

DIRECT DETERMINATION OF TRACE METALS IN SALINE WATER SAMPLES
USING GFAAS

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The Faculty of the Department of Chemistry
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Master of Arts

by
Michael J. Wassell
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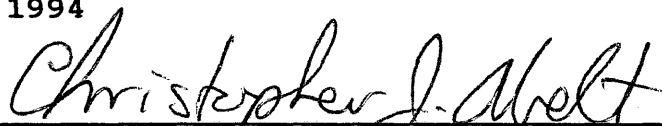
APPROVAL SHEET

This theses is submitted in partial fulfillment of
the requirement for the degree of
Master of Arts



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ABSTRACT

Methods for the direct determination of As, Cd, Co, Cr, Cu, Pb, Mn, and Ni in saline waters using graphite furnace atomic absorption spectroscopy were evaluated and developed. Methods from the literature were evaluated for their applicability to the GFAAS used in this study. Simple aqueous standards and some modifications of methods were used for producing calibration curves in the analysis of Co, Cr, Cu, Pb, Mn, and Ni. The development of matrix matching techniques was used for producing calibration curves in the analysis of Cd.

**DIRECT DETERMINATION OF TRACE METALS IN SALINE
WATER SAMPLES USING GRAPHITE FURNACE ATOMIC
ABSORPTION SPECTROPHOTOMETRY**

CHAPTER I

INTRODUCTION AND BACKGROUND

The analytical determination of trace metals in saline waters is very important due to the known toxicity of some elements. Trace metals can be defined as those metals that occur at quantities less than 0.01 percent in a substance, i.e., biological tissues, waters, sediments, etc. Many of these trace metals are essential to maintain life but at higher concentrations can act as pollutants and cause a variety of toxic effects. For example, Cu is considered an essential trace metal in the diet, however a lack of Cu produces an anemic or iron deficient condition because of interactions in the body with iron in some metabolic processes. At excess doses Cu causes diarrhea, vomiting, and other metabolic disorders.

Table 1 is a list of some metals that are likely to be found in polluted saline waters with known toxicological information and sources. Many of these metals vary dramatically in their toxicity and their toxic effects. This occurs because of the different metabolic reactions that can arise in biological systems.

TABLE 1. Examples of trace metals found in polluted waters^a.

| ELEMENT/ CHEMICAL STATE | ESSENTIAL IN NUTRITION | TOXICITY/ TOXIC EFFECTS | SOURCES | FEDERAL LIMIT ($\mu\text{g/L}$)^b |
|--|---|--|--|---|
| As/ AsO_2^- | no / although possible biological functions have been proposed ^c | high/ kidney failure, mental disturbance | fossil fuel combustion, detergents, smelting, pesticides, bronzing | 50 |
| Cd/ Cd^{2+} | no | high/ high blood pressure, kidney damage, red blood cell loss | metal plating, by-product in the treatment of Zn, Cu, and Pb, mining, cigarette smoke | 10 |
| Co/ Co^{2+} | yes | low/ not characterized | electroplating, metallurgy | |
| Cr/ CrO_4^{2-} | yes | medium/ suspected carcinogenic | electroplating, metallurgy | 50 |
| Cu/ Cu^{2+} | yes | low/ liver damage | mining, metal plating, copper pipes | 1000 |
| Pb/ Pb^{2+} | no | high/ anemia, kidney failure, mental retardation, convulsions | lead piping, lead paints, auto emissions from leaded gasoline | 50 |
| Mn/ Mn^{2+} | yes | low/ not well characterized | industrial waste, acid mine drainage | 50 ^d |
| Ni/ Ni^{2+} | possible biological functions have been proposed ^c | medium/ suspected carcinogenic | electroplating, metallurgy | |
| Zn/ Zn^{2+} | yes | low/ not characterized | metal plating, wastes, acid mine drainage | 5000 |

^aReference 1^bU.S. Public Health Service Limits^cReference 2^dLimits on manganese is not determined by toxicity, but because it stains clothing and ceramic plumbing fixtures.

Life has evolved from a balanced environment of trace elements found in the sea. Marine plants and simple organisms obtain necessary elements from the seawater habitat which in turn provides these nutrients to fish and aquatic mammals. A deficiency of an essential trace element can cause diseases in both plants and animals whereas high concentrations of essential trace elements can be toxic and lead to substantial loss of life. Thus when the balance is disturbed by either natural or manmade events, the results can be disastrous.

Non-essential or toxic trace elements in excessive amounts may enter living systems and interfere with the actions of essential trace elements. Elements within a group of the periodic table have similar properties and tend to undergo the same chemical reactions but display systematic differences. The systematic differences, which can be related to the vertical position of the element in the group, include the atomic radius, the melting and boiling points, and densities. When tissues have an affinity for a certain element, or are structured by it, they have some affinity for all other elements within the same group. Similarity of atomic structures can bring about the replacement of one element with a heavier element in a system and cause biochemical alterations that affect immunological systems and induce disease. Examples of displacement include the replacement of the essential elements Zn and P with Cd and As respectively, both of which are non-essential elements and

highly toxic. When Cd displaces Zn in biochemical systems, changes occur to the Zn containing enzymes causing a considerable loss in activity. The Zn containing enzyme catalyzes the reaction of CO₂ and water, which can affect the immunological system and cause disease.

Pollution by toxic metals is considered by some to be a much more serious and insidious problem than is pollution by organic substances such as pesticides, herbicides, etc². Most organic compounds are naturally degradable although in some cases it may take a considerable amount of time, but no metal is degradable. Metals in elemental form or as salts can exist indefinitely to the point where they are eventually leached by rains into rivers and ultimately into the sea. Therefore, every effort must be made to slow the build up of these toxic trace metals in the environment that concentrate in marine organisms which in turn could be destined for human consumption. Continued research into more economical and expedient ways to detect these metals at very low concentrations is necessary to curtail the eventual environmental impacts.

Considerable difficulties have been encountered in both sampling and analysis of saline water samples for trace metals. These difficulties arise from extremely low trace metal concentrations (0.02-10 µg/L) coupled with the spectral and chemical interferences arising from the variable concentrations of dissolved salts (up to 35 g/L) in the sample

matrix. The concentration of dissolved salts in the sample matrix depends primarily on the sample location, which can pertain to seawater, bay water, estuarine water, brackish river water, etc.

Many methods of sample preparation encountered are designed to both preconcentrate the trace metals and separate them from the interfering components before analyses. These methods are time-consuming, tedious, increase sample handling, use relatively large amounts of reagents, and require contact of the sample with numerous container surfaces. Such methods can result in unacceptable high analytical blanks and possible contamination. These problems are also compounded by the lack of standard reference materials that can allow for detection of errors such as contamination, analyte loss during sample manipulation, and the presence of chemical or spectral interferences effecting instrument response.

A variety of analytical instrumentation and techniques have been used to determine trace metals in saline waters. These methods can be divided into nonspectroscopic techniques and spectroscopic techniques. Nonspectroscopic techniques include: electroanalytical techniques, neutron activation analysis, ion chromatography, and specific ion electrodes. Another important nonspectroscopic technique is mass spectrometry, which more specifically includes isotopic dilution mass spectrometry and inductively coupled plasma mass spectrometry. Spectroscopic techniques include: X-ray

fluorescence, flame and graphite atomic absorption spectrometry, and inductively coupled plasma atomic emission spectrometry. These methods tend to rely on separations and preconcentration of the trace metals, however direct analysis by graphite furnace atomic absorption spectrometry is possible.

Flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) are the most widely used instrumental methods for trace metal determinations, each of which will be briefly discussed.

FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS)

FAAS is a rapid, simple, and precise method of trace metal analysis. Determinations of analyte concentrations in the mg/L concentration range are routine for most metals with a typical analytical working range of two to three orders of magnitude. An advantage of FAAS is that the determination of a single element requires only 3-10 seconds. However, FAAS requires specific light sources such as hollow cathode lamps or electrodeless discharge lamps and different optical parameters for each element to be determined. Different elements may also require different flame gases and burner heads for determinations. Although FAAS can be used for

multielement analysis it is considered a single element technique.

Analysis of major elements and higher concentrations of minor elements in water samples with simple matrices make FAAS the instrument of choice. But for trace metal analysis in saline waters FAAS is a very tedious and time-consuming method. The determination of analyte concentrations at $\mu\text{g/L}$ and below by FAAS requires the use of preconcentration techniques. Preconcentration can be accomplished by several methods including liquid-liquid extraction with a small volume of organic phase (e.g., ammonium pyrrolidine dithiocarbamate in methyl isobutyl ketone)³ relative to a large volume of aqueous phase. The analyte can also be separated and preconcentrated by ion exchange⁴, co-precipitation⁵, and electrochemical methods⁶. The high concentration of salts in saline water samples can cause burner clogging and both chemical and spectral interferences for some trace metals⁷.

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

(ICP-AES)

ICP-AES is the most widely accepted multielement atomic spectroscopy technique. Operator skill requirements are intermediate between FAAS and GFAAS. ICP-AES detection limits are comparable to FAAS detection limits, but ICP-AES has an analytical working range of up to six orders of magnitude. ICP-AES offers significant speed advantages over atomic

absorption for multielement analyses since no source lamps are used. By monitoring selected analytical emission wavelengths for each element, either all at once or in a programmed sequence, many elements in a given sample can be determined in one automated analysis.

Determination of trace metals in saline waters by ICP-AES typically requires a separation of the analyte from the matrix. High concentrations of salts in solution tend to clog the sample orifice of the ICP torch. High alkali and alkaline metal concentrations tend to suppress ion emissions, which are normally the most sensitive analytical wavelengths for the determination of a number of metals. Preconcentration factors of at least 100, and preferably 200-500, are required for analysis of uncontaminated seawater samples⁸. Such sample manipulations are very time-consuming and create difficulties in controlling analytical blanks and contamination problems.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

The major attractiveness of ICP-MS is that it combines the multielement capability and broad linear analytical working range of ICP-AES with the exceptional detection limits of GFAAS, which is in the ng/L concentration range. ICP-MS requires operator skills comparable to those for GFAAS and ICP-AES. Sample throughput for ICP-MS is only slightly less than that of ICP-AES. For ICP-MS, the ICP is used as the ion source for a quadrupole mass spectrometer. Since ICP-MS is

not a spectroscopic technique, spectral interferences do not occur, but interferences from mass overlaps due to other isotopes and polyatomic species produced in the plasma can occur. These interferences may provide erroneous results unless corrections can be applied.

ICP-MS has proven to be a powerful instrument for the determination of trace metals in various matrices. Trace metal determination in saline waters by ICP-MS can however be very time consuming and tedious. Salts must be removed before analysis or interferences corrected during analysis due to mass overlaps. Either salts are removed by chemical separation procedures⁸, or interferences are corrected by procedures such as principle component analysis⁹ or the use of multivariate calibration¹⁰. Separation procedures include solvent extraction from the aqueous solution to an immiscible organic solvent or ion exchange, which relies on the ionic equilibria between the sample solution and a particular ion exchange resin. Interfering polyatomic ions can also be separated from the analyte atomic ions by using a high resolution mass spectrometer¹¹ but the additional instrumentation costs offset the analytical advantages.

GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAAS)

By far the most advanced and highly sensitive atomization technique for atomic absorption is the graphite furnace. Detection limits for most elements are in the ng/L range, but

GFAAS has a limited analytical working range of a little over two orders of magnitude. GFAAS has a relatively low sample throughput because of the need to temperature program the system for electrothermal atomization of samples and to change the specific light sources for each element to be determined as in FAAS.

A single routine GFAAS determination normally requires two to three minutes because of the multiple step temperature program required. These programs typically consist of several controlled and timed temperature parameters for drying, charring, and atomizing the sample. Operator skill requirements are somewhat more extensive than skills required for FAAS.

Determinations of trace metals in saline waters by GFAAS can be accomplished by using several techniques. Most publications describe methods to deal with interference problems that arise from the salt matrix. These include extraction¹² and preconcentration^{6,13} techniques, method of standard additions^{14,15,16,17}, or the use of closely matched standards¹⁸. Detection limits for GFAAS are such that trace metals concentrations can be determined directly¹⁹ from saline waters and verified to be less than the U.S. EPA maximum allowable concentrations. Indeed, GFAAS is the only method explored that has the potential for the direct determination of trace metals in saline water samples using simple aqueous standards. Thus, the specific methods through which this can

be accomplished as given in the associated literature will be discussed in detail.

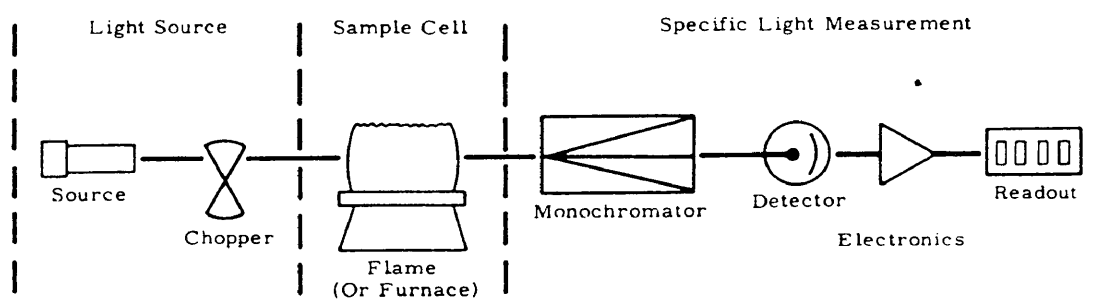
CHAPTER II

GENERAL OVERVIEW OF GFAAS PRINCIPLES

A basic atomic absorption system is shown in Figure 1. In this technique the sample container is a graphite tube, which is placed between the light source and the monochromator of an atomic absorption spectrometer. A small aliquot of analyte (typically 5-100 μL) is quantitatively placed into the tube. An autosampler is normally used to deposit the analyte into the tube through a sample injection hole and onto a flat platform called the L'vov platform. The graphite tube is then heated through a programmed series of elevated temperatures to sequentially remove the solvent and produce the ground state atoms needed for absorption to occur. The absorbance of the radiation source by the atoms is detected by a photomultiplier tube. Integrated peak areas or peak heights are used for quantitation of the analytical signal.

RADIATION SOURCES

Atoms only absorb radiation at energies associated with discrete electronic transitions, thus the radiation source must be monochromatic in order for Beer's Law to be applied to

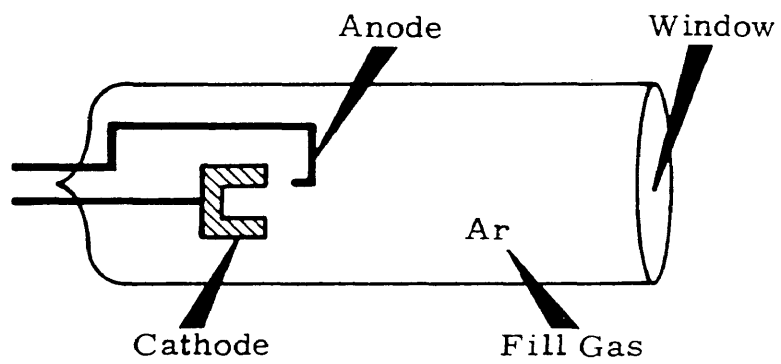
FIGURE 1. Schematic of a basic atomic absorption instrument.

such narrow wavelengths of absorption. This is accomplished by using a line source that emits the specific wavelength that can be absorbed by the element of interest. The most commonly used sources are hollow cathode lamps (HCL) and electrodeless discharge lamps (EDL).

