis of mercury in natural waters. It has been used to analyze water samples that are about 10 ppt in mercury.

Cold Vapor Atomic Absorption and Fluorescence Analysis of Mercury

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TO MOM AND SHARON

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COLD VAPOR ATOMIC ABSORPTION AND FLUORESCENCE ANALYSIS OF MERCURY

I. INTRODUCTION

Mercury in the environment is of great current interest because of its toxicological effect on plant and animal life. Sources of mercury are man-made such as industrial wastes, pesticides and fungicides or natural such as mineral deposits. To pinpoint the sources of mercury contamination and to evaluate the levels of mercury contamination in a host of materials, extensive research on mercury analysis has been conducted. This is evidenced by a number of review articles (1-4). Atomic spectrometric techniques have been applied to mercury analysis with the greatest success. In particular the cold vapor atomic absorption and atomic fluorescence methods have received the greatest attention because these techniques normally provide detection limits on the order of 0.5-1.0 ppb and are relatively simple and free from most interferences. The best detection limit reported (66) for these techniques is about 0.02 ppb of mercury (II).

Analysis of mercury in natural water is a particular problem because mercury levels in natural water is often below 0.03 ppb (5, 6). This fact indicated the need for a more sensitive instrument for the direct analysis of mercury in natural waters.

The purpose of this research was to critically study the cold

vapor method for atomic absorption and atomic fluorescence analysis of mercury in order to improve the instrumentation, to lower the detection limit for mercury, and to improve the precision of analysis at sub-part-per-billion mercury concentrations. In addition, it was desired to obtain a more fundamental understanding of variables that affect the technique and of the factors that affect the precision and accuracy of anlaysis.

In brief, modifications to the normal apparatus used for the cold vapor atomic absorption and atomic fluorescence analysis of mercury have been made by reducing the dead volume of the apparatus, by increasing the efficiency of diffusion of elemental mercury into the carrier gas, and by optimizing the instrumental parameters. The time of analysis, sample volume, and the detection limit have been greatly reduced. For a one milliliter sample, the concentration detection limit is 0.001 ppb of mercury(II). The relative standard deviation for 0.05-10 ppb of mercury(II) is approximately two percent. At concentrations below 0.10 ppb Hg(II), imprecision is due mainly to the fluctuations from the radiation source and at concentrations above 0.10 ppb Hg(II), sampling imprecision is limiting. To prevent mercury losses, an oxidizing agent and acid should be used as a preservative and to prevent contamination all glassware must be adequately cleaned with the oxidizing solution.

II. HISTORICAL

Molecular Spectroscopy

Molecular Absorption

The first quantitative spectroscopic method of analysis for mercury was based on the molecular absorption of the mercury-dithizonate complex (7-20). The method was used in the analysis of biological, soil, rock, and air samples. After a sample is digested, the digest is buffered to a pH of 4 to avoid photodecomposition of the complex. The mercury in the digest is extracted into a dithizone-chloroform solution. Spectrophotometric measurements of the mercury-dithizonate complex in chloroform are made at 490 nm. The molar absorptivity of the mercury-dithizonate complex in chloroform has been reported to be 70, 000 l cm^{-1} $mole^{-1}$ (17). With a one centimeter path length spectrophotometric cell, the detection limit of mercury is approximately 0. 1 ppm. The relative standard deviation for 0. 4 ppm mercury-dithizonate was 28% and for 90-97 ppm mercury-dithizonate was 3. 6%.

Metallic interferences must be eliminated before analysis. Three major techniques have been employed and will be briefly reviewed. Two of the techniques involve masking metal interferences with EDTA. However, the major interference, copper, can

still be complexed into the dithizone-chloroform solution. In one method, an aqueous bromide or iodide solution is used to back extract mercuric ions from the organic phase. The mercuric ions in the aqueous phase are re-extracted with a dithizone-chloroform solution and the absorbance of the mercury-dithizonate complex is measured. In the other method, the total absorbance due to mercury and copper dithizone complexes is measured and then the mercury is extracted with an aqueous iodide solution from the organic phase. The absorbance of the copper-dithizonate complex and the excess dithizone is measured and is subtracted from the previous absorbance reading. The difference is the absorbance of the mercury-dithizonate complex.

The final method is based upon the reduction of the mercuric ions by tin(II) chloride and the subsequent aeration of the mercury vapor into a permanganate solution where it is collected and concentrated about four fold. The mercury is extracted into a dithizone-chloroform solution to provide a ten fold concentration and the absorbance is then measured (18).

Molecular Fluorescence

Recently, molecular fluorescence has been applied to the determination of mercury by Holzbecher and Ryan (21). The results to date report the first instance of mercury-induced molecular fluorescence. The determination is based on the oxidation reaction

of mercuric ions with thiamine to produce highly fluorescent thiochrome. The excitation wavelength is 375 nm and the fluorescence intensity is measured at 440 nm. Linear response over 10-500 ppb mercury was reported. The relative standard deviation of the analysis of 50 ppb of mercury(II) was 4.1%. Interferences were less critical than in molecular absorption analysis, although CN^-, I^-, $S^=$, and EDTA quench the fluorescence.

Atomic Spectroscopy

Atomic Absorption (AA)

General. Atomic absorption spectroscopy has been used extensively in the trace analysis of mercury. This technique involves the absorption of resonance radiation by neutral ground state atoms. Atomization of mercuric ions to elemental mercury atoms can be carried out by a flame, by a furnace, or by a graphite atomizer, but the most common means is with chemical reduction followed by aeration. The most commonly used resonance line for mercury is at 2537 Å, but some researchers have used the 1849 Å line because the oscillator strength is 50 times greater than that of the 2537 Å line. In order to measure the absorption at 1849 Å, the apparatus must be evacuated or purged with an inert gas since air absorbs this radiation. The radiation source employed is either a mercury hollow cathode tube, a low pressure mercury vapor lamp, or an electrodeless

discharge tube. Conventional detection systems consist of a monochromator, a photomultiplier tube, an amplifier, and readout device. The following sections describe the various methods of atomization.

Flame Techniques. The development of atomic absorption flame spectroscopy enabled researchers (22-30) to lower the detection limits for the analysis of mercury. Presently, the detection limit for direct aspiration of a Hg(II) solution into a flame is 0.5 ppm of mercury (22).

In 1967, Hingle et al. (24) mixed the mercury solution with tin(II) chloride, a reducing agent, before aspiration into a commercial AA. The atomization efficiency is increased since the reducing agent converted the mercury ions to the neutral ground state. The increase in sensitivity is 16 fold for Hg(II) solutions and four fold for Hg(I) solutions. Without the addition of tin(II) chloride to the solutions, the sensitivity for Hg(I) solutions is greater than Hg(II) solutions. The explanation of this discrepancy lies in the disproportionation of Hg(I) into elemental mercury and Hg(II) ions. Thus, Hg(I) solutions contain elemental mercury atoms before introduction into the flame which increases the concentration of elemental mercury atoms in the flame. To obtain good reproducibility the absorbance is measured immediately after addition of tin(II) chloride to avoid volatilization losses. Non-linearity in calibration curves over 0-50 ppm of mercury was attributed to line broadening in the flame and

self-reversal in the mercury radiation source.

Another method is to preconcentrate by organic extraction the Hg(II) before atomization. Tindall reported extracting Hg(II) as the tetraiodomercurate(II) ion into methyl isobutyl ketone (27). Pyrih and Bisque (25) achieved a six-fold concentration of Hg(II) into a dithizone-methyl isobutyl ketone solution before aspiration into an air-acetylene flame. A detection limit of 50 ppb of mercury in a one gram sample was reported.

Modifications to the normal flame system were first employed in 1958 by Lindstrom (23). Solutions are aspirated into an oxygen-hydrogen flame and the exhaust gases are sent through condensers and cotton filters to remove water vapor and salt mist. The mercury vapor passed into an absorption cell, a glass cylinder with quartz windows at each end and with inlet and outlet ports. The reproducibility was 1.0% for aqueous solutions with 25-500 ppb Hg(II) and the detection limit was 1.0 ppb. Poluektov and Vitkun (26) modified the technique by changing the fuel gases to propane or butane, the aspirator, and the length of the absorption cell. Atomization to neutral mercury atoms is initiated inside the aspirator before entry to the flame by reduction of the Hg(II) ions. The reducing agent, tin(II) chloride, at a flow rate of 0.07-0.4 ml/min and a Hg(II) solution at a flow rate of 8-9 ml/min is premixed with air to produce a mist which is carried into the flame. Upon entry to the flame, the

mercury vapor passes into an absorption cell, either 22 cm or 68 cm long. The reproducibility for 30-200 ppb Hg(II) solutions is about 4.0% and the detection limit is about 10 ppb Hg(II).

Another method suitable for 1-10 ng of mercury involved preconcentration of Hg(II) ions by extraction into a dithizone-chloroform solution (29). The organic phase containing the mercury vapor evolved is passed into an absorption cell where the absorbance is measured. In the final modification, the sample is placed in a tantalum boat and heated in a flame. Mesman et al. (28) preconcentrated mercury in samples by extraction with ammonium-pyrrolidino dithiocarbamate and methyl isobutyl ketone. Two tenths of a milliliter is placed in the boat and solvents were allowed to evaporate before atomization. Moffit and Kupel (30) concentrated the mercury by reducing the Hg(II) ions to mercury atoms with tin(II) chloride. A carrier gas transports the mercury atoms over activated charcoal to absorb the mercury. The activated charcoal is placed in a tantalum boat and heated in a flame. The detection limit is 20 ng of mercury.

Non-flame Thermal Techniques. Non-flame thermal techniques involve the atomization of mercury by direct combustion of samples in an electrically heated furnace or graphite atomizer. Preconcentration methods before introduction into the furnace have been used. The following material describes these methods of atomization.

Furnace atomizers have been employed in the direct combustion

of samples (31-37). Goleb reported one of the lowest detection limits, 0.01 ng of mercury, and a relative standard deviation for a 1.79 ppb mercury sample of 2.8% (36). A rock sample is placed in a furnace and heated, and the resulting vapor is swept into an absorption cell. Thomas et al. (37) developed a method for the direct determination of mercury in fish. Fifty to 150 mg samples are heated in a 900° C air stream. The exhaust gases are passed over copper oxide to insure complete combustion of organic matter and through a heated silver wire, a caustic scrubber, and an Anhydrone-Ascarite filter to remove halides and oxides of sulfur and nitrogen from the gas stream. The remaining mercury vapor passed into an absorption cell and the absorbance was integrated to improve precision. The response is linear between 0.05-3.0 ppm with a relative error of ±10%, and a single analysis took eight minutes.

The popular graphite atomizers for direct combustion of samples have been used in mercury analysis. L'vov and Khartsyzov (38) used a carbon rod atomizer and monitored the absorbance of mercury at 184.9 nm.

Later Robinson et al. (39) applied the graphite atomizer to the analysis of mercury in the atmosphere. As air is drawn through a bed of hot carbon, the oxygen is converted to carbon monoxide and mercury compounds in the air are reduced to the atomic state either by reaction with the hot carbon or with carbon monoxide. The

spectrographically pure carbon is heated to 1350° C with a radio-frequency coil and the absorption cell is heated to 900° C. Compressed air was found to contain no measurable amounts of mercury. Comparisons were made between the 184.9 nm and 253.7 nm lines for a mercury pen lamp, for an ozone lamp, for a commercial mercury hollow cathode tube, and for two demountable hollow cathode tubes (one with a solid copper hollow cathode with amalgamated mercury and the other filled with mercury(II) chloride and fused at 280° C). No significant differences in sensitivity were noted except for the demountable hollow cathode with the mercury(II) chloride cathode which yielded a much higher sensitivity compared to all the other lamps at 184.9 nm and to all lamps at 253.7 nm. The result was attributed to the fact that this lamp had less free mercury to cause self-reversal and self-absorption. The detection limit is 0.5 $\mu g/m^3$ of mercury in the air. Although a number of designs have been used for the graphite atomizers, the detection limit for a 1 μl sample of 0.45 ng reported by L'vov is little different from the 0.1 ng detection limit reported for the more recent mini-Massman carbon rod (40).

Preconcentration by collection of the mercury on cadmium sulfide pads (41-45) and by amalgamation on copper (46-48), silver (49-52), and gold (53-62) has been employed. In the first method Hg(II) solutions were filtered through cadmium sulfide pads on which

the Hg(II) precipitated as the HgS salt. The mercury impregnated pads were heated in a furnace, and a nitrogen carrier gas transported the mercury atoms into an absorption cell where the absorption at 253.7 nm can be measured, down to 0.01 μg of mercury (45).

Most amalgamation techniques involve collection of mercury from an air stream. First, the mercury in the sample is atomized either in a furnace or by reduction with tin(II) chloride and the mercury atoms pass over an amalgamator in a carrier gas. For collection from a solution, mercury is directly amalgamated on silver metal placed in the solution. After collection is completed, final atomization is carried out by heating the amalgamator in a furnace or by direct electrical heating of the metal. The resultant mercury atoms are transported to an absorption cell by a carrier gas and the absorbance is measured.

Recently, Long et al. (52) made an extensive study on the collection of mercury from ambient air. The collector capacity of gold wire, silver gauze, and silver wool was compared and the silver wool showed the highest collection capacity. Mercury calibration curves extend from 0.5-594 ng and the relative standard deviation of analysis is within 11% at 0.5 ng and 3% above 6 ng of mercury. The detection limit is 0.3 ng of mercury.

Cold Vapor Technique. The reduction-aeration cold vapor technique involves the atomization of Hg(II) ions to neutral mercury

atoms by chemical reduction with a suitable reducing agent. The sample solution is purged with a carrier gas which transports the neutral mercury atoms to an absorption cell where the absorbance is measured (63-86). A number of variations of the basic technique are possible by modification of the overall mercury transport system. In a closed system, the carrier gas is continually circulated through the apparatus to provide a steady-state signal (63-66). In an open system, without recirculation, a peak absorbance signal is produced (67-84). Another method without transport of the mercury by a carrier gas has been developed. After thorough reduction and mixing in a closed container, the mercury vapor above the solution is extracted with a syringe and injected into an absorption cell (82, 83).

An overall description of the reduction-aeration apparatus will be presented, followed by a review of studies made with open and closed systems. Since the Water Quality Control Laboratories of the Environmental Protection Agency have adopted a standard closed system, this system will be described along with the lowest detection limits reported. In conclusion, methods used to overcome interferences and mercury losses will be reviewed.