A typical diagram of an HCL is shown in Figure 2. An HCL consists of a tungsten anode and a cathode made from a hollow metal cylinder constructed entirely or in part of the metal whose absorbance is to be measured. The anode and cathode are sealed in a glass tube filled with either argon or neon at a reduced pressure of less than 10 torr. When a small current of 5 to 30 mA is applied between the electrodes, some gas atoms are ionized at the anode. The potential developed between the anode and cathode accelerates the positively charged gas ions to the negatively charged cathode. Collisions of the gas ions with the cathode dislodge individual metal atoms in a process called sputtering to produce an atom cloud of the cathode material. Kinetic energy transferred from the gas ions excite the metal atoms, which then emit radiation of their own characteristic wavelengths while returning to the ground state. The radiation passing through the window of the HCL, which is composed of quartz, is then focused through the graphite tube.

It is sometime possible to construct the cathode out of several metals of interest. These multielement lamps can be used as a radiation source for any of the elements used to

FIGURE 2. A typical hollow cathode lamp.



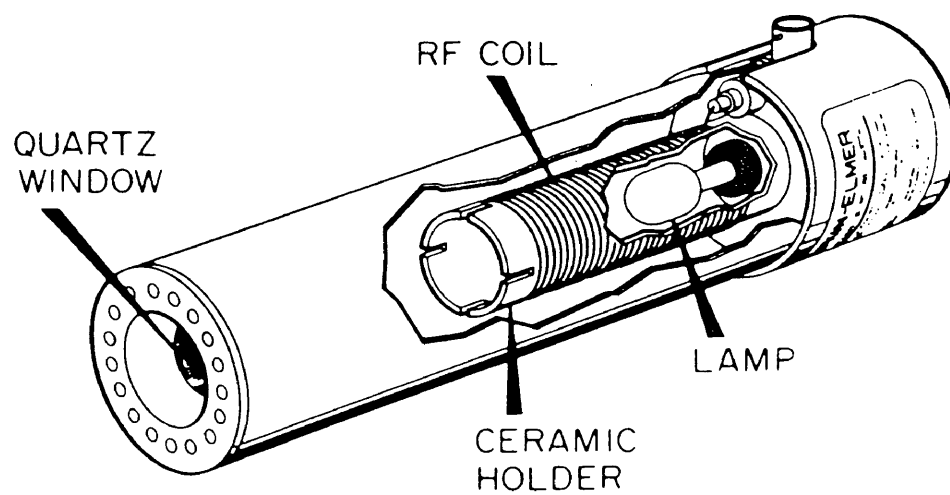
construct the cathode. Only certain elements can be used in combination to construct multielement lamps. Analytical considerations must be taken when using multielement lamps because their intensity is not as great as single element lamps. When high precision or low detection limits are required it may not be advantageous to use multielement lamps due to this loss of intensity.

Each HCL functions at a specific current for optimum performance. Higher currents tend to produce greater emission intensity and less baseline noise. However as the current is increased spectral line broadening will occur, resulting in a reduction of sensitivity and analytical working range.

HCLs have a finite lifetime of one to two years depending on the element, average current used, amount of use, and problems due to leakage of gas-fill. Fill gas absorption onto the inner surfaces of the lamp is also another cause for lamp failure.

A typical EDL design is shown in Figure 3. The EDL is constructed by sealing a small amount of the metal or the metal salt of the element for which the source is to be used into a quartz bulb or tube. The size of the tube or bulb is typically three to eight cm in length and one cm or less in diameter. The bulb is filled with an inert gas and placed inside a ceramic cylinder on which an antenna wire from a radio frequency generator is coiled. When a radio frequency field of adequate power is applied, the coupled energy

FIGURE 3. Cutaway of an electrodeless discharge lamp.



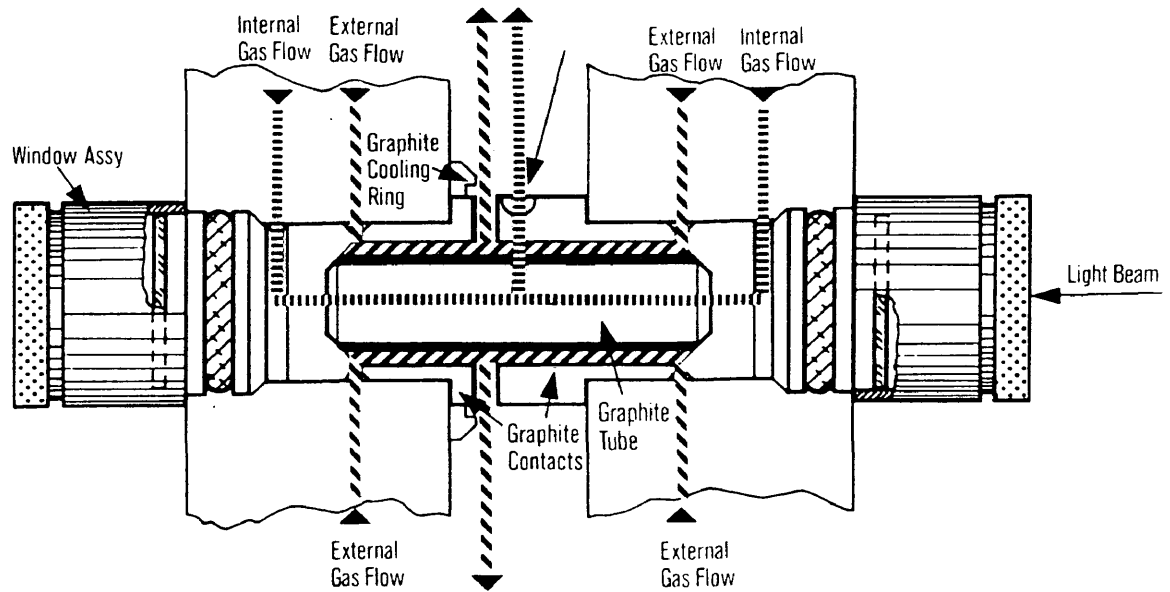
vaporizes and excites the atoms inside the bulb to produce emissions of the wavelength of interest. In order to operate an EDL a separate power supply and a warm up time of 30 minutes is required.

EDLs generally have a much higher intensity and can provide greater sensitivity than HCLs. EDLs provide a definite analytical advantage when analysis is limited by HCL intensities by providing better sensitivity and lower detection limits. Specific situations that require higher intensities involve the volatile elements where low intensity and short lamp life are a problem. EDLs are recommended for As, Sb, Bi, Cd, Pb, Hg, Se, Te, and Sn. Besides the analytical advantages EDLs also have a much longer useful lifetime than HCLs do for the same element. The benefits of EDL performance can only be observed in instruments designed for their use because the optical image for the EDL is markedly larger than that for an HCL.

SAMPLE CELL

A typical graphite furnace atomizer assembly is illustrated in Figure 4. The graphite tube is aligned horizontally in the path of the radiation source and serves as the sample cell. The tube is about 5 cm long and has an internal diameter of less than 1 cm. The electrodes and graphite tube are contained within a water cooled metal jacket assembly and are purged with two separate inert gas streams.

FIGURE 4. A graphite furnace atomizer assembly.



A quartz window at each end of the assembly allows the light source to pass through the graphite tube and forces the gas purge through the graphite tube. The analyte solution, which is usually measured by an autosampler, is deposited through a small hole in the top of the tube onto the inner tube wall or a L'vov platform. The graphite tube fits snugly between two larger graphite cylinders, which are at each end of the water cooled jacket and provide electrical contact. The current is applied across the graphite tube through the graphite electrical contacts, which resistively heats the tube at rates up to 2000 °C per second.

An external inert gas flow is used to minimize oxygen contact on the outside walls of the tube during heating to prevent oxidization of the graphite. A separate purge gas is used through the tube during all programmed heating steps except the atomization step when the absorption is measured. This gas stream not only excludes air but removes the volatilized species during the drying and char steps, which could interfere with the absorption process. The gas flow is stopped during the atomic absorption step to increase residence time of the atomized sample in the tube and thus increase absorption.

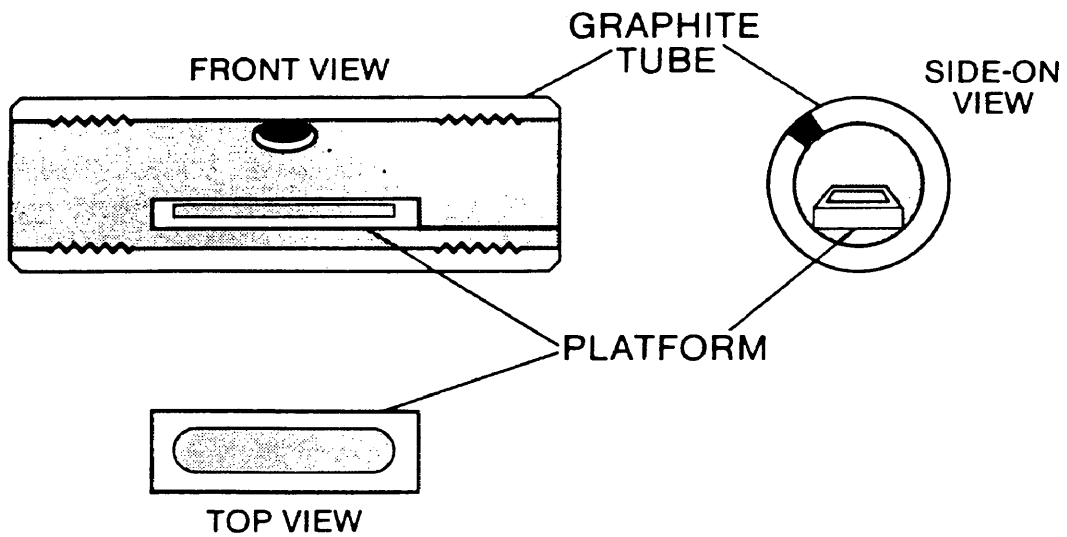
In order to produce sharp, narrow absorption peaks rapid heating rates are required. When the atomization step is initiated, the temperature of the tube wall rises rapidly. Heat is transferred principally by conduction from the tube

wall to the sample. Without a L'vov platform, when the tube reaches the atomization temperature atoms are released into the inert gas atmosphere and are cooled because the temperature of the gas lags behind the temperature of the tube wall. The atomization of the analyte is then inhibited by this cooling and chemical interferences result due to the possible recombination of atoms.

A diagram of the graphite tube with the L'vov platform is shown in Figure 5. When a L'vov platform is used to contain the sample, the temperature of the platform lags behind the temperature of the tube wall. The sample is then atomized when it is at the same temperature as the inert gas environment and not at the temperature of the tube wall. During the atomization step both the gas atmosphere and the platform are heated mainly by radiative heat transfer. Very little convection occurs because there is no flow of gas in the tube during the atomization step and conduction is minimized by the poor physical contact of the platform with the tube wall. When atomization does occur, the platform temperature is in equilibrium with the gas environment temperature, thus interferences are reduced.

L'vov platforms also extend tube life. Unlike the graphite tubes, which are only coated with pyrolytic graphite, the platforms are constructed entirely out of solid pyrolytic graphite. This makes the platforms must more resistant to chemical attack by caustic agents. The platform also prevents

FIGURE 5. A graphite tube with the L'vov platform.



the sample from spreading out over a large surface area, which increases signal reproducibility between the sample and standards if the solutions have different surface tensions.

OPTICS AND WAVELENGTH ISOLATION

Single Beam System

A single beam atomic absorption spectrophotometer is illustrated in Figure 6. A single beam system is based on the absorbance measurements from the varying intensity of one beam of light. Radiation emitted by the HCL is modulated by a chopper or a modulated power source so the detector can differentiate between the emissions from the lamp and the blackbody radiation generated from the electrothermal atomizer. Gated electronics synchronized with the chopper drive or the modulated power source measure a net signal from the HCL and produces a true absorbance signal.

Double Beam Systems

A double beam atomic absorption spectrophotometer is illustrated in Figure 7. The lamp emission is equally split into two beams by a mirrored chopper. One beam is directed around the sample cell as the reference beam, (P_r) and the other beam is directed through the sample cell as the sample beam, (P). Both beams are then directed onto a half-silvered mirror where they are focused through the monochromator. Computer controlled electronics synchronized with the chopper drive sequentially measures the intensity of the sample and

FIGURE 6. Schematic of a basic single beam atomic absorption spectrophotometer.

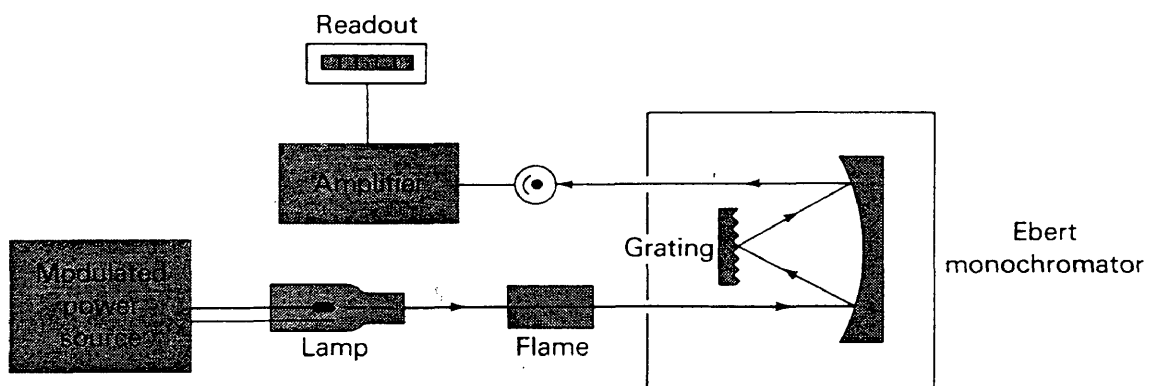
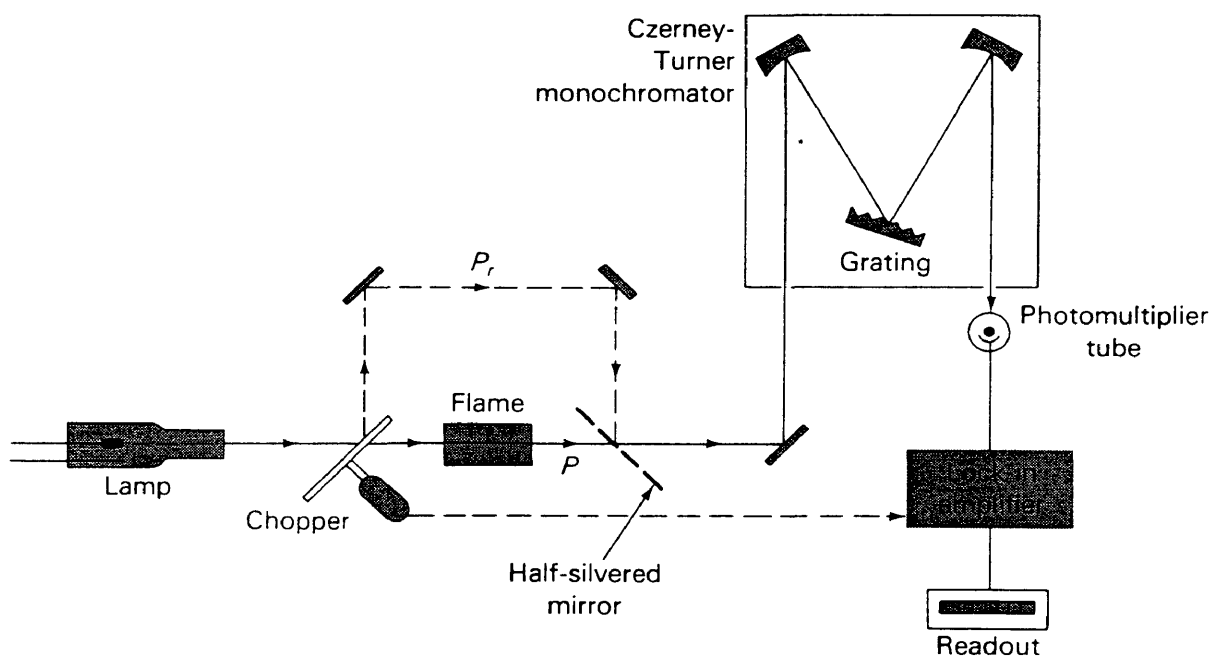