The atomization apparatus used consists of a reduction vessel, an aeration device, a water vapor trap, and an absorption cell. The reduction vessels used include 20 ml test tubes, 30-150 ml Büchner

filter funnels, 100-250 ml round bottom flasks, 250 ml suction flasks, 300 ml BOD bottles, and 50 ml midget gas impingers. Aeration devices inserted into the reduction vessel have been glass tubes, glass tubes with fused fritted glass ends, and the fritted glass disc in the Büchner filter funnels. An exhaust port in the reduction vessel is connected to a water trap which consists of a drying tube filled with $Mg(ClO_4)_2$ or a normal flask trap (86). The absorption cells are 10-30 cm long cylinders of 5-40 mm internal diameter with quartz windows at each end and with inlet and outlet ports placed approximately one inch from each end. The carrier gases used are air, argon, or nitrogen at flow rates from 216-2000 ml/min. The reducing agent is either tin(II) chloride, tin(II) sulfate, or hydrazine hydrate.

After the sample is placed in the reduction vessel, the reducing agent is added, and the sample is aerated. Depending on the size of the reduction vessel, sample volumes ranged from 1-1000 ml and the reducing agent volumes ranged from 0.5-50 ml.

Studies have been made on the effects of the flow rate, aeration device, sample volume, reducing agent, and carrier gas. Poluektov, Vitkun, and Zelyukova (67) first noticed that an optimum carrier gas flow rate existed which gave a maximum peak absorbance and similar data have been reported by other researchers (68, 73, 74, 77). Linstedt found that fastening a sintered glass filter to the end of the aeration tube resulted in a 50% increase in the peak absorbance (68).

Gilbert and Hume have shown that smaller volumes provide lower absolute detection limits (0.5 ng of Hg for a 5 ml sample and 2.0 ng of Hg for a 50 ml sample). However, they also indicate that larger sample volumes provide lower concentration detection limits (0.12 ppb Hg(II) for a 50 ml sample and a 0.05 ppb Hg(II) for a 100 ml sample) (77). Hwang, Ullicci, and Malenfant reported that hydrazine hydrate is a bettter reducing agent than tin(II) chloride for the analysis of organomercury compounds and of mercury in air. However, both reagents work equally well for fish and water samples. In the analysis of urine, tin(II) chloride worked best. It was reported that a greater response was obtained with argon than air as the carrier gas (74). All the above studies were made with open systems.

A standard closed system was established by Kopp, Longbottom, and Lobring (66) for use in Water Quality Office Laboratories. The reduction vessel is a 300 ml BOD bottle with a stopper which contained the aeration device and exit tube. The aeration device is a glass tube with a coarse porosity frit attached to the end. Following the exit tube is a drying tube filled with $Mg(ClO_4)_2$. The absorption cell is a glass cylinder 10 cm long with a 2 cm internal diameter with quartz windows. A peristaltic pump capable of providing a 1 l/min flow rate is used. Five milliliters of a 10% ($\frac{w}{v}$) solution of tin(II) sulfate is used as the reducing agent. The sample volume is usually 100 ml; however, to lower the concentration detection limit

a sample volume of 200 ml is sometimes used. The time for maximum response is approximately 30 seconds. The concentration detection limit is a 0.025 ppb Hg(II) for a 200 ml sample which yields an absolute detection limit of 5 ng of mercury.

For a closed system without preconcentration of the mercury, the lowest concentration detection limit ever reported (84) is 0.015 ppb Hg(II) with a one liter seawater sample which yields an absolute detection limit of 15 ng of mercury. Finally, for an open system the lowest concentration and absolute detection limit reported is 0.2 ng of Hg for a one milliliter sample volume (74).

Interferences to the Cold Vapor Technique. The major interferences to the reduction-aeration cold vapor atomic absorption technique are spectral in nature. Erroneously high absorbances are obtained when water mist or certain volatile organic molecules are present in the absorption cell with mercury (74, 87-89). A drying tube will eliminate water mist.

To correct for molecular absorption, the absorbance measured with a hydrogen lamp is manually or electronically subtracted from the mercury hollow cathode absorbance to yield the absorbance only due to mercury (88). Windham used a palladium chloride absorber with a closed system. The total absorbance is measured first, then the gas stream is passed over palladium chloride which removes only the mercury by oxidation to Hg(II). The resulting absorbance is

due only to molecular absorption. Subtraction of the two signals gives the mercury absorbance (89). Incomplete digestion or oxidation of the sample may be the cause for organic contaminants. Kopp et al. (66) suggested complete oxidation of samples with a permanganate-persulfate solution. Molecular absorption by chlorine may occur if samples containing high levels of chloride were oxidized. Any volatile molecular species such as Cl_2 can be removed by bubbling air through the sample before analysis.

Atomic Fluorescence

General. Atomic fluorescence analysis has been based on mercury atomization by the flame (90-94), by a furnace (95), and by the reduction-aeration method (96-98). Neutral ground state mercury atoms are excited at either 253.7 nm or 184.9 nm by a suitable mercury lamp and the resultant fluorescence radiation is measured at a right angle with respect to the path of the radiation impingent on the fluorescence cell. Detection of the fluorescence at 253.7 nm is made with a monochromator and photomultiplier tube or with a solar blind photomultiplier tube without a wavelength isolation device.

Flame Techniques. In 1969, the atomization technique used by Poluektov and Vitkun for atomic absorption (i.e. the addition of tin(II) chloride before atomization) was applied to atomic fluorescence to yield a detection limit of 2 ppb (58). Recently, Kirkbright et al. (59)

measured mercury atomic fluorescence in a nitrogen-separated air acetylene flame with excitation at 184.9 nm. The stepwise fluorescence signal at 253.7 nm results from excitation at 184.9 nm of the 6^1S_0-6^1P_1 transition. The 6^1P_1 state crosses over to the 6^3P_1 state because of spin orbital coupling and finally the emission at 253.7 nm ($^3P_1$-$^1S_0$) is observed. When the excitation path between the source and flame is purged with nitrogen to minimize the absorption of the 184.9 nm line by air, an increase in sensitivity was noted. A solar blind photomultiplier tube was used with the monochromator. The fluorescence emission measured corresponded to 15% resonance fluorescence at 253.7 nm and to 85% stepwise-line fluorescence at 253.7 nm stimulated at 184.9 nm. The detection limit is 0.025 ppm and the calibration curve is linear up to 100 ppm for mercury(II).

Non-flame Thermal Techniques. Graphite atomizers have also been applied to the atomic fluorescence of mercury. Robinson et al. (95) applied the same technique described previously for atomic absorption by passing air which contained mercury compounds over hot carbon rods. Fluorescence measurements were made at the 253.7 nm line with the conventional monochromator-photomultiplier detection system. Results showed that carbon monoxide and nitrogen quenched the fluorescence of the mercury. Studies confirmed the

strongest quencher to be the carbon monoxide generated upon heating the carbon rod in contact with air. It was concluded that the technique was unsuitable for direct determination of mercury in air.

Cold Vapor Techniques. In 1971, Muscat and Vickers (96) published results for atomic fluorescence of mercury by using a closed system. The mercury vapor is passed into a fluorescence cell made of square Pyrex tubing (2 cm x 2 cm x 4.5 cm) with two Vycor windows approximately 2 cm by 2.5 cm on adjacent sides and with an inlet at the bottom and an outlet at the top. The excitation source is a mercury pen lamp. External optics focused the excitation radiation on the cell. A monochromator with a solar blind photomultiplier tube is employed to monitor the fluorescence. To 50 ml of sample, three milliliters of ten percent tin(II) chloride is added. The flow rate is adjusted to 4 l/min and within one minute a steady signal is obtained. Calibration curves are linear over the concentration range of 3-600 ng of mercury with the limit of detection being 3 ng or 0.06 ppb. The relative standard deviations for the atomic fluorescence technique were 7% for 40 ng, 3% for 70 ng, and 2% for 130 ng of mercury. The signal for a 70 ng mercury sample increases linearly with slit width over the range of 100-200 μm. The background signal is due chiefly to randomly reflected 253.7 nm radiation and exhibits no measurable noise at slit widths of 1000 μm or less. The signal-to-noise ratio is approximately constant for a 1000 μm or greater slit width. All

subsequent fluorescence measurements were made with a slit width of 500 μm.

The atomic absorption technique and the atomic fluorescence technique were compared with inconclusive results. Blank effects were more serious for atomic absorption measurements due to possible broad band absorption and scatter in the long path cell. When the mercury pen lamp was used for AA measurements, instead of a mercury hollow cathode, the slope of the analytical curve decreased by a factor of two due to the greater width of the 253.7 nm line produced from the pen lamp. The pen lamp is approximately 1,000 times more intense than the hollow cathode tube.

Later, Muscat et al. (97) developed an open system which used for initial atomization the reduction-aeration method or the direct furnace combustion method. The generated mercury vapor from the initial atomization is collected on a silver amalgamator which is then heated for final atomization. In the reduction-aeration method, a mercury(II) solution is reduced with a tin(II) chloride and the resultant mercury vapor is swept into the silver amalgamator by bubbling argon gas through the solution. In the furnace method, solid samples are heated to 800° C in a tube furnace and argon is used to sweep the mercury into the amalgamator. The furnace tube is a fused silica tube with the central part placed in a furnace. A trap containing lead acetate to remove volatile sulfides from the gas

stream is placed between the furnace and the amalgamator. The amalgamator consists of 36 gauge silver wire closely packed in a fused silica tube. Five feet of resistance wire connected to a variable transformer is used to heat the amalgamator for 35 seconds before the mercury is swept into the fluorescence cell.

Standard mercuric chloride solutions are used with the reduction-aeration method. Mercury vapor standards are used to prepare analytical curves for the furnace method. Air in a polyethylene container is saturated with mercury at room temperature. Knowledge of the container temperature allows calculation of the nanograms of mercury per cubic centimeter of air from tabulated values of the vapor pressure of mercury. At 20° C there is 13.1 ng of Hg per cubic centimeter of air. The slope of the analytical curve for the vapor pressure method is greater than the slope of the reduction-aeration analytical curve. The greater sensitivity of the furnace method makes it possible to use smaller samples. A 0.6 ng mercury sample gives a signal twice the blank value and the relative standard deviation for three measurements is 10-20%. The monochromator-photomultiplier tube detector system was replaced by a solar blind photomultiplier since the scatter of radiation is very small. A one millimeter aperture is placed in front of the solar blind detector. This system performed as well as the monochromator-photomultiplier tube system, thus simplifying the instrumentation.

The same month that Muscat and Vickers (96) published their results for the closed system, Thomas and Reynolds (98) reported an open system with the reduction-aeration method. The unit consists of two vessels, one for the reduction-aeration and the other to smooth out the flow rate and to prevent carry over of solution into the fluorescence area. The mercury vapor released does not flow into a fluorescence cell but exists freely from a glass delivery tube. The radiation from a mercury vapor lamp is optically focused on the exiting region. The fluorescence intensity is measured with a conventional monochromator-photomultiplier tube system. Quenching of the fluorescence signal is observed when air, nitrogen, and organic solvents are present. Argon was chosen for the carrier gas. The relative standard deviation for 60 ng of Hg(II) in a one milliliter sample is 5% and the detection limit is 2 ng of mercury.

Atomic Emission. Flame emission spectroscopy (99) provides a detection limit of about 10 ppm for Hg. The development of inert gas plasmas produced by d. c. discharge or induction-coupled high frequency generators has resulted in much lower atomic emission detection limits for mercury. Most systems utilize the standard reduction procedure to produce elemental mercury vapor which is then swept into the plasma for excitation at 253. 7 nm or 184. 9 nm and detected in the usual manner.

In 1970, April and Hume (100) designed a reduction-aeration

vessel from a 30 ml, coarse grade, fritted glass filtering funnel. A rubber stopper with an injection port and an outlet is placed tightly over the top of the funnel. The stem of the funnel is used as the inlet port for the carrier gas. A ten milliliter mercury(II) sample is injected into the funnel and purged with inert gas. Then 0.5 ml of two percent tin(II) chloride is injected into the vessel. The signal reached a maximum in approximately 20 seconds and returned to the baseline in about two minutes. The helium plasma is generated in a torch chamber which has a quartz chimney and an RF coil wound around the entire assembly. The detection limit is 2 ng of Hg for a ten milliliter sample or 0.2 ppb.

One year later Braman (101) developed a membrane probe in which a helium carrier gas transported the mercury vapor to a plasma after the mercury atoms diffused through a latex balloon membrane. The mercury in a 200 ml sample is reduced with three to ten drops of ten percent sodium borohydride. The helium plasma is generated by discharge between two platinum electrodes in a 0.32 ml quartz cell with an inlet and outlet. Mercury emission is stimulated at 253.7 nm. The signal reaches a maximum in approximately two minutes. The concentration detection limit is 0.02 ppb of Hg(II) with an absolute detection limit of 4 ng. The relative precision of analysis ranged from two to five percent. The system was modified for low sample volumes of two to five milliliters to yield an absolute

detection limit of 0.4 ng with a 30 second response time. Braman found that the signal increased with temperature since the rate of diffusion increased.

Next, Lichte and Skogerboe (102) developed a very simple argon plasma emission system in which the dead volume was minimized. The mercury is generated by reduction with tin(II) chloride and the carrier gas in argon. Typical volumes are five milliliters of reducing agent and 0.1-0.5 ml of sample solution. The flow rate is 600 ml/min. Typical relative standard deviations are two percent, the absolute detection limit is approximately 0.1-0.6 ppb, and the accuracy is approximately ±10% or better.

Recently, Kirkbright et al. (103) used an induction-coupled high frequency argon plasma for emission studies on mercury using the 184.9 nm line. The mercury(II) solutions are aspirated directly into the plasma without prior reduction. The monochromator and the path between the entrance slit of the monochromator and the plasma are purged with nitrogen. Results showed that the emission intensity at 253.7 nm is the greatest; however, the signal-to-background and signal-to-noise ratios are much poorer than those for the 184.9 nm emission line. The signal emission at 184.9 nm is less because of absorption by air or quartz and because of the lower response of the photomultiplier tube at the 184.9 nm line. The detection limit is 2 ppb for Hg(II) at the 184.9 nm line. The

calibration curves are linear up to 700 ppm for Hg(II).

Other Techniques

X-ray Fluorescence

X-ray fluorescence has been used to determine mercury in solid and liquid organic samples (104). The accuracy is ±1 ppm in the range of 2-40 ppm for mercury. The average time requirement for each analysis, including sample preparation, was 45 minutes.

Spark Source Mass Spectrometry

Spark source mass spectrometry has been applied to the analysis of mercury in apples from trees that were treated with organic mercury fungicides (105). The mercury is extracted with a dithizone-chloroform solution, mixed with a silver internal standard and graphite powder, and pressed into an electrode. Upon sparking the intensities of silver (m/e) 107, and mercury (m/e) 198, 199, 200, 201, and 202, and the corresponding backgrounds are recorded on photographic film. The mercury to silver ratio is determined by the exposure ratio of mercury to silver after correction was made for the background and the isotopic abundance. The detection limit is about 2 ppb of mercury.

Neutron Activation Analysis

Neutron activation has been employed in the analysis of trace quantities of mercury in various types of samples by many researchers (106-113). The procedures differ mainly in the sample preparation methods. Analysis usually is based upon the reaction Hg^{196} (n, γ) Hg^{197} because it has a half-life of 65 hours, has the largest activation cross-section (4.5 barns), and has a relatively short activation time compared to other mercury isotopes. The electromagnetic radiation emitted by Hg^{197} is about 75% of 68 KeV X-rays and 25% 77 KeV gamma rays. In order to eliminate short-lived interferences, the sample is aged 2-3 days after irradiation. Irradiation conditions vary from thermal neutron fluxes of 10^{12} n cm^{-2} sec^{-1} for 2-3 days to 10^{13} n cm^{-2} sec^{-1} for 2-4 hours. The total counts from the 68 KeV and 77 KeV peaks are related to the amount of mercury in the sample. The lowest detection limit found was reported by Weiss and Bertine (113) at 0.3 ng of mercury.

Sample preparation after activation has been carried out by three major methods. In one method mercury ions are reduced with tin(II) chloride, dissolved in aqua regia, then reprecipitated as the sulfide. The HgS is collected and counted or dissolved and counted. Another method involves the combustion of the sample followed by adsorption of mercury on selenium paper or by liquefaction of

mercury in a liquid nitrogen trap. The collected mercury is placed in a vial and counted. In the last method, the tetrachloromercurate(II) complex is formed and then collected on an anion exchange filtering disc which is placed in a container to be counted. The latter method has a linear calibration curve with 100% recovery for 0.05-250 μg of mercury. In most of the methods a mercuric ion carrier is used to maximize the extraction efficiency.

Electrochemical Analysis

In general, electrochemical methods are less sensitive than spectrophotometric methods for mercury analysis. In one technique (114), mercury is measured by its catalytic effect on the rate of the reaction:

$$Fe(CN)_6^{-4} + 3\ o\text{-phen} \rightarrow Fe(o\text{-phen})_3^{+2} + 6\ CN^-.$$

After a fixed time period, the reaction is stopped and the released cyanide is titrated with electrically generated iodine. Silver must be absent since it exerts a catalytic effect twice that of mercury. The technique is linear over the concentrations of 0.1-1.0 μg of added Hg(II). One other technique (115) involved titration of Hg(II) with iodide and endpoint detection with an iodide-selective electrode. Useful results were obtained down to about 10 μg of Hg(II).

Gas Chromatography

Organomercury compounds in fish have been analyzed by gas chromatography. Chromatographic techniques vary in the procedures used for sample extraction prior to injection into the column. An extraction technique was developed for methylmercury compounds by Westoo (116). The sample is homogenized, acidified with HCl(c), and the methylmercury compounds extracted with benzene. However, the procedure is time consuming and only 70% was extracted. Hartung (117) modified Westoo's technique in order to determine monomethylmercury compounds and dimethylmercury in the same sample. By buffering the sample at a pH of 8.2 with a cysteine-borate buffer, dimethylmercury is stabilized while free monomethylmercury forms a water soluble cysteine adduct. The dimethylmercury is extracted into toluene and then converted to methylmercuric bromide which has a stronger electron affinity and hence sensitivity with the electron capture detector. The remaining sample is analyzed by Westoo's technique although the extraction is made with toluene. Typically, 2-5 foot Carbowax columns at 60-150°C have been used for separation. Electron capture (118), mass spectrometry (119), and a microwave helium plasma emission spectrometer (120) have been used as detectors.

Longbottom (121) separated the organomercury compounds with a gas chromatograph, atomized these compounds with a furnace or

flame, and finally measured the mercury with atomic absorption at the 253.7 nm line. For dimethylmercury the detection limit is 0.02 ng, the response is linear from 0.05 ng to 100 ng, and the relative standard deviation was 1.72% for 5 ng.

Chemical Problems - Mercury Losses

A serious problem in the analysis of mercury is the loss of mercury by volatilization from the solution and by adsorption on the walls of the container. The solutions to the problem are complex and have resulted in contradictory results among a number of researchers. The relative importance of volatilization or of adsorption as the mechanism of loss has not yet been established.

Lindstrom (23) first indicated that losses due to volatilization were important. Later researchers (122, 123) illustrated this importance with the following experiment. Two Petri dishes containing the same concentration of radioactive mercury(II) chloride solution were placed side by side. One Petri dish contained potassium permanganate, and after 24 hours the concentration of the radioactive mercury in it had increased. The Petri dish without the permanganate decreased in its radioactive mercury concentration. It was suggested that the potential needed to reduce the Hg(II) to Hg(I) is small enough that almost any reducing substance could convert Hg(II) to Hg(I). After conversion to Hg(I) disproportionation occurs

$$Hg_2^{+2} \rightleftharpoons Hg^0 + Hg^{+2}$$

with the volatilization of metallic mercury.

Rosain and Wai (124) reported that volatilization losses were negligible compared to adsorption on the walls of the container. Various container materials have been studied for adsorption effects with inconclusive results (124, 125). Corner and Rigler (126) found that bacteria increase adsorption on the container surfaces; however, in bacteria-free mercury solutions, volatilization losses were greater than adsorption losses.

Preservation techniques are not consistent. Acidification to a pH < 2 is recommended by the EPA (127). However, some researchers recommend a pH < 1 (128, 129) and others a pH < 0.5 (124). Potassium permanganate has been used to prevent losses (73, 122). Chloride ions in aqueous or in acid solutions prevent the binding of mercuric ions to the container (130). Container materials studied show that Pyrex glass may be more suitable than polyethylene containers (124, 125, 23). Recently, Feldman studied distilled water solutions containing 0.1-10 ppb Hg(II) stored in borosilicate glass and polyethylene containers for ten days. Those which were untreated or treated with HNO_3, $H_2SO_4 + KMnO_4$, or $K_2Cr_2O_7$ lost substantial fractions of their mercury in this period independent of the container. However, solutions stored in polyethylene and treated with 5% ($\frac{v}{v}$) HNO_3 + 0.05% ($\frac{w}{v}$) $K_2Cr_2O_7$ stayed at full strength for at least ten

days. Solutions stored in glass and treated with 5% ($\frac{v}{v}$) HNO_3 + 0.01% ($\frac{w}{v}$) $K_2Cr_2O_7$ stayed at full strength for as long as five months. The causes of losses in distilled and natural waters were related to suspended and dissolved impurities which can adsorb, complex, and/or reduce any mercury present (131).

III. EXPERIMENTAL

Solution and Glassware Preparation

The stock solutions were prepared from reagent grade chemicals and distilled water as indicated in Table 1.

Table 1. Solution preparation

Reductant:	1 g $SnCl_2$ + 1 ml HCl(c) diluted to 100 ml (1% ($\frac{w}{v}$) $SnCl_2$)
Oxidant:	0.2 g $KMnO_4$ diluted to 100 ml (0.2% ($\frac{w}{v}$) $KMnO_4$)
Mercury:	0.1354 g $HgCl_2$ + 50 ml HNO_3(c) diluted to 1 liter (100 ppm Hg(II) stock solution)

All standards contained 1% ($\frac{w}{v}$) HNO_3(c) and 0.002% ($\frac{w}{v}$) $KMnO_4$ as a preservative and were prepared by dilution of the 100 ppm mercury stock solution and analyzed within eight hours after preparation.

Glassware was stored for 24 hours with a nitric acid-permanganate solution. Afterwards, the glassware was washed with HCl(c), rinsed with distilled water, washed with HNO_3(c), and rinsed with distilled water.

Instrumentation

Atomic Absorption (AA)

For AA both single and double beam systems were employed. The block diagram of the single beam AA instrument is shown in

Figure 1 and the specific components are identified in Table 2. During analysis, the carrier gas, air, flows from the compressed air tank (breathing quality) through a T-bore stopcock, the reduction vessel, a drying tube, the absorption cell, another T-bore stopcock, a flowmeter, two mercury oxidizing traps (chromic acid and acid-permanganate solutions in filtering flasks), and finally into the hood. The two T-bore stopcocks can be turned 90° to allow the solution in the reduction vessel to be evacuated into the filter flask without drawing the oxidizing solutions in the traps back into the line. The drying tube is made from tygon tubing, filled with $Mg(ClO_4)_2$, and sealed with quick-connect ends. Different lengths and diameters of tubing were used as discussed in a later section. The reduction vessel is constructed from a glass sealing tube with a 1 cm porous fit. The structure and dimensions are shown in Figure 2. One end is tapered and the other end is widened to house tightly a no. 20 sleeve type rubber stopper for injection of samples. A glass exit tube is placed beneath the stopper. Pointed impressions are made to stop bubbles from creeping out the exit tube.

The absorption cell was constructed by attaching one inch diameter quartz windows with apiezon wax to the ends of glass tubing. Inlet and outlet ports (3/16" od) were attached about 1 mm from each end. Different lengths and cell diameters were studied as discussed in a later section. To align the absorption cell, it is mounted with

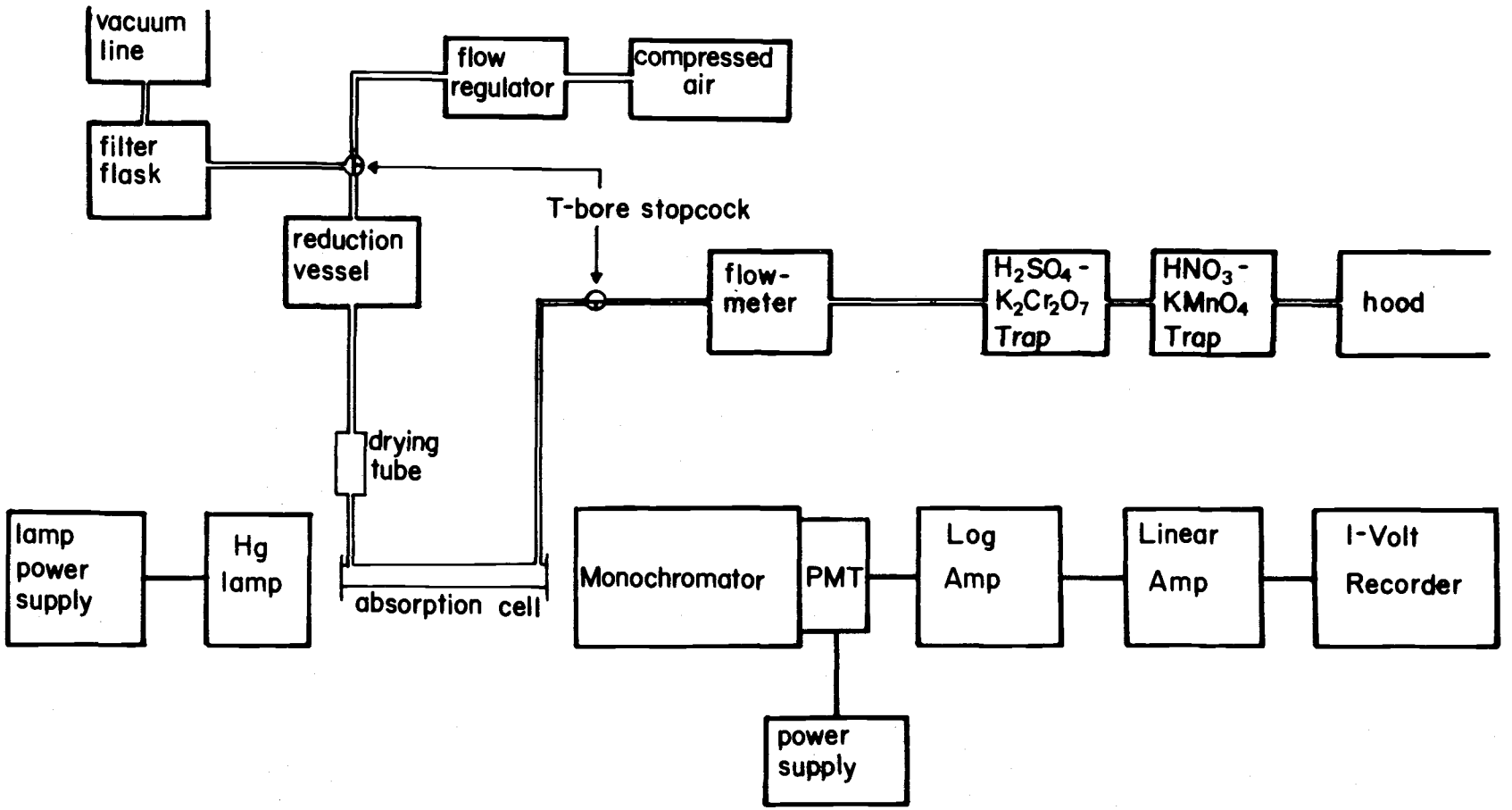


Figure 1. Single beam AA

Table 2. Components of instrumentation

	Item	Supplier and Model
1.	Sources and power supplies	
	mercury pen lamp	Ultra-Violet Prod. -11SC-1C
	AC power supply	Ultra-Violet Prod. -SCT-1
	DC power supply	E/M Co.
	mercury hollow cathode tube	Westinghouse-WL 22847A
2.	Monochromator	Heath-EU-700/E
3.	Photomultiplier tubes, power supplies, and holders	
	sample PMT	RCA-1P28
	power supply	Heath-EU-42A
	holder	Heath-EU-701-93
	reference PMT	HTV-R166 solar blind
	power supply	Keithley-84489
	holder	McKee-Pedersen-MP-1021
4.	Log amplifier	
	log module	Teledyne-Philbrick-4351
	power supply	Analog Devices-915
5.	Log ratio amplifier	
	log ratio module	Teledyne-Philbrick-4361
	power supply	Analog Devices-915
6.	Linear amplifier	
	operational amplifier	Function Models-3801
	power supply	Analog Devices-915
7.	Potentiometric amplifier	Heath-EU- 200-01
8.	Strip chart recorder	Heath-EU-205-11
9.	Flowmeter	Gilmont - F7260
10.	Flow regulators	Matheson - 1 L-AF Matheson - 70 Victor - SR-200