FIGURE 7. Schematic of a basic double beam atomic absorption spectrophotometer.



the reference beam signals. The measured absorbance is appropriately determined from a ratio of the sample beam and the reference beam signals in the data acquisition system. The reference beam monitors discrepancies in the signal due to abnormalities in the system electronics and drifting lamp intensity. The observed absorbance is therefore free from anomalies due to drifting lamp intensities and electronic abnormalities that effect both sample and reference beams similarly. The double beam design can also reduce analysis time and increase the lamp lifetime by eliminating the need for a warm up period for power stabilization.

A monochromator is used to isolate the analytical wavelength of interest emitted by the primary radiation source from other emissions situated close to the source spectrum as well as emissions from the electrothermal atomizer. Photomultiplier tubes are typically used for detectors.

GRAPHITE FURNACE AUTOMATED PROGRAMS

A typical GFAAS instrument can perform the following functions and store them in memory for automated sampling when conducting identical analysis on multiple samples:

1. temperature program control
2. gas flow control
3. autosampler volume and sequence control
4. optics and monochromator control
5. lamp current control

6. automated calibration curve production
7. calculation of sample concentrations

A graphite furnace analysis involves the measuring and dispensing of a 5-100 μL aliquot of sample into the graphite tube. The sample is then subjected to a sequenced series of timed temperature steps. The program also allows selection of gas flow rates and choice of purge gases during each step. When the temperature is increased to the point where atomization takes place, the absorption measurement is made.

Selections of both the temperature program parameters and the modifier have the most potential to reduce interferences in direct GFAAS analysis. Temperature programming will be briefly discussed in this section, and modifier selection will be explored later.

Variables under operator control in the temperature program include:

1. the final temperature of each step
2. the ramp time for the temperature increase to the final temperatures
3. the hold time for maintaining the final temperatures
4. the internal gas flow rate and type of gas

A typical graphite furnace temperature program consists of three to five steps. The program usually includes:

1. a drying step
2. a charring step
3. a pre-atomization cool down step

4. an atomization step
5. a clean out step

Drying Step

The purpose of this step is to remove the solvent and/or other volatile liquids from the sample. Drying times and temperatures are dependent on sample volumes and the solvent used. Drying temperatures for water can range from 90 to 250 °C but typical drying temperatures usually range from 100 to 160 °C. Recommended hold times range from 15 seconds for a 10 μ L sample to 60 seconds for a 100 μ L sample. Temperatures must be low enough to avoid splattering from excessive heating, which reduces analytical precision. If a higher drying temperature is needed, a ramped temperature increase over a fixed time period is used to avoid splattering. During the drying step, the internal gas flow is normally set at a maximum of 300 mL per minute.

Charring Step

The charring step is used to remove any components of the sample matrix that are more volatile than the element of interest. During this step the temperature is increased as high as possible to volatilize matrix components but below the temperature at which analyte loss would occur to decrease the possibility of interference due to broad band absorption from molecular species. The selection of char temperatures is a function of the sample matrix, the modifier, and the element of interest. Temperatures and times are usually suggested in

the literature. Ramped times are normally used during the char step. Again the gas flow is normally kept at the maximum during the char step to remove the volatilized matrix components.

Pre-atomization Cool Down Step

It is frequently advantageous to cool the tube to ambient temperatures before atomization of the sample. For most furnaces the heating rate is a function of the temperature range to be covered. When the temperature range is increased, the heating rate is increased. A cool down step before atomization increases the heating rate and creates a larger isothermal zone in the tube immediately after heating, which improves sensitivity and reduces peak trailing for some elements. The use of a cool down step can reduce or eliminate interferences that could not otherwise be controlled¹⁹.

Atomization Step

One of the most critical processes in the GFAAS procedure is to generate atoms in the ground state, from the ions or molecules present in the sample, in order for absorption to occur. As with the char step, the sample matrix, the modifier, and the element of interest are important to consider when selecting atomization temperatures. Temperatures and times are usually suggested in the literature.

The atomization temperature is usually attained as quickly as possible, therefore ramp times are normally not

used during the atomization step except in cases where the analyte and matrix atomize in the same temperature region. In such cases a selective volatilization technique can be used, which uses a ramped time during the atomization step to volatilize one component before the other. The gas flow is stopped during the atomization step to increase residence time of the atom vapor in the path of the radiation and increase sensitivity.

Clean Out Step

After the atomization step the temperature of the graphite tube is usually increased to a maximum (2600–2800 °C) to burn off any residue that may remain in the graphite tube.

QUANTITATIVE ANALYSIS BY ATOMIC ABSORPTION

Light at the analytical wavelength of initial power (P_0) is focused into the graphite tube. Ground state atoms are excited by the absorption of the light energy at the specific analytical wavelength. The initial power is decreased by some amount determined by the atom concentration in the graphite tube. The residual radiation is then focused onto the photomultiplier tube where the reduced power (P) is measured. The amount of light absorbed is determined by comparing the initial power to the reduced power.

Several terms must be defined in order to discuss Beer's Law. The transmittance is defined as the fraction of the

original light that passes through the sample and decreases as the attenuation of the original light becomes greater.

$$T = P/P_0$$

A more useful quantity is the absorbance defined by

$$A = \log (P_0/P) = - \log T$$

In contrast to transmittance, the absorbance increases as the attenuation of the beam becomes greater. Absorbance is the most convenient term for characterizing light absorption in spectrophotometry. Beer's Law states this quantity follows a linear relationship with concentration for a fixed set of instrument conditions as given by,

$$A = abc$$

where A is the absorbance, a is the absorption coefficient, b is the sample cell length, and c is the concentration. The absorption coefficient is characteristic of the substance and is also used for unit conversion since the product abc must be dimensionless.

This direct proportional behavior between absorption and concentration is used for quantitative analysis in GFAAS. The absorbance of standard solutions containing known concentrations of analyte is measured and the absorbance data plotted against the concentrations to create a calibration curve. The concentration of analyte solutions can then be determined by correlating their absorbance values to the calibration curve. Although the use of simple aqueous standards is quite suitable for the analysis of trace elements

in a wide variety of matrices, there are instances where it becomes critical that the matrices of the standards are closely matched to that of the samples. Different samples can have different types of interferences that affect the absorbance and background signals producing non-quantitative calibration curves.