Table 2. (Continued)

	Item	Supplier and Model
11.	Beam splitter housing interference filter (254 nm)	 McKee-Pedersen-MP-1017 Pomfret Res. Optics-20-2357-1
12.	Quartz windows	ESCO Optics Prod.
13.	Syringes (1 ml)	Hamilton-1001-LT Becton, Dickinson and Co. - K179
14.	Optical rail	Oriel - B-22-064
15.	X-Y translation stages	OSU Physics shop
16.	Vertical translator	OSU Physics shop
17.	Tube holders	OSU Physics shop
18.	Sleeve Type Rubber stoppers	VWR 16170-167

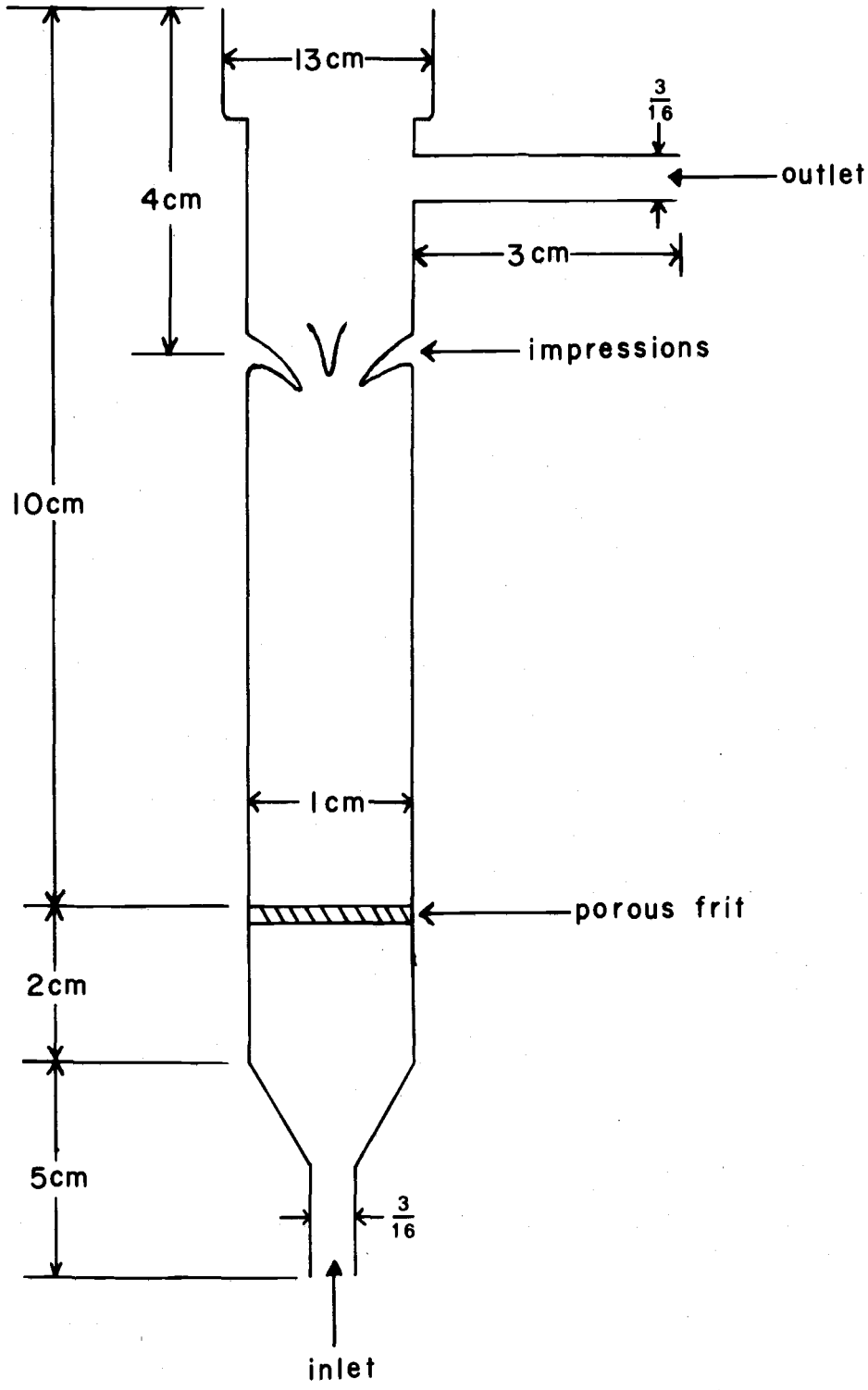


Figure 2. Reduction vessel

tube holders on vertical translators upon an optical rail secured to a horizontal translation stage. The DC lamp power supply for the pen lamp was constructed from a 0-600 voltage source in series with a 20 KΩ ballast resistor and a 20 ma current meter. The linear amplifier was constructed from an OA, power supply, and appropriate connectors mounted in a metal box. Rotary switches allow selection of various feedback precision resistors and of different input precision resistors. The linear amplifier can be used as a current-to-voltage converter with 10^4-10^8 Ω feedback resistors or as a voltage amplifier with gains of 1-10^4. The logarithmic amplifier was constructed from a commercial log amplifier, power supply, appropriate switches, and connectors mounted in a metal box. The operation of the logarithmic amplifier is described by equation 1

$$E_o = k \log_{10} (i_s/i_r) \qquad (1)$$

where

E_o = output voltage, V

k = logarithmic slope, 1V per decade

i_s = input photoanodic current from PMT anode

i_r = reference current, internally fixed to 10^{-5} A.

To improve stability, this single beam system was modified to a double beam system (Figure 3) by addition of a beam splitter between the mercury pen lamp and the absorption cell, by replacement

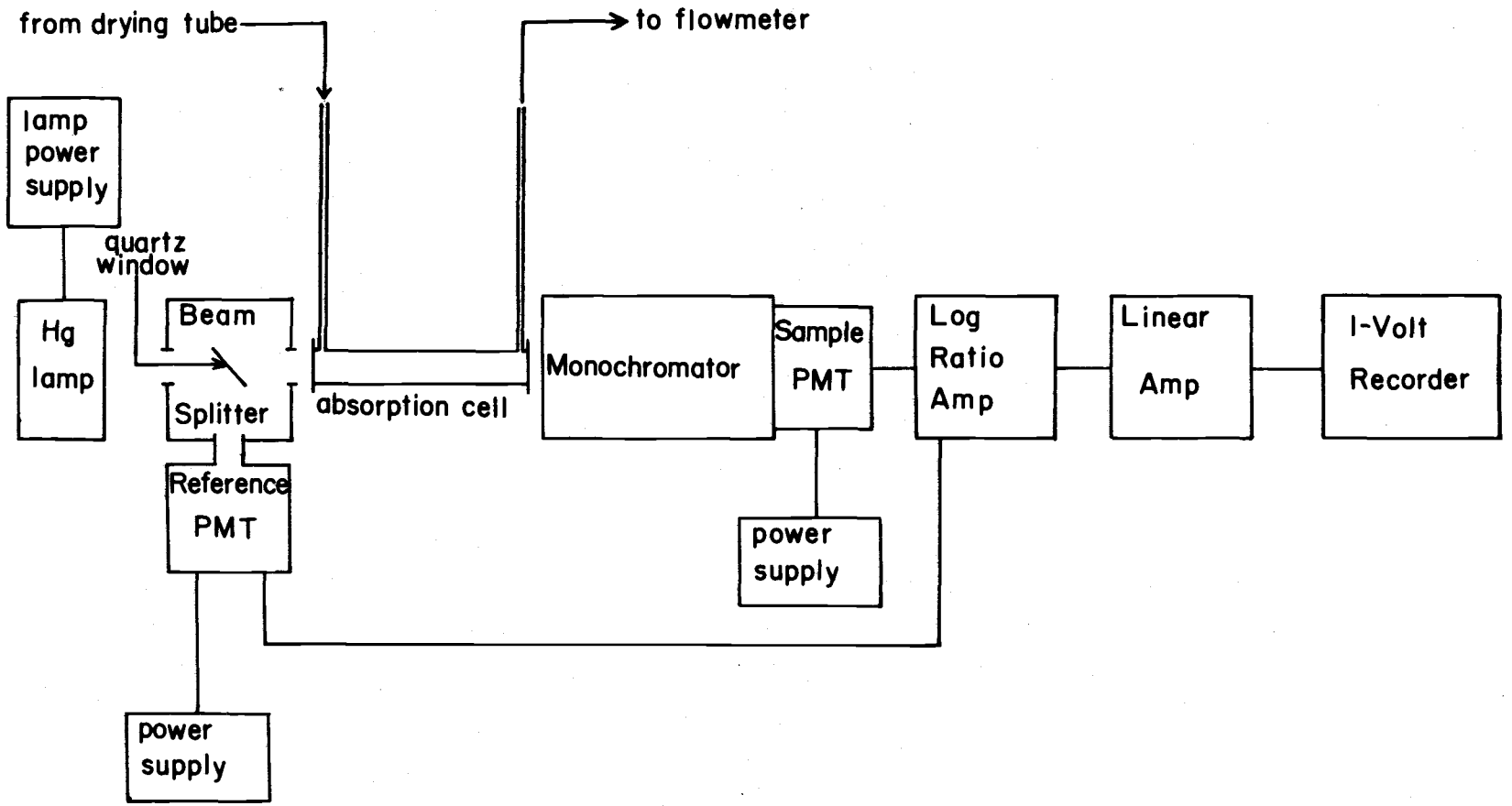


Figure 3. Double beam AA

of the logarithmic amplifier with a logarithmic ratio amplifier, and by addition of another photomultiplier tube and power supply. The logarithmic ratio amplifier was constructed from a commercial log ratio module, in a manner similar to the construction of the logarithmic amplifier already discussed, and its operation is also described by equation (1). However, the reference current is derived from the anode of the reference photomultiplier tube in order to provide double beam operation. The beam splitter is a quartz window placed in the center of a sample holder. A small percentage of the source radiation is reflected 90° and passes through a 3 mm aperture and a 254 nm interference filter to the reference photomultiplier tube.

Atomic Fluorescence (AF)

The atomic fluorescence instrument is illustrated in Figure 4. The linear amplifier is used as a current-to-voltage converter. The mercury pen lamp powered by the AC power supply is oriented at 90° with respect to the cell-monochromator axis. The fluorescence cell shown in Figure 5 is made from transparent rectangular plexiglass blocks cemented together. To make inlet and outlet ports, holes are drilled and glass tubing connected to the top and bottom sections of the cell. Quartz windows are glued to the cell and the cell is mounted about 1.5 cm from the slit of the monochromator.

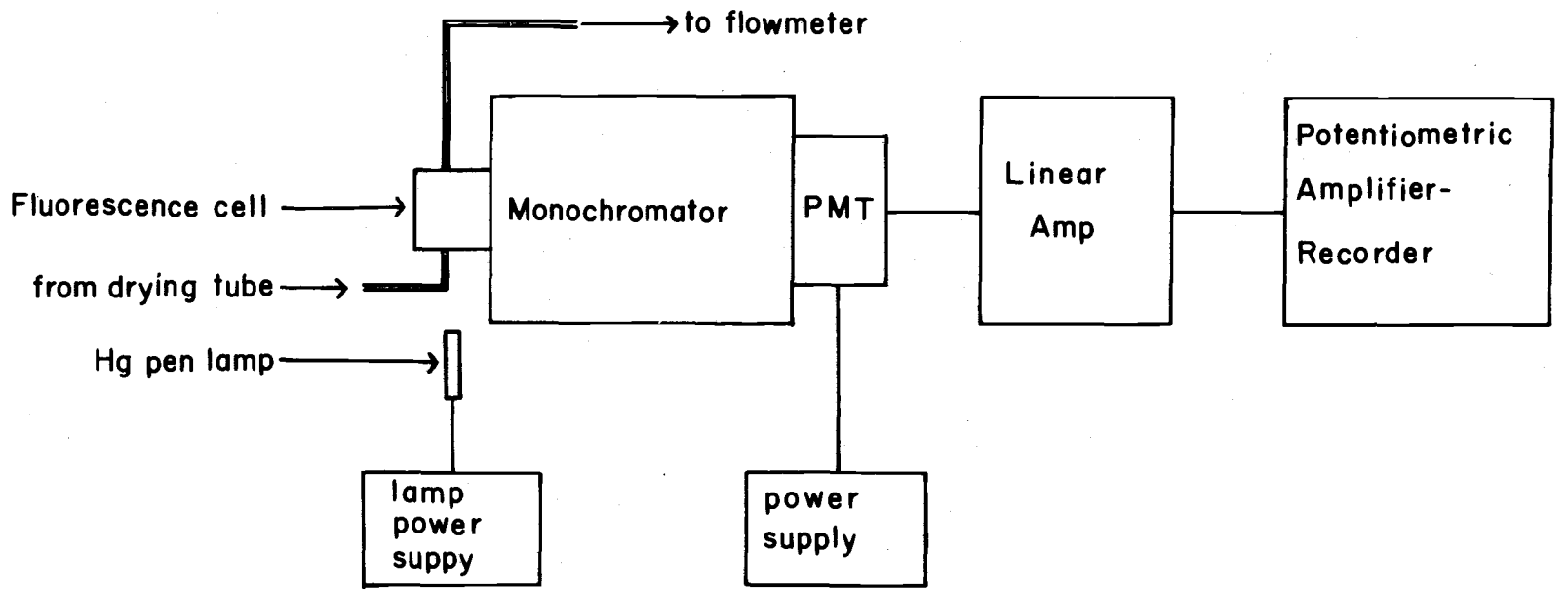
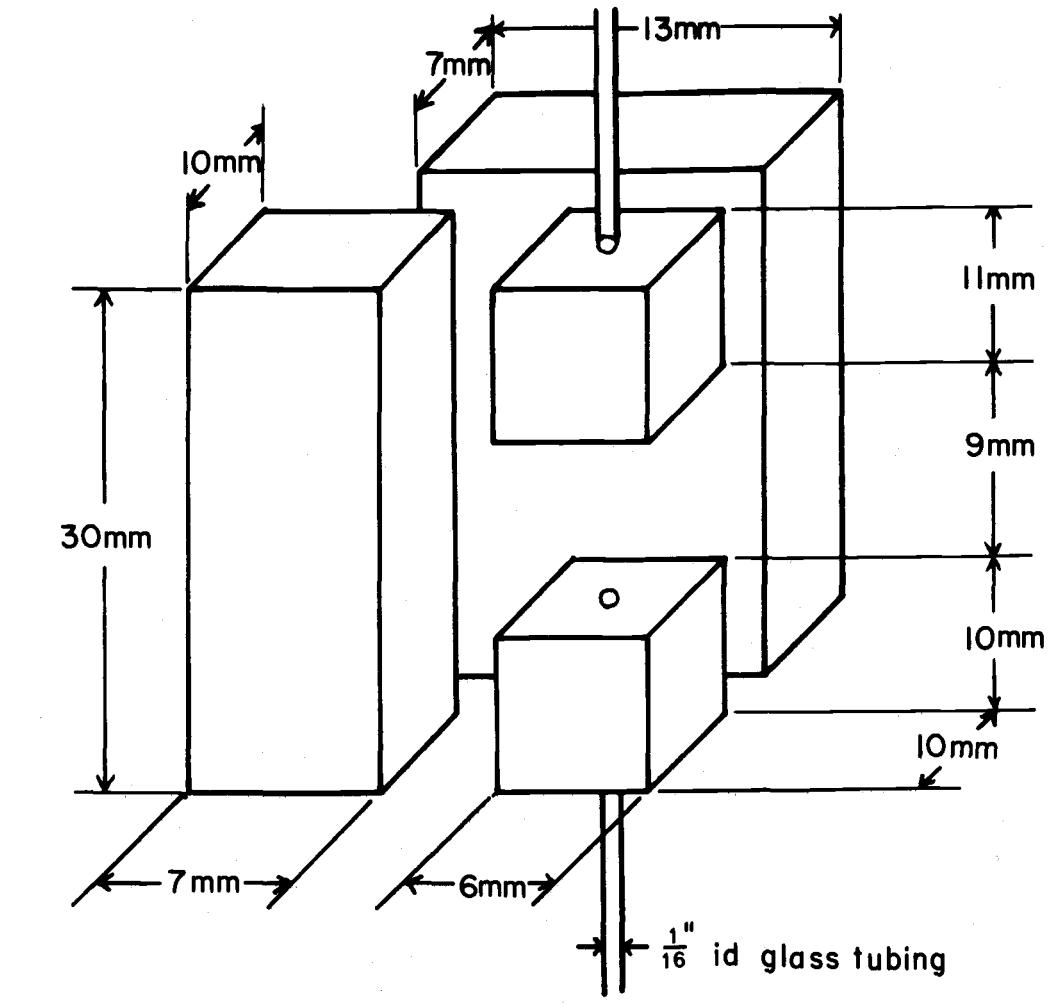


Figure 4. Atomic fluorescence instrument



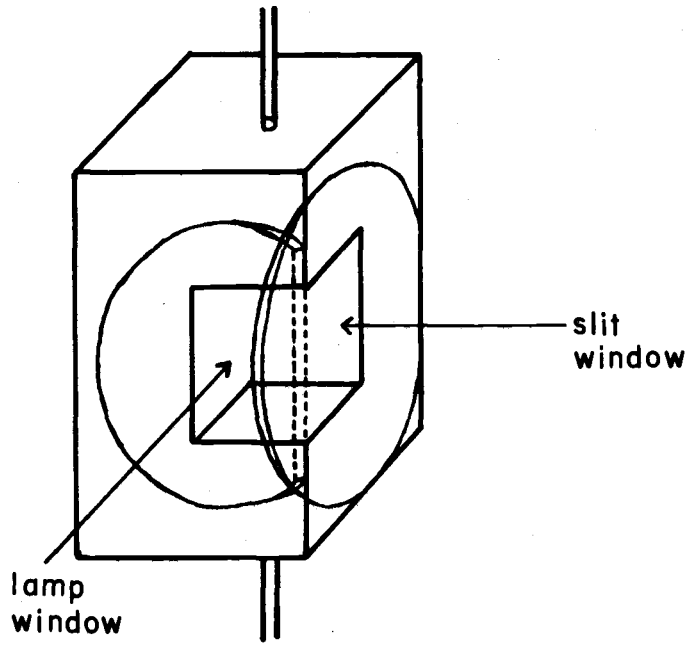


Figure 5. Atomic fluorescence cell

Alignment of the pen lamp is made with X-Y translation stages. Argon is used in place of air for the carrier gas since air quenches the fluorescence of mercury.

Procedure

AA Measurements

The final procedure used for analysis and for optimization is discussed below. Instrumental variables are adjusted to the values noted in Table 3 after optimization of the cell position. For the single beam AA, the photomultiplier supply voltage is adjusted to achieve a 10^{-5} A photoanodic current and a zero volt output from the log amplifier. For the double beam system, both the sample and reference photomultiplier power supplies are adjusted to produce 10^{-5} A photoanodic currents. One-tenth of a milliliter of reductant is injected with a 1 ml syringe into the reduction vessel after the carrier gas flow has been initiated through the frit. After the recorder pen has returned to the baseline, 1 ml of Hg(II) standard is injected with a 1 ml syringe into the reduction vessel. A typical recorded absorption peak under optimum conditions is shown in Figure 6. The beginning of the peak is observed about 3 seconds after injection. Within 7 seconds the peak absorbance is recorded and within 20 seconds the pen has returned to the baseline.

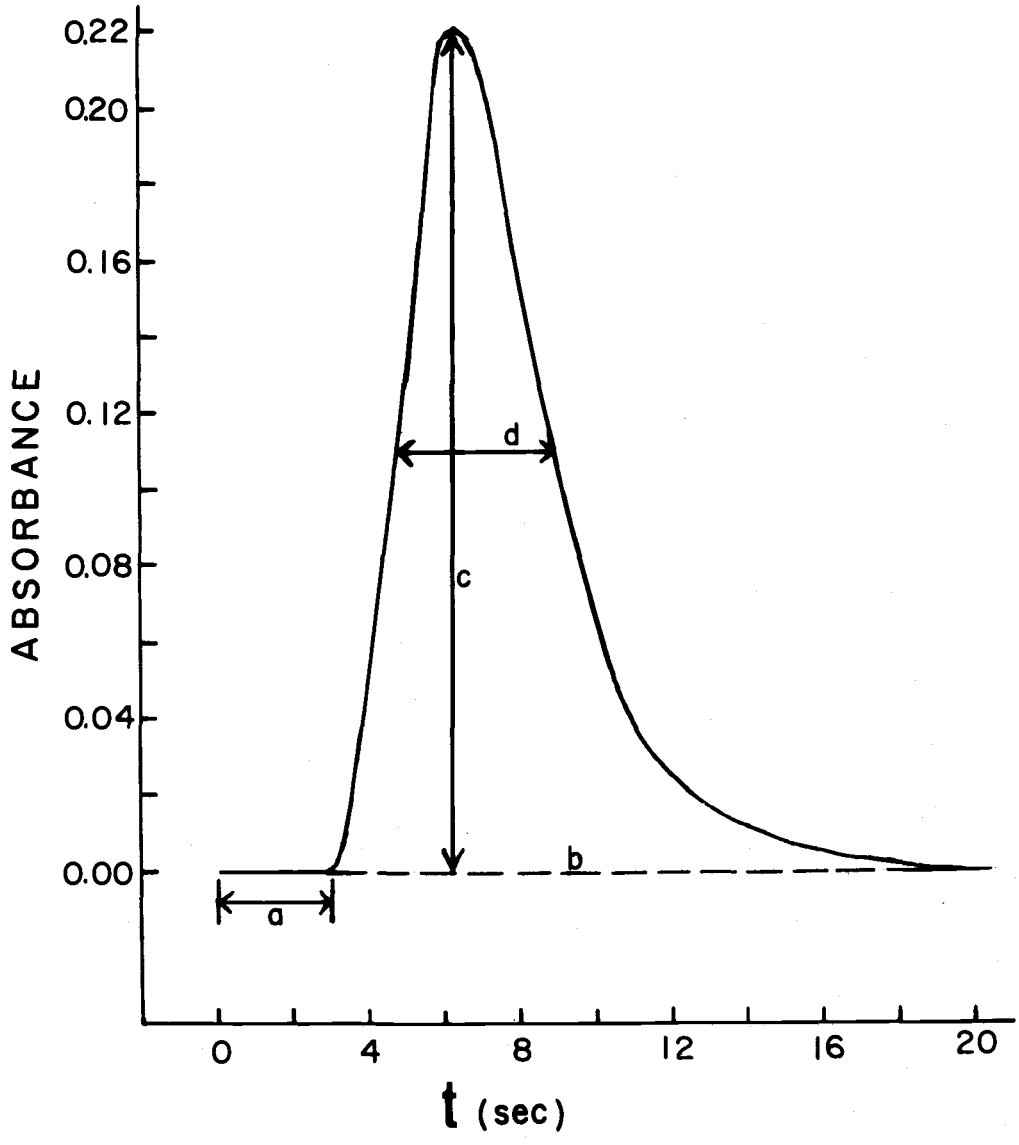


Figure 6. Typical observed absorbance peak for a 10 ppb Hg(II) standard with a 2 mm dia x 20 cm long absorption cell at optimum conditions

a - time of injection to response
b - baseline interpolation
c - peak absorbance
d - half-width (peak width at one-half the height)

Table 3. Optimal variables for analysis

Variable	A.A.	A.F.
Flow rate	140 ml/min	140 ml/min
Frit grade	medium	medium
Drying tube	5 cm long x 12 mm dia $Mg(ClO_4)_2$	5 cm long x 12 mm dia $Mg(ClO_4)_2$
Gas carrier	air	argon
Volume of reductant	0.1 ml	0.1 ml
Volume of sample	1.0 ml	1.0 ml
Slit width	1000 um	2000 um
Absorption cell	20 cm long x 2 mm id 60 cm long x 2 mm id	--
Fluorescence cell	--	1 cm x 9 mm x 6 mm
Radiation source	Hg pen lamp (DC)	Hg pen lamp (AC)
Lamp current	9-10 ma	17 ma
RC time constant	0.32 sec	1 sec
System	Double beam	--
Photoanodic current	10^{-5} A	--
Photomultiplier supply voltage[1]	500-600 V	700-800 V
R_f[1]	--	10^6 Ω

[1] Adjusted as described in procedure

To measure the peak absorbance, a peak baseline is interpolated by drawing a line between the baseline before injection and after the peak returned to the baseline. The difference between the absorbance at the peak and the absorbance of the interpolated baseline under the peak is taken as the peak absorbance.

The sample is evacuated and a 1 ml blank is flushed through the frit to eliminate memory effects above 1 ppb Hg(II) levels. The rubber stoppers must be replaced after 20 injections and samples can be analyzed at a rate of about 40 per hour.

AF Measurements

The final instrumental variable settings used for AF measurements are also shown in Table 3. After optimization of the cell position, the feedback resistor of the linear amplifier, the gain of the potentiometric amplifier, and the photomultiplier supply voltage are adjusted to yield a reasonable peak deflection for analysis. The actual analysis procedure is identical to that for AA.

Optimization

AA

General. In this section, the studies of the effects of various instrumental or physical variables on the observed peak height,

width, and shape on reproducibility, and on S/N are discussed. The effects of the variables will be discussed one at a time. Unless stated otherwise, a 10 ppb Hg(II) standard, a 20 cm long-5 mm diameter absorption cell, the single beam AA instrument, and the other settings for the variables listed in Table 3 were employed. The basic analysis scheme described in the previous section was used for all optimization studies.

To understand the influence of different variables on the data and to understand why the described system is superior to previous systems in a number of respects, one must first understand the basic processes that occur in analysis. When a Hg(II) solution is injected into the reduction vessel with the bubbling Sn(II) solution, the Hg(II) ions are reduced to neutral mercury atoms which diffuse from the solution into the carrier gas and are carried through the reduction vessel to the drying tube and finally to the absorption cell. Essentially all of the mercury atoms will diffuse from the solution into a given volume of carrier gas. This volume of carrier gas which contains mercury will be denoted the plug. Ideally, the plug would be of uniform concentration but in reality the plug's concentration profile will decrease with respect to time.

The diffusion out of the reduction vessel will be controlled by the size and shape of the reduction vessel, the volume of reductant and Hg(II) solution, the efficiency of aeration, the effective solution

surface area during aeration, and the rate constant for diffusion of mercury through a solution of unit depth into the carrier gas. If diffusion of mercury in the carrier gas is important, then the volume of the plug is expected to increase as it moves through the apparatus.

The plug of mercury will first be observed when it enters the front of the cell and the maximum value will be observed when the plug just reaches the end of the cell. The observed peak height or peak absorbance will be dependent on the effective concentration of the plug or of the front portion of the plug in the cell. The observed width will depend on the volume of the mercury plug entering the cell and the cell volume. If either volume is reduced, the observed width will be reduced. However, if the cell volume is much smaller than the plug volume the cell volume should have little effect on the observed width. If the flow rate of carrier gas is doubled but the volume of the plug is unchanged, then the mercury will diffuse out of the solution twice as fast, the velocity of the plug through the system will be twice as fast, and the peak width in time will be reduced.