INTERFERENCES IN ATOMIC ABSORPTION SPECTROSCOPY

Interferences in GFAAS are associated with both chemical and spectral phenomena. Chemical interferences are those interferences caused by various chemical processes that occur during the atomization step that adversely affect the analytical signal being measured. Free ground state atoms of the analyte element must be present in the light path of the spectrophotometer for atomic absorption to take place. Chemical interferences occur when the sample matrix inhibits the formation of free atoms. An example would be the formation of oxides of the analyte which will decrease the concentration of the free analyte atoms measured.

Spectral interferences are due to the incomplete isolation of the analyte signal from the interfering species signal. This occurs when the absorption or emission of an interfering species either overlaps or is sufficiently close to the analyte absorption line that the monochromator cannot differentiate between the two signals. The most common sources of spectral interferences in GFAAS are light

scattering and molecular absorption²¹. Molecular absorption can result from the presence of molecules produced from the recombination of the matrix and/or analyte atoms in the atomization process that exhibit broad band absorption. Light scattering may become a problem due to incomplete atomization of an organic matrix which can form carbonaceous particles and lead to substantial background absorbance²².

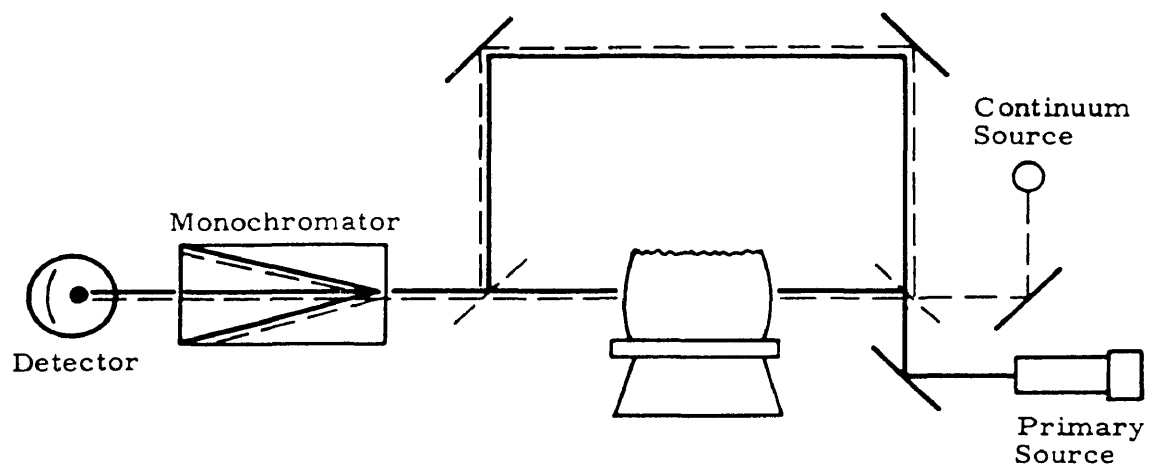
Background absorption due to spectral interferences can also cause severe measurement problems in GFAAS. It is a nonspecific attenuation of radiation at the analyte wavelengths caused by the sample matrix. Background absorption tends to be primarily due to broad band molecular and is a function of the sample matrix being investigated.

TECHNIQUES FOR REDUCTION OF BACKGROUND INTERFERENCES

Continuous Source Background Correction

Continuous source background correction uses a deuterium lamp to provide a source of continuous radiation throughout the ultraviolet and visible region. Figure 8 shows a basic continuous source background correction system. A mirrored chopper alternates the line source radiation and the continuous source radiation through the graphite tube. Since the analyte only absorbs radiation at very narrow and discrete wavelengths it will not measurably affect the intensity of the deuterium lamp, which emits broad band radiation. But the background, which can absorb over a very broad spectral range

FIGURE 8. Schematic of a basic continuous source background correction system.



will noticeably attenuate the continuous source as well as the line source. The data acquisition system gives a corrected absorbance by subtracting the absorbance of the continuous source from the total absorbance of the line source.

The performance from continuous background correction is frequently flawed because two radiation sources are used. The deuterium source contains the background component of the signal, while the HCL or EDL measures the total uncorrected signal. If the two lamps are not in perfect optical alignment and pass through different parts of the atom cloud, erroneous results will occur. Continuous background correction is inaccurate for structural background absorption such as light scatter because the two sources can be attenuated to different degrees. It has been shown that continuous background correction can result in considerable positive and negative errors due to under or over compensation when correcting for high background levels in GFAAS²¹.

Zeeman Background Correction

Zeeman background correction relies on the principle that splitting of electronic energy levels of atoms takes place when the atomic vapor is subjected to a strong magnetic field. This alters the atomic spectra by forming several closely spaced absorption lines for each electronic transition. These altered electronic states may split into several components symmetrically displaced about the normal wavelength position. The sums of the absorbance of the split lines are equal to the

absorbance of the original line from which they were formed. This phenomenon is known as the Zeeman effect.

Radiation exiting the lamp is passed through a rotating polarizer, with one-half plane polarized and the other half polarized 90 degrees to the direction of the magnetic field. This alternating beam of radiation then passes through the graphite tube, which is surrounded by a permanent magnet. The analyte will only absorb radiation that is plane polarized in the direction of the magnetic field. No absorption takes place by the analyte from the radiation polarized 90 degrees in relationship to the direction of the magnetic field. During the entire cycle broad band molecular absorption and light scattering can occur, which is absorbed in all planes. The data acquisition system can produce a corrected background signal by calculating the difference between the two absorption signals measured during a complete cycle.

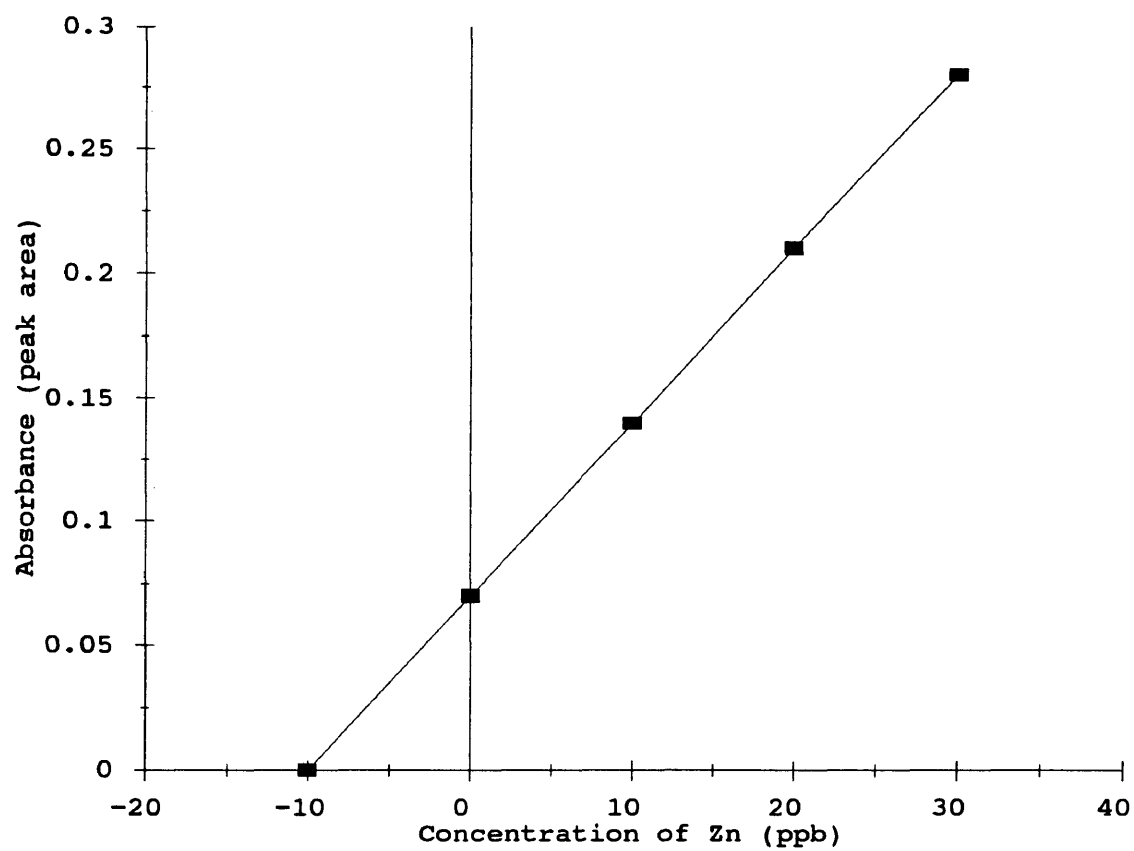
Instruments with Zeeman background correction provide a more accurate correction for background interferences than do continuous background correction instruments. As mentioned earlier, the decomposition of organic compounds in some matrices can lead to substantial background absorbance, which can readily be corrected for using Zeeman background correction. Another advantage of Zeeman background correction is that it requires only one light source and thus does not require alignment and intensity matching of two light sources.