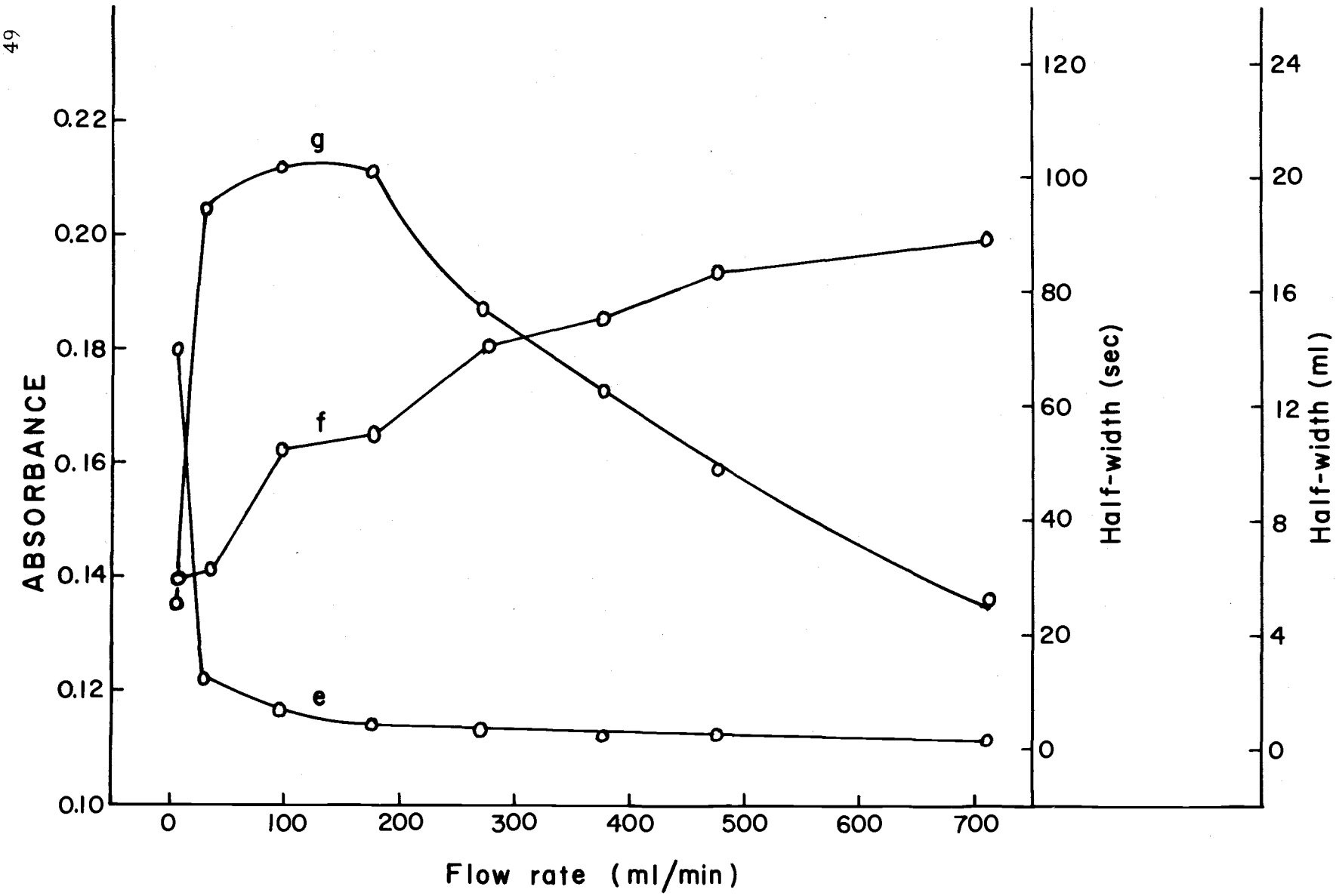
Flow Rate. The effect of carrier gas flow rate on the peak parameters was studied. The flow rate was evaluated from the flow-meter setting and a calibration curve provided by the manufacturer. Figure 7 is a plot of peak absorbance, peak half-width in seconds and peak half-width in milliliters versus flow rate. The peak half-width in milliliters is the half-width in seconds times the flow rate.

Figure 7. The relationship of peak parameters to flow rate

e - Half-width (sec)

f - Half-width (ml)

g - Peak absorbance


ABSORBANCE
0.22
0.20
0.18
0.16
0.14
0.12
0.10
g
f
e
0
100
200
300
400
500
600
700
Flow rate (ml/min)
120
100
80
60
40
20
0
Half-width (sec)
24
20
16
12
8
4
0
Half-width (ml)

Experimentally, it was found that approximately 90% of the peak was contained within 2 half-widths of the initial rise of the peak. The half-width in milliliters should be related to the volume of the plug or the volume of the most concentrated part of the plug.

The half-width in seconds continually decreases with increasing flow rate which indicates the mercury plug is flowing faster through the absorption cell. The half-width in milliliters and hence the volume of the plug increases with flow rate which indicates the efficiency of mercury diffusion decreases with increasing flow rate. The peak absorbance basically decreases with higher flow rates since the mercury plug volume increases and becomes more dilute. The product of the half-width in milliliters and the peak absorbance is proportional to the area of the peak in milliliters if the peak shape remains constant and this product is essentially constant above a flow rate of 95 ml/min. This is expected if the area is proportional to the total number of mercury atoms passing through the absorption cell. At the lowest flow rates, the bubbling efficiency is visually reduced and the diffusion efficiency may be reduced and also gas diffusion of mercury in the gas phase may be relatively more important and cause peak broadening. A flow rate of 140 ml/min was chosen for further studies since this yielded maximum absorbance that was fairly independent of flow rate fluctuations of ±20 ml/min.

Reduction Vessel. Three grades of porous frits: coarse,

medium, and fine in the reduction vessel were studied. The peak absorbance obtained with the fine frit was only 2% higher than for the medium frit and 5% higher than for the coarse frit. A medium frit was chosen for all succeeding studies since the fine frit easily clogs and requires the most time to evacuate. A reduction vessel made from a 30 mm diameter medium frit sealing tube with reduced ends gave about a 13% lower peak height than the 10 mm diameter coarse fritted reduction vessel.

Drying Tube. Drying tubes from 5 cm to 10 cm in length and 12 mm to 8 mm in diameter were tested. The peak absorbance observed was essentially independent of the drying tube size although a 5 cm long drying tube with a 12 mm internal diameter was used for the following studies and was changed after 20 analyses.

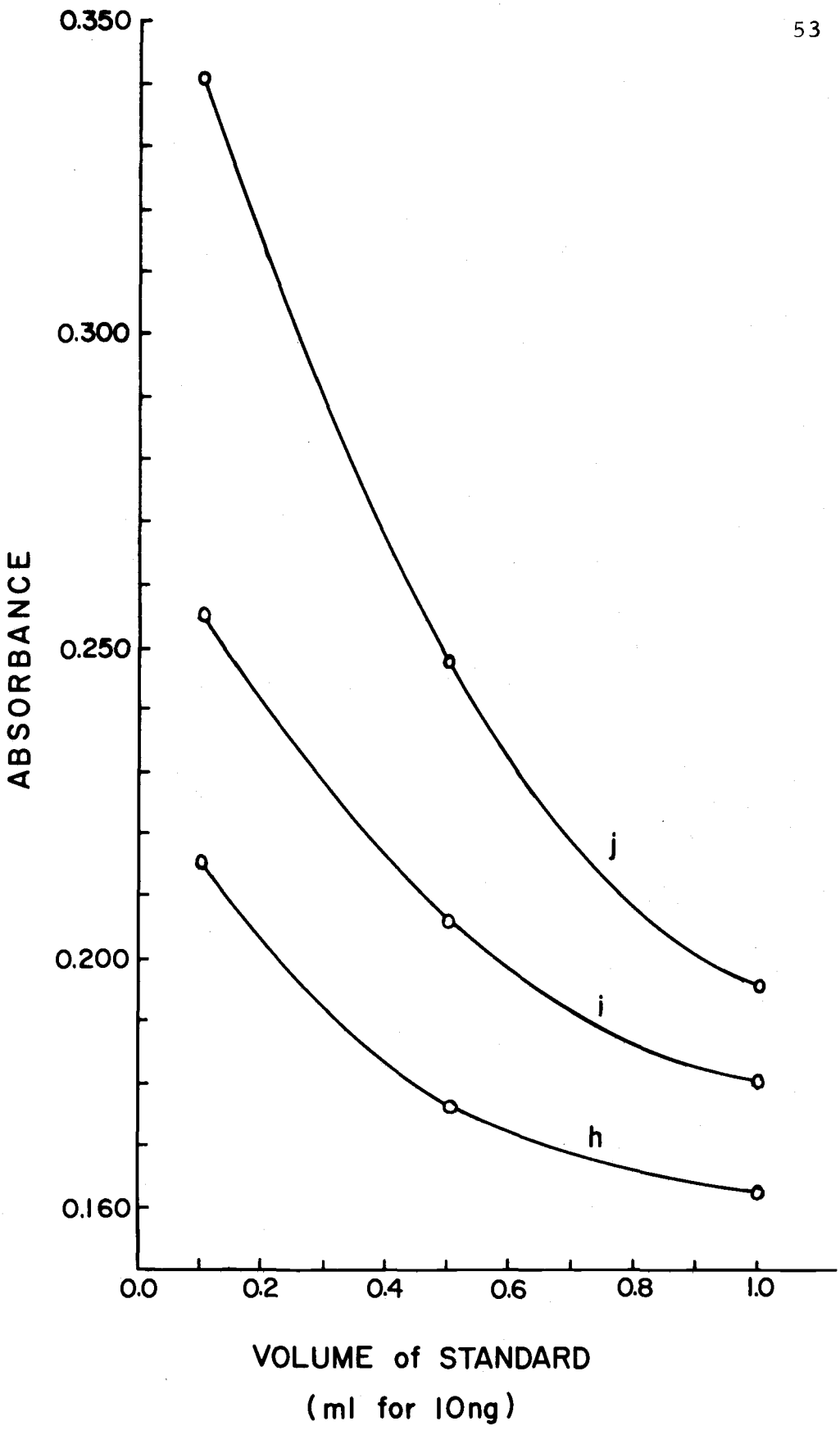
Volume Study. The effect of the volume of solution in the reduction vessel on the peak absorbance for a constant absolute amount (10 ng) of mercury was studied. This was done by mixing 0.1 ml of 100 ppb, 0.5 ml of 20 ppb, or 1.0 ml of 10 ppb of a Hg(II) standard solution with 0.1 ml, 0.5 ml, or 1.0 ml of the tin(II) chloride solution. The results are shown in Figure 8 and clearly illustrate that for a given volume of reductant, the peak absorbance increases with decreasing sample volume and for a given sample volume, the peak absorbance increases with decreasing reductant volume. These results suggest that the primary reasons for the decrease in peak

Figure 8. Effect of solution volume in reduction vessel on peak absorbance

h - 1.0 ml of $SnCl_2$

i - 0.5 ml of $SnCl_2$

j - 0.1 ml of $SnCl_2$


0.350
0.300
0.250
0.200
0.160
ABSORBANCE
j
i
h
0.0
0.2
0.4
0.6
0.8
1.0
VOLUME of STANDARD
(ml for 10ng)

absorbance as the solution volume increases is that the diffusion rate depends on the volume of solution from which the mercury atoms must diffuse before entering the air stream. For smaller solution volumes the diffusion is faster, and for a given flow rate and absolute amount of Hg(II) the plug volume is smaller and hence of higher concentration. The peak half-widths were more narrow for small solution volumes which also indicates a faster diffusion rate or smaller plug. One milliliter Hg(II) standard volumes and 0.1 ml of reductant were chosen for final solution parameters. Smaller volumes of Hg(II) standards increase the absolute response (A/ng) but produce a much poorer concentration response (A/ppb).

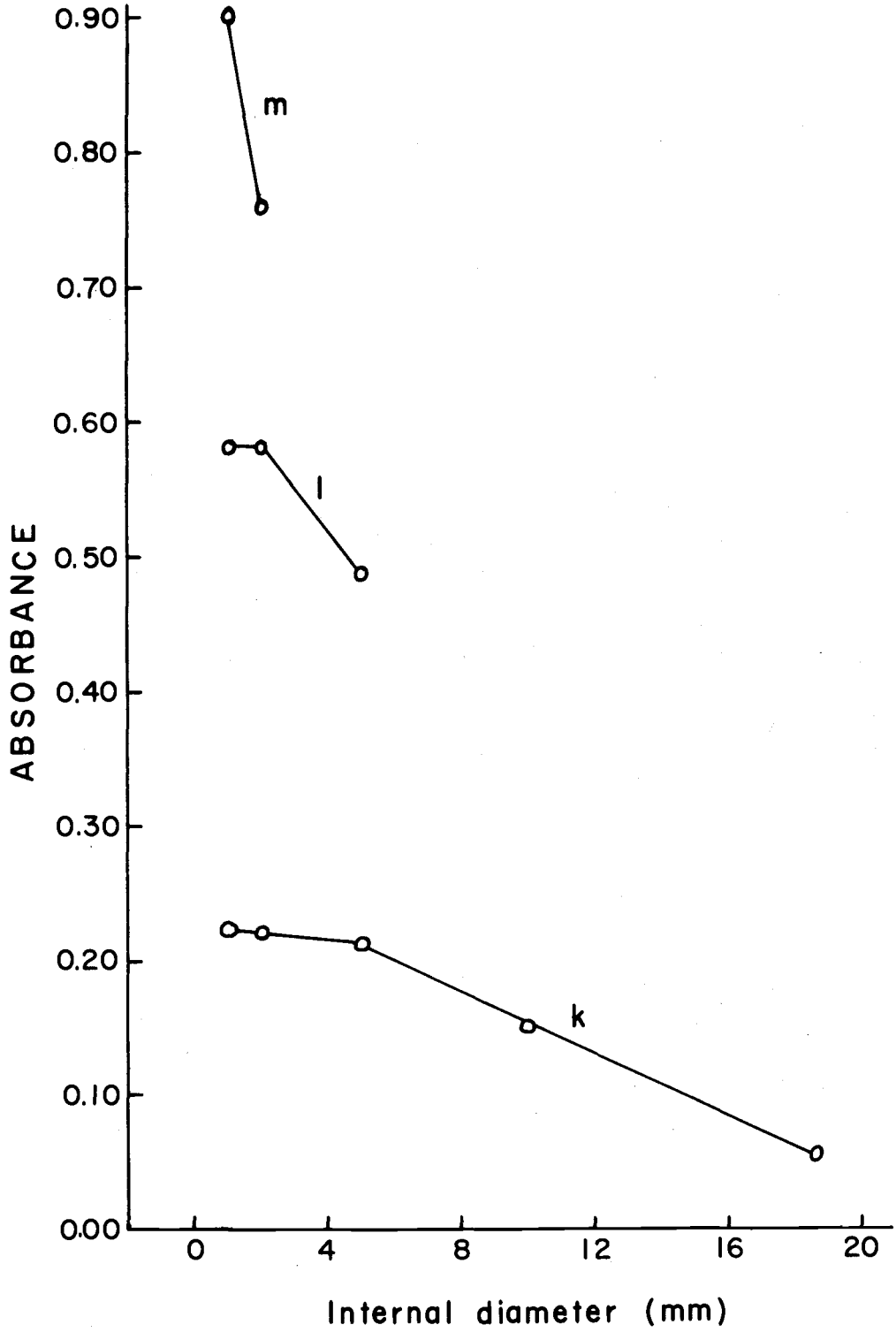
Absorption Cell. Alignment of the radiation source with respect to the slit of the monochromator is made by positioning the lamp in both vertical and horizontal directions to achieve the greatest photoanodic current. The absorption cell is then placed in the tube holders upon the optical rail and is oreinted in the X-Y planes with the translators to achieve a maximum photoanodic current. The peak absorbance was measured for absorption cells which varied in length from 20 to 120 cm and in internal diameters from 18.6 mm to 1 mm and the results are shown in Figure 9. For a given cell length, the absorbance increases with decreasing cell diameter and approaches a limiting value. The increase in absorbance as the cell diameter decreases occurs because the average concentration in the absorption

Figure 9. Effect of cell dimensions on peak absorbance

k - 20 cm length

l - 60 cm length

m - 120 cm length


0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
ABSORBANCE
m
l
k
0
4
8
12
16
20
Internal diameter (mm)

cell increases as the volume of the absorption cell decreases until the cell volume becomes small enough to contain the initial and most concentrated part of the mercury plug. The volumes of the cells studied varied between about 0.16 ml and 54 ml and the volume of the plug was estimated (twice the half-width in ml) to be about 20 ml. The total volume of the cell must be less than about 4 ml to achieve near maximum peak absorbance.