Method of Standard Additions

Accurate determinations of analyte concentrations in interfering matrices are possible using the method of standard additions. This method makes it possible to work in the presence of a matrix interference without eliminating the interference. The major disadvantage of this method is that it must be repeated for each determination, thus it is very tedious and time consuming.

Increasing concentrations of a standard solution containing the element of interest are added to sample aliquots that are all diluted to the same volume. This method allows any interferences present in the sample to also affect the calibration standards similarly. A typical graph produced using the method of standard additions is shown in Figure 9. For example consider the determination of Zn in seawater. A 100 $\mu\text{g/L}$ Zn standard can be added in volumetric increments of 0, 10, 20, and 30 mL to four 100 mL volumetric flasks each containing 50 mL aliquots of seawater and diluted to volume with deionized water. The final standard concentrations of Zn in the four flasks will be 0, 10, 20, and 30 $\mu\text{g/L}$.

The measured absorbance values and the concentrations of the standard additions are then plotted. The slope is used to extrapolate the calibration line back to the zero intercept of the absorbance axis. The intersection of the calculated linear regression line with the absolute value of abscissa

FIGURE 9. A typical method of standard additions plot.

indicates the concentration of Zn contained in the unspiked sample.

Matrix Modification

The use of matrix modification in GFAAS analysis was first introduced by Ediger²². Matrix modifiers are compounds added to the sample to free the analyte element from matrix effects and/or enhance analyte atomization, enabling detection of trace metals at the lowest possible levels. This can be accomplished in several ways, including increasing or decreasing the volatility of the analyte metal or the interfering matrix, or converting the interfering species to compounds exhibiting lower levels of molecular absorption. Decreasing the volatility of the analyte metal allows for higher char and atomization temperatures, causing the volatilization of the interfering matrix to occur before the atomization of the analyte metal. An example of this type of modifier is a mixture of palladium and magnesium nitrates, which stabilize certain elements to allow the use of substantially higher char and atomization temperatures. The mechanism of the stabilization has not been investigated in detail but it is believed that the palladium forms an alloy with the analyte which increases the atomization temperature²³.

Increasing the volatility of the interfering matrix will permit for volatilization before the metal analyte is atomized. ° The use of ammonium nitrate to eliminate interferences of sodium chloride during sea water analysis is

one example of this type of modifier²⁴. The lower volatilization temperatures of ammonium chloride and sodium nitrate allow elimination of these interfering salts before the atomization of the analyte metal.

Selective Volatilization

Selective volatilization involves the use of different temperatures and temperature programs to volatilize interfering compounds from the sample before atomization is attempted. The char step is used for this purpose but the success of such an approach depends on the atomization temperature of the analyte. Temperature ramping has been successfully used for separation of the analyte from interfering matrix components¹⁵. When the analyte and matrix atomize in the same temperature range a ramped time for the atomization step can be used to volatilize one component before the other. The analyte absorption can be detected by using precise integration times.

CHAPTER III

GFAAS METHODS FOR SALINE WATER ANALYSIS

This study ultimately concentrated on the GFAAS determination of As, Cd, Co, Cr, Cu, Mn, Ni, and Pb in saline waters. Modern GFAAS instrumentation typically produces, from programmed memory, the recommended parameters for the determination of each element. A list of recommended parameters and matrix modifiers used for the GFAAS determination of these elements with a Perkin Elmer GFAAS is given in Table 2. The detection limits and conditions given for these elements are based on simple aqueous standards. Detection limits given in Table 2 are enhanced significantly for most of these elements relative to using no modifiers.

In 1983 Manning and Slavin reported the successful development of procedures for the direct determination of 12 trace elements in natural waters using the stabilized temperature platform furnace¹⁹. Only simple aqueous standards were used for calibrations and the method of additions was not required. A Perkin Elmer Model 5000 atomic absorption spectrophotometer equipped with an HGA 500 graphite furnace and AS-40 autosampler was used. All background corrections

TABLE 2. Perkin Elmer recommended parameters and matrix modifiers for selected elements studied^a.

| ELEMENT | WAVE LENGTH (nm) | SLIT WIDTH (nm) | MATRIX MODIFIER ^b | TEMPERATURE (°C) | | DETECTION LIMIT (µg/L) |
|---------|---------------------|--------------------|--|---------------------|------|---------------------------|
| | | | | CHAR | ATOM | |
| As | 193.7 | 0.7 | 0.015 mg of Pd and 0.01 mg of Mg(NO ₃) ₂ | 1300 | 2300 | 0.5 |
| Cd | 228.8 | 0.7 | 0.2 mg of PO ₄ | 700 | 1600 | 0.02 |
| Co | 240.7 | 0.2 | 0.05 mg of Mg(NO ₃) ₂ | 1400 | 2500 | 0.4 |
| Cr | 357.9 | 0.7 | 0.05 mg of Mg(NO ₃) ₂ | 1650 | 2500 | 0.08 |
| Cu | 324.8 | 0.7 | NONE | 1000 | 2300 | 0.25 |
| Mn | 279.5 | 0.2 | 0.05 mg of Mg(NO ₃) ₂ | 1400 | 2200 | 0.6 |
| Ni | 232.0 | 0.2 | NONE | 1400 | 2500 | 0.8 |
| Pb | 283.3 | 0.7 | 0.2 mg of PO ₄ | 700 | 1800 | 0.15 |

^aReference 26 and 27

^bAssume a typical sample size of 20 µL.

were made using either a tungsten-iodide lamp or a deuterium lamp depending on the analytical wavelength.

All determinations were based on 20 μL sample aliquots with 5 μL of matrix modifier. Magnesium nitrate in 2% HNO_3 was used as the matrix modifier for Al, Be, Co, Cr, Mn, and Ni. A combination of magnesium nitrate and ammonium phosphate modifiers in 2% HNO_3 was used for Cd and Pb. Nickel dissolved in 20% HNO_3 was used for As and Se. No matrix modifiers were required for Cu and V. The HNO_3 was not only used to preserve the modifiers but also to prevent a precipitate from forming when preparing the Cd and Pb modifiers. A magnesium phosphate precipitate forms if the hydronium ion concentration is not sufficient to keep the salt soluble.

The recommended matrix modifier concentrations and temperature settings are shown in Table 3. A drying step of 250 $^\circ\text{C}$ for 45 seconds and a clean out step of 2600 $^\circ\text{C}$ for 6 seconds were used for each element.

Conformation of the method was corroborated by recovery experiments in which the samples were spiked at four different concentration levels of the elements to verify signal integrity in the sample matrix. The simple recovery experiments satisfactorily confirmed freedom from chemical interferences. The detection limits in the natural waters approached 0.1 $\mu\text{g}/\text{L}$ for most of the elements with a precision of 10 to 15%.