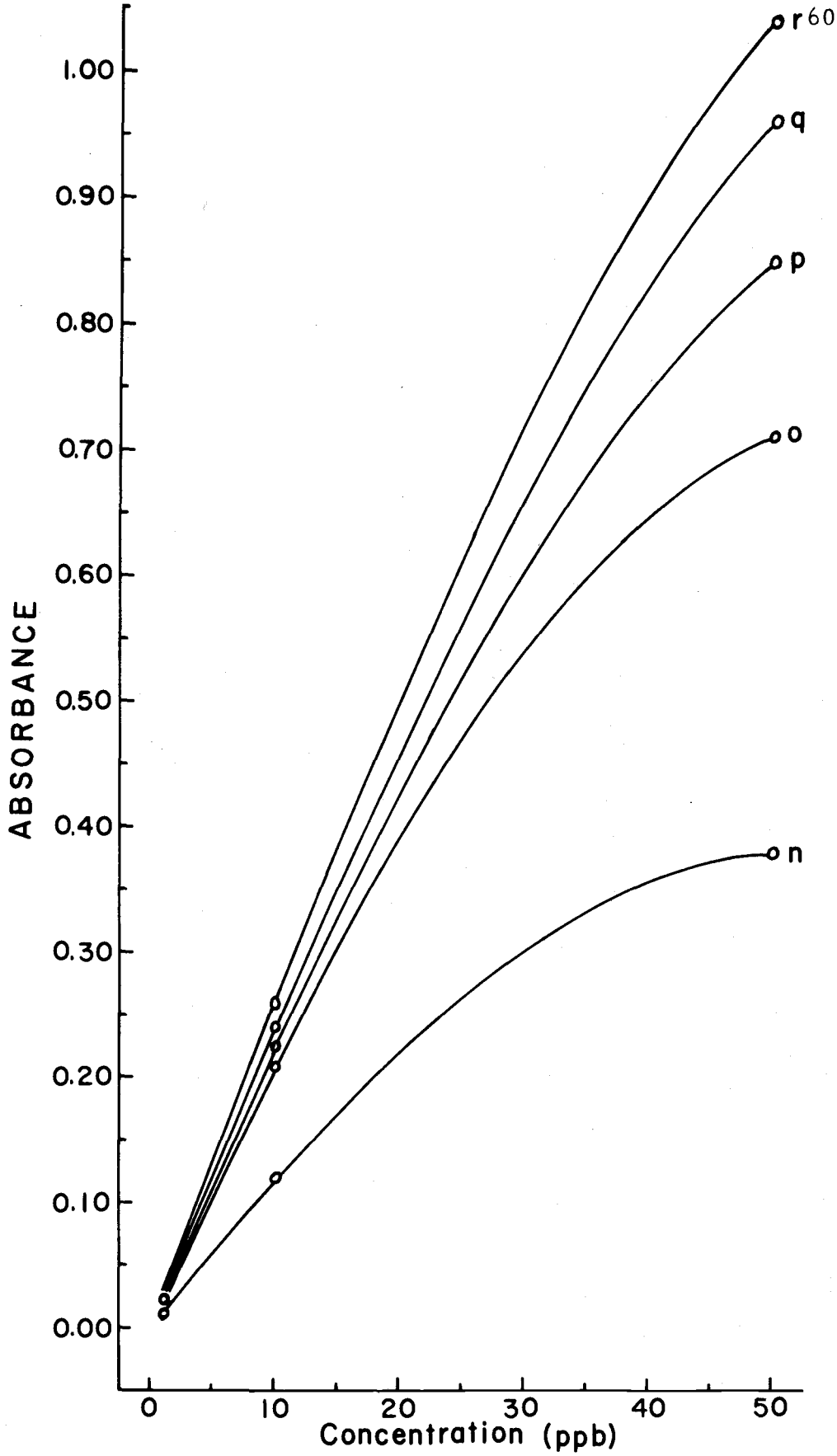
For a constant cell diameter of 2 mm, the signal increased 2.6 times from the 20 cm length to the 60 cm length and 3.5 times from the 20 cm length to the 120 cm length. The increase in absorbance with cell length for small diameters can be explained in terms of Beer's law. The absorbance is directly proportional to the length if the analyte concentration is uniform throughout the cell. The negative deviations to Beer's law evident for the 60 cm and 120 cm long cells may be due to the non-uniform mercury plug concentration profile from the 10 ppb Hg(II) solution. However, at mercury concentrations below 1 ppb, the absorbance with the 60 cm length cell is 3 times the absorbance with the 20 cm length cell, thus conforming to Beer's law. For practical purposes the 120 cm long and 1 mm diameter absorption cells are very difficult to align and it is difficult to maintain the alignment. Therefore, 2 mm diameter absorption cells with 20 cm and 60 cm lengths were chosen as the optimum dimensions.

Slit Width. The noise in the log amplifier output was measured at various slit widths for the single beam system. The photoanodic current was maintained at 10^{-5} A with the photomultiplier power supply. From 2000-50 μm, the low frequency noise was the most significant contributor to the noise and was independent of the slit width. Below a 50 μ slit width, the amount of noise increased rapidly and was higher frequency in nature. A 1000 μ slit width was chosen to insure that the signal shot noise was negligible.

Radiation Sources. A mercury hollow cathode tube and a mercury pen lamp were evaluated as atomic absorption sources with the 2 mm x 20 cm length cell. Figure 10 shows the calibration curves constructed from peak absorbance measurements for three different Hg(II) concentrations for the two lamps operated under different current conditions. The data indicate that the slope or sensitivity in absorbance units per ppb and the linearity are better for the hollow cathode tube, for lower currents with either lamp and for DC rather than AC operation with the pen lamp. Below 6.5 ma DC the pen lamp will not operate. Although the hollow cathode tube provides the greatest slope, a lens was needed to focus and collimate the radiation in order to produce the same light level impingent upon the photomultiplier tube as produced with the pen lamp without optics; without the lens, the signal from the hollow cathode radiation was shot noise limited. For further analysis, the mercury pen lamp was chosen

Figure 10. The effect of the type of lamp and lamp conditions on calibration curves

Pen lamp:	n - 14 ma AC
	o - 10 ma DC
	p - 6.5 ma DC
Hollow Cathode:	q - 10 ma DC
	r - 5 ma DC


r 60
q
p
o
n
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
ABSORBANCE
0
10
20
30
40
50
Concentration (ppb)

since it was more intense, since it could be used with longer 2 mm diameter absorption cells, and since it was easier to align. Finally, a 9-10 ma DC current was used to provide the best stability.

Time Constant. The response time of the linear amplifier was changed by varying the RC time constants. It was desired to choose the largest possible time constant which would reduce the noise but not reduce the peak absorbance. Experimentally, this value was found to be 0.32 seconds.

Single Beam-Double Beam. Comparison of the single and double beam system indicated that the double beam system exhibited a factor of six less short term source flicker noise and a factor of ten less drift.

Atomic Fluorescence

Most of the optimized settings used for AA were also used for AF. However, the following variables required optimization for AF: the volume of the fluorescence cell, the slit width, the alignment of the mercury pen lamp and of the fluorescence cell, the RC time constant, and the type of lamp and current conditions. The atomic fluorescence cell volume of 0.54 cm^3 was chosen because it was about equal to the optimum volume of 0.16-0.63 cm^3 found for the atomic absorption cells. The slit width, the alignment of the pen lamp and fluorescence cell, and the RC time constant were varied

to yield the largest signal-to-noise ratio and, for final values, a 2000 μm slit width and a 1 second time constant were chosen. The mercury pen lamp was the most intense source and was operated on AC since DC operation provided no improvement.

Chemical and Physical Problems

Storage Losses

Mercury losses with polyethylene and borosilicate glass containers were studied under different conditions. Such studies at concentrations below 20 ppb had not been made by other researchers. After preparation of solutions and placement in containers, absorption measurements were made every hour for 14 hours with the final measurement made after 24 hours. The percent loss over the 24 hour period for different Hg(II) concentrations and conditions are listed in Table 4. In general, the loss is linear or exponential with time. The data indicate that open containers are worse than closed containers: that, in general, relative losses are more serious at lower concentrations; and that the 1% ($\frac{v}{v}$) HNO_3(c) preservative suggested by some researchers is not adequate for 1 ppb Hg(II) solutions nor is a 0.6% ($\frac{v}{v}$) HNO_3(c) + 0.0006% ($\frac{w}{v}$) $KMnO_4$ solution suitable as a preservative. The 1% ($\frac{v}{v}$) HNO_3(c) + 0.002% ($\frac{w}{v}$) $KMnO_4$ preservative was found to be much more suitable for mercury storage over a 24 hour period.

Table 4. Percent losses of mercury over 24 hours

Solution	H_2O		1% (v/v) HNO_3(c)		1% (v/v)HNO_3(c) +0.002% (w/v) $KMnO_4$	0.6% (v/v)HNO_3(c) +0.0006% (w/v) $KMnO_4$
	polyethylene		polyethylene		borosilicate	borosilicate
	closed	open	closed	open	closed	closed
Blank	--	--	--	--	16	29
0.01 ppb	--	--	--	--	6	29
1.0 ppb	80	90	60	80	10	28
10 ppb	28	28	20	20	1	12

Mercury Contamination and Blank Problems

The blank solution will give a positive absorbance reading or mercury solutions will give erroneously high absorbances if the blank or mercury solutions pick up mercury. Mercury contamination results from residue mercury in the distilled water, in the reagents, from the air, or from the surfaces of the volumetrics, of the reduction vessel, or of the syringes. The cleaning procedures outlined in the procedure section should reduce some of the extent of contamination from some of the sources. Untreated house distilled water produces no blank signal. The following solutions were made from house distilled water: a 1% ($\frac{v}{v}$) HNO_3(c) solution, a 0.002% ($\frac{w}{v}$) $KMnO_4$ solution, and a 1% ($\frac{v}{v}$) HNO_3(c) + 0.002% ($\frac{w}{v}$) $KMnO_4$ solution. The absorbance of the above three solutions was measured. Only the last solution gave a measurable blank value and after diluting

this solution 1:2 with house distilled water, the blank value remained constant. Therefore, it was concluded that in the strong oxidizing environment of the acid-permanganate preservative solution, the mercury was released from organomercury compounds, bacteria, or particulate matter in the distilled water. Finally, double distilled water in the preservative solution exhibited the same characteristics as stated above; however, the blank value was reduced by about one-half to one-third.

Mist Studies

Mist from the reduction vessel can enter the absorption cell, scatter the source radiation, and increase the absorbance. To prevent this problem a number of approaches were taken such as heating the entry tube and the absorption cell to vaporize the mist, freezing the entry tube to crystallize the water before it enters the absorption cell, and trapping the mist in a molecular sieve, glass wool, or $Mg(ClO_4)_2$ before it enters the absorption cell. Results showed the molecular sieve was most effective but it did not pass the mercury. The $Mg(ClO_4)_2$ drying tube which was finally used did pass some mist to produce a small steady state absorbance signal which did not change with injection of distilled water into the reduction vessel.

Trouble Shooting

Table 5 presents a number of common problems encountered in analysis and their respective remedies.

Table 5. Trouble shooting

	Problem	Remedy
1.	Unusually high blank values	clean flask, syringe, reduction vessel
2.	Non-reproducible blank values	clean syringe, reduction vessel
3.	Steady decreasing blank values	clean syringe, reduction vessel
4.	At low concentrations the signal returns below the initial baseline	replace drying tube
5.	Blank value increases with time of solution in flask	clean blank flask
6.	Non-reproducibility of standards	replace drying tube or correct erratic flow rate
7.	Unusually low peak values for standard	replace tin(II) chloride
8.	D. C. pen lamp-flicker increases or shuts off	switch polarity on electrodes

IV. RESULTS

Calibration and Precision Data

After the system was optimized, the linearity and precision of both the AA and AF cold vapor systems were evaluated with the final parameters indicated in Table 3. Tables 6, 7, and 8 show the relationship between concentration and the absorbance or fluorescence signals and the absolute and relative standard deviation in these signals. All standard deviations are calculated from 5 or more independent measurements and the symbols are defined below:

A = peak absorbance of sample solution

A_b = peak absorbance of the blank solution

A_s = peak absorbance corrected for absorbance of the blank solution

σ_A = standard deviation in measurement of A

σ_{A_b} = standard deviation in measurement of A_b

σ_{A_s} = standard deviation in measurement of A_s; $(\sigma_A^2+\sigma_{A_b}^2)^{\frac{1}{2}}$

$\frac{\sigma_A}{A}$ = relative standard deviation in A

$\frac{\sigma_{A_s}}{A_s}$ = relative standard deviation in A_s

E_s = peak fluorescence signal of sample, V

σ_f = standard deviation in measurement of E_f, V

Table 6. Calibration and precision data for AA with the 20 cm long x 2 mm diameter absorption cell

Concentration of standard (ppb)	A	A_s	σ_A	σ_{A_s}	$\frac{\sigma_A}{A}$	$\frac{\sigma_{A_s}}{A_s}$
Blank	1.9×10^{-4}	---	3.1×10^{-5}	---	3.2×10^{-1}	---
0.01	4.7×10^{-4}	2.8×10^{-4}	2.8×10^{-5}	4.2×10^{-5}	6.0×10^{-2}	1.5×10^{-1}
0.05	1.28×10^{-3}	1.09×10^{-3}	3.5×10^{-5}	4.7×10^{-5}	2.7×10^{-2}	4.3×10^{-2}
0.10	2.50×10^{-3}	2.31×10^{-3}	6.3×10^{-5}	7.9×10^{-5}	2.5×10^{-2}	3.4×10^{-2}
1.0	2.24×10^{-2}	2.22×10^{-2}	4.3×10^{-4}	4.3×10^{-4}	2.0×10^{-2}	2.0×10^{-2}
10.0	2.19×10^{-1}	2.19×10^{-1}	5.6×10^{-3}	5.6×10^{-3}	2.5×10^{-2}	2.5×10^{-2}
50.0	7.14×10^{-1}	---	---	---	---	---

Table 7. Calibration and precision data for AA with the 60 cm long x 2 mm diameter absorption cell

Concentration of standard (ppb)	A	A_s	σ_A	σ_{A_s}	$\frac{\sigma_A}{A}$	$\frac{\sigma_{A_s}}{A_s}$
Blank	2.1×10^{-4}	---	4.0×10^{-5}	---	1.9×10^{-1}	---
0.005	5.1×10^{-4}	3.0×10^{-4}	5.6×10^{-5}	6.9×10^{-5}	1.1×10^{-1}	2.3×10^{-1}
0.01	8.7×10^{-4}	6.6×10^{-4}	3.6×10^{-5}	5.3×10^{-5}	4.1×10^{-2}	8.1×10^{-2}
0.05	3.54×10^{-3}	3.33×10^{-3}	6.9×10^{-5}	8.0×10^{-5}	2.0×10^{-2}	2.4×10^{-2}
0.10	6.76×10^{-3}	6.55×10^{-3}	1.8×10^{-4}	1.8×10^{-4}	2.7×10^{-2}	2.8×10^{-2}
1.0	6.41×10^{-2}	6.39×10^{-2}	1.2×10^{-3}	1.2×10^{-3}	1.9×10^{-2}	1.9×10^{-2}
10.0	5.17×10^{-1}	5.17×10^{-1}	5.4×10^{-3}	5.4×10^{-3}	1.0×10^{-2}	1.0×10^{-2}

Table 8. Calibration and precision data for AF

Concentration of standard (ppb)	E_f	σ_f	$\frac{\sigma_f}{E_f}$
Blank	0	4.0×10^{-5}	----
0.01	9.3×10^{-4}	4.6×10^{-5}	5.0×10^{-2}
0.05	1.90×10^{-3}	5.5×10^{-5}	2.9×10^{-2}
0.10	9.20×10^{-3}	2.3×10^{-4}	2.5×10^{-2}
1.0	1.87×10^{-2}	4.5×10^{-4}	2.4×10^{-2}
10	1.82×10^{-1}	5.7×10^{-3}	3.1×10^{-2}
50	8.90×10^{-1}	2.6×10^{-2}	2.9×10^{-2}
100	1.75	6.4×10^{-2}	3.7×10^{-2}

$\frac{\sigma_f}{E_f}$ = relative standard deviation in E_f.

Note that, for AA measurements of mercury standards, it is necessary to correct for the absorbance of the distilled water blank, and thus the absolute and relative standard deviations of analysis (σ_A and σ_A/A_s) take into account the variability of the separate blank measurement. Correction for blank absorbance is not necessary for real AA samples to which distilled water is not added (i.e. $\sigma_{A_s} = \sigma_A$) or for AF measurements since the blank measurement is zero.

The linearity of AA measurements is obvious from Tables 6 and 7 and Figure 10. For the 20 cm cell, the slope of the AA calibration curve is 0.0219 ppb^{-1} and is linear up to about 10 ppb of Hg(II). At 50 ppb Hg(II) the slope of the calibration curve is about a factor of three less. For the 60 cm cell, the slope of the calibration curve is 0.0638 ppb^{-1} and is linear up to about 3 ppb Hg(II). As illustrated by Figure 10, serious negative deviations occur for concentrations which yield absorbances above 0.5.

To analyze solutions of higher Hg(II) concentrations it would be desirable either to use the pen lamp at 6.5 ma DC or the hollow cathode tube or to reduce the absorbance to a linear region by dilution of the sample or by use of a smaller path length absorption cell.

The absorbance data also indicate that measurements can be made with a relative precision better than 10% above 10 ppt and

better than 3% above 50 ppt.

The slope of the AF calibration curve is 0.0180 V ppb^{-1}. From Table 8, non-linearity is reasonably small up to 100 ppb and the relative precision of measurements is better than 5% above 50 ppt Hg(II).

Detection Limit

The detection limits for AA and AF were calculated with equations 2-3.

$$\text{AA:}\quad c_l = z\,\sigma_{A_s}/m\sqrt{n} \tag{2}$$

$$\text{AF:}\quad c_l = z\,\sigma_f/m\sqrt{n} \tag{3}$$

where all standard deviations are measured near the detection limit and all terms have been defined except

c_l = concentration or absolute amount at the detection limit

m = slope of the calibration curve

n = number of measurements (n=1)

z = test statistics for a given confidence level (z=2, 97.7%).

Table 9 shows the detection limits for AA and AF.

Table 9. AA and AF detection limits

Instrument	c_l				c_l^*	
	ppt		pg			
	real	standard	real	standard	ppt	pg
AA 20 cm cell	3	4	3	4	3	3
60 cm cell	1	2	1	2	1	1
AF	7	7	7	7	7	7

*Common detection limit, defined as the concentration which yields a signal twice the standard deviation of the blank measurement.

Analysis

Atomic absorption analysis of the mercury content in regular tap water, in regular house distilled water, in double distilled water, in 1% ($\frac{v}{v}$) HCl(c), and in the Willamette River water were made with the 60 cm absorption cell. The water samples were analyzed directly and also after addition of acid and permanganate. In the latter case, to 490 ml of the water sample were added 5 ml of 1% ($\frac{v}{v}$) HNO_3(c) and 5 ml of 0.2% ($\frac{w}{v}$) $KMnO_4$ and the samples were analyzed immediately. No difference in peak height was noted if the samples were analyzed 15 hours after treatment.

The data shown in Table 10 indicate that the apparatus can be used for the direct analysis of water samples after treatment with the acid-permanganate which releases the mercury, that each distillation step reduces the mercury content by about a factor of 3, and that our HCl(c) has about 1 ppb Hg(II) which is considerably more than in HNO_3(c).

Table 10. Water analysis

Sample	Hg(II) ppt without preservative	Hg(II) ppt with preservative
tap water	0	10
distilled	0	3
twice distilled	0	1
1% ($\frac{v}{v}$) HCl(c)	15	--
Willamette River	0	9

Noise Sources

Recent studies (132) have considered the effect of different types of noise on the precision of AA measurements. For the AA cold vapor instruments described in this work, amplifier-readout noise, background radiation noise, analyte emission noise, dark current shot noise, and transmission flicker noise were found to be negligible compared to other types of noise. Under these conditions, the literature expressions for a single beam linear absorbance instrument reduce to

$$\sigma_A = [(0.4343)^2 (mK/i_r + mK/i_s + 2\xi_1^2) + \xi_3^2 A^2]^{\frac{1}{2}} \qquad (4)$$

where

i_s = peak signal photoanodic current, A

i_r = reference or baseline photoanodic current, A

m = current gain of the sample photomultiplier, dimensionless

$K = 2e\triangle f(1+\alpha)$, A

e = charge of an electron, coulombs

α = secondary emission factor, dimensionless

$\triangle f$ = noise equivalent bandwidth of amplifier-readout system, sec^{-1}

ξ_1 = source flicker factor, dimensionless

ξ_3 = sampling flicker factor, dimensionless

This equation takes into account the shot noise in the photoanodic

signals, the source flicker noise in the photoanodic signals, and the reproducibility of sampling.

For the double beam system, equation 4 must be slightly modified to yield

$$\sigma_A = [(0.4343)^2(2m'K/i_r + mK/i_r + mK/i_s + 4\xi_1^2) + \xi_3^2 A^2]^{\frac{1}{2}} \quad (5)$$

where m' = current gain of the reference photomultiplier.

For fluorescence measurements,

$$\sigma_f = [mR_f K(E_b+E_f) + \xi_1^2 (E_b+E_f)^2 + (\xi_3 E_f)^2]^{\frac{1}{2}} \quad (6)$$

where

E_b = background reflection and scattering signal, V

R_f = feedback resistance of current-to-voltage converter, Ω .

The above theoretical standard deviations were compared to the experimental standard deviations (i.e. σ_A and σ_f) to ascertain whether shot noise was important and to calculate the values of the flicker factors. First, the right sides of equations 4-6 were evaluated at low absorbances where $i_r = i_s$, $E_b = E_f$, and sampling flicker ($\xi_3 A$ or $\xi_3 E_f$) is negligible. The resulting expressions were set equal to the experimental standard deviation at zero absorbance and were solved for ξ_1. It was assumed that $2e(1+\alpha) = 4.08 \times 10^{-19}$ coulombs and that $\triangle f = 0.86$ Hz as determined by the RC time constant of the linear amplifier. The photomultiplier gains were calibrated against a vacuum phototube as described in a recent paper (132). The

reference current, i_r, was 10^{-5} A and the sample current was calculated from the measured peak absorbance.

Next the appropriate experimental standard deviations for a 10 ppb Hg(II) solution were set equal to the right side of equations 5 and 6 and the resulting equations solved for ξ_3. The value of ξ_1 calculated near zero absorbance was used and i_s was evaluated from the measured absorbance.

For the AA and AF systems, equations 4-6 can be reduced to

AA: 60 cm cell

single beam

$$\sigma_A = [1.8 \times 10^{-7} + (9.2\times10^{-11})/10^{-A} + (1.0\times10^{-4})A^2]^{\frac{1}{2}} \quad (7)$$

double beam

$$\sigma_A = [3.1 \times 10^{-9} + (9.2\times10^{-11})/10^{-A} + (1.0\times10^{-4})A^2]^{\frac{1}{2}} \quad (8)$$

AF:

$$\sigma_f = [3.6\times10^{-8}(E_b+E_f) + 5.9 \times 10^{-7}(E_b+E_f)^2 + 7.2\times10^{-4} E_f^2]^{\frac{1}{2}} \quad (9)$$

These expressions indicate that near the detection limit for double beam AA measurements the noise is about 2/3 source flicker noise and 1/3 signal shot noise, for AF measurements shot and flicker noise are about equal, and for single beam AA measurements flicker noise is dominant. As expected, the source flicker factor ξ_1 is about

the same (7×10^{-4}) for the single beam AA and AF systems. For the double beam AA system, the source flicker factor is reduced to about 8×10^{-5} because of compensation.

For higher absorbances, σ_A and σ_f are limited by sampling flicker (1-2%). This limit corresponds to the expected reproducibility of the injection of 1 ml samples into the reduction vessel with a syringe.

V. SUMMARY

With a few basic modifications to the normal apparatus for the cold vapor atomic absorption and fluorescence analysis of mercury, the detection limits, the sample volume, and the analysis time have been reduced significantly. The improvement in the technique is due largely to the unique design of the reduction vessel which allows the mercury to be swept efficiently out of the solution into the small volume of carrier gas to provide a much more concentrated mercury plug compared to previous reduction vessels. The new reduction vessel coupled with the small sample volumes, small apparatus dead volume, and optimized absorption cell dimensions results in a greater calibration sensitivity or larger peak absorbance per ppb or per ng of Hg(II). For a given length absorption cell, it is shown that the total cell volume must be reduced to some critical volume in order to maximize the absorbance.

The increased calibration sensitivity and the low noise and drift in the double beam AA system result in extremely low detection limits as evidenced by comparison to detection limits for the normal apparatus. For AA the concentration detection limit has been reduced from 0.025 ppb (66) to 1 ppt Hg(II) and the absolute detection limit has been reduced from 0.2 ng (74) to 1 pg of mercury. For AF the concentration detection limit has been reduced from 0.06 ppb

(96) to 7 ppt Hg(II) and the absolute detection limit has been reduced from 3 ng (96) to 7 pg of mercury. These low detection limits make it possible for the first time to analyze mercury levels on the order of 10 ppt which occur in natural waters by the cold vapor AA or AF technique without preconcentration methods. The capability to carry out direct analysis saves considerable time and prevents contamination or loss of mercury that can occur in concentration procedures.

With the mercury hollow cathode tube normally used, the above detection limits would not be possible because of shot noise limitations. The use of the much more intense mercury pen lamp operated in the unconventional DC current mode and of double beam compensation allows peak absorbances of 10^{-4} absorbance units to be detected.

The fast analysis time of 2 minutes per sample is brought about by the reduction vessel design which utilizes small sample volumes (100 times less than some systems) that can be handled quickly and which allows rapid evacuation of the sample after analysis without replacement of the reduction vessel. Automation should be easy to implement.

Both AA and AF can be used with a relative precision of 3% or better above 0.1 ppb up to 50 ppb or 100 ppb of Hg(II) and AA can be used with a relative precision of 10% or better down to about 5 ppt. Both techniques are limited by shot noise and source flicker noise

for concentrations near the detection limit and by the sampling precision of injecting samples into the reduction vessel at higher concentrations. Comparison of the AA and AF techniques shows little difference except that the AA detection limit is seven times lower than that of AF, that AA measurements are slightly more precise, and that AF has a larger dynamic range in terms of linearity. With the samples utilized, difficulties with scattering and molecular absorption in AA measurements as discussed by other authors were not apparent.

The problems of mercury loss and contamination at the sub-ppb levels studied are critical. A 1% ($\frac{v}{v}$) HNO_3(c) + 0.002% ($\frac{w}{v}$) $KMnO_4$ solution was shown to be adequate for storing standard Hg(II) solutions for a day without contamination. All glassware with which sample solution came into contact must be rinsed with oxidizing solutions to remove mercury adsorbed on the surface. Memory effects from glassware in contact with more concentrated Hg(II) solutions can be limiting without scrupulous rinsing.

Although a number of improvements have been realized, further studies would be useful. Redesigning the reduction vessel to eliminate all possible dead pockets and to improve the aeration efficiency to enable the mercury to diffuse into the smallest possible volume of carrier gas should be studied. A more rigorous theoretical treatment of the diffusion processes from the solution into the

carrier gas stream and of diffusion in the carrier gas should be investigated. The present open AA system could be modified to a closed system with a smaller total volume. This might increase the total effective mercury concentration in the absorption cell and allow long term signal integration to improve precision. The precision and detection limit of the AF system could be considerably improved by use of double beam compensation and by redesign of the fluorescence cell to reduce the background reflection signal and noise.

Many physical and chemical problems deserve more study. The mechanisms of mercury loss and contamination are still uncertain. The effects of preservation techniques and oxidizing solutions on different organomercury compounds or on bound mercury are unclear.

The improvements of this technique are not restricted to mercury analysis but are applicable to other systems which are based on the reduction and/or diffusion of an analyte from a solution into a carrier gas stream before detection. It may also be possible to analyze for other metal ions indirectly by the reduction of Hg(II) with metal ions and measurement of the mercury released.

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