TABLE 3. Manning and Slavin recommended matrix modifiers and temperature parameters.

| ELEMENT | MATRIX MODIFIER ^a | CHAR TEMPERATURE | ATOMIZATION TEMPERATURE |
|---------|---|------------------|-------------------------|
| As | 20 μg of Ni as nitrate | 1500 °C - 45 s | 2500 °C - 6 s |
| Cd | 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 200 μg of $\text{NH}_4\text{H}_2\text{PO}_4$ | 1000 °C - 45 s | 1600 °C - 6 s |
| Co | 50 μg of $\text{Mg}(\text{NO}_3)_2$ | 1400 °C - 45 s | 2400 °C - 10 s |
| Cr | 50 μg of $\text{Mg}(\text{NO}_3)_2$ | 1600 °C - 45 s | 2400 °C - 10 s |
| Cu | none | 1300 °C - 45 s | 2300 °C - 6 s |
| Mn | 50 μg of $\text{Mg}(\text{NO}_3)_2$ | 1400 °C - 45 s | 2300 °C - 6 s |
| Ni | 50 μg of $\text{Mg}(\text{NO}_3)_2$ | 1400 °C - 45 s | 2400 °C - 10 s |
| Pb | 2 μg of $\text{Mg}(\text{NO}_3)_2$ and 10 μg of $\text{NH}_4\text{H}_2\text{PO}_4$ | 1100 °C - 45 s | 1800 °C - 6 s |

^aassumes a 5 μL aliquot

Schlemmer and Welz proposed the use of palladium and magnesium nitrates as a universal modifier for the determination of As, Bi, In, Pb, Sb, Se, Sn, Te, and Tl by GFAAS²⁴. The authors claimed that thermal pretreatment temperatures of 900-1400°C could be used with this mixture of modifiers for the separation of the analyte from the matrix.

A Perkin Elmer Zeeman Model 3030 atomic absorption spectrophotometer equipped with an HGA 600 Zeeman graphite furnace and AS-60 autosampler was used. EDLs were used as line sources for all determinations. Wavelength, slit width, and lamp power were set according to recommended specifications. Typical temperature programs were used with the exception of elevated char and atomization temperatures.

The mixture of palladium and magnesium nitrates was shown to be an excellent modifier for GFAAS determination of Group 3A through 6A elements of the periodic table. The palladium and magnesium nitrates modifiers allowed use of char temperatures of at least 900-1000 °C for all investigated elements. These higher char temperatures allowed effective removal of biological matrices and removal of inorganic contaminants before atomization. This modifier allowed for the use of common conditions for all elements investigated with a minimum of sacrifice in sensitivity.

An example of a complete temperature program used for lead with the Pd/Mg(NO₃)₂ modifier as suggested by Schlemmer and Welz is given in Table 4. The Pd/Mg(NO₃)₂ modifier

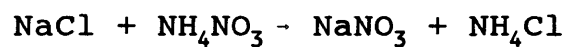
TABLE 4. Schlemmer and Welz recommended temperature program for Pb.

| STEP | FURNACE TEMP (°C) | RAMP TIME (s) | HOLD TIME (s) | INTERNAL GAS FLOW (mL/min) | READ SIGNAL |
|-------------|----------------------------------|------------------------------|------------------------------|---|------------------------|
| Dry #1 | 90 | 1 | 9 | 300 | |
| Dry #2 | 120 | 10 | 30 | 300 | |
| Char | 1000 | 10 | 30 | 300 | |
| Atomization | 1900 | 0 | 4 | 0 | yes |
| Clean Out | 2650 | 1 | 6 | 300 | |
| Cool Down | 20 | 1 | 5 | 300 | |

contained 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 15 μg of $\text{Pd}(\text{NO}_3)_2$ per 10 μL of modifier solution used per sample aliquot. No sample volumes were given. This method was not used to quantitatively determine lead in the seawater but rather for screening purposes of polluted shoreline waters. No calibration curves were developed for Pb in seawater. The detection limit, which was calculated to be 1 μg Pb/L of seawater was used for screening purposes. This modifier allowed for a 300 °C higher char temperature and a 100 °C higher atomization temperature than typical temperatures used for Pb. These elevated temperatures implied that the direct determination of Pb in saline waters could be achieved by allowing for volatilization of the matrix before the Pb was atomized.

Ediger Peterson and Kerber used ammonium nitrate for the direct determination of Cu in saline water by GFAAS coupled with the methods of additions¹⁶. They reported that the sodium chloride interferences could be minimized by volatilizing the salt matrix during the char step for removal prior to atomization. Any remaining background absorption could usually be compensated for by using deuterium background correction.

A large excess of an NH_4NO_3 solution dried with a NaCl solution supposedly forms a NaNO_3 and NH_4Cl mixture. This reaction along with the melting points and boiling points are shown in Table 5. The NH_4NO_3 , NaNO_3 , and NH_4Cl are removed by volatilization during the charring step at about 500 °C.

TABLE 5. The effect of ammonium nitrate on sodium chloride.

| COMPOUND | MELTING POINT (°C) | BOILING POINT (°C) |
|--------------------------|-----------------------|-----------------------|
| NaCl | 801 | 1413 |
| NH_4NO_3 | 170 | 210-decomposes |
| NaNO_3 | 307 | 380-decomposes |
| NH_4Cl | 355-sublimes | |

The analysis was carried out by combining 50 μL of sample and 20 μL of 50% NH_4NO_3 solution in the graphite furnace using a nitrogen gas purge. The solution was dried at 120 $^\circ\text{C}$ for 30 seconds, charred at 1000 $^\circ\text{C}$ for 60 seconds, and atomized at 2500 $^\circ\text{C}$ for 10 seconds. The analysis was done by the method of additions with deuterium background correction.

For conformation of the Ediger et al. method a set of 14 samples was taken off the coast of New York City, air filtered and stored in acid. The samples were analyzed by two independent laboratories by both direct injection into a GFAAS using the Ediger et al. method and after an ammonium pyrrolidine dithiocarbamate/methyl isobutyl ketone (APDC/MIBK) extraction. The results of the two methods were in reasonable agreement. The same procedure was used on samples spiked with As and a relative standard deviation of 5.6% was reported. Another important phenomenon reported in this paper was the depressive effect the sample matrix had at increasing concentrations on the analyte signal. This occurrence will be discussed later in this paper as related to our experimental observations.

Montgomery and Peterson also used ammonium nitrate as a matrix modifier in the direct analysis of seawater for Cu, Fe, and Mn by GFAAS²⁵. They also reported that the sodium chloride interferences in seawater were eliminated by volatilizing the salt matrix during the char step for removal prior to atomization.

This report also focused on decreases in sensitivity of various lots of graphite tubes caused by the prolonged use of ammonium nitrate as a matrix modifier. The analysis of seawater for Cu by GFAAS using NH_4NO_3 as a matrix modifier was strongly dependent on the quality of the pyrolytic coating on the graphite tubes. The seawater itself could decrease the sensitivity obtainable by forming corrosive halogen compounds that degrade the pyrolytic coating. This suggestion was substantiated by the fact that the sensitivity with a coated tube tended to decline to values obtained with uncoated tubes. Further, the sodium oxide formed by thermal decomposition of the matrix modifier could react with the hot graphite coating of the pyrolytic coating, forming carbon monoxide. It was suggested that a 50% dilution of the seawater with deionized water be used for analysis and that the sensitivity be checked every 10-20 atomizations by comparisons to a standard.

The direct determination of manganese in natural waters by GFAAS using ammonium nitrate was reported by McArthur²⁸. Different temperature programs were examined in this report. A 20 μL aliquot of 30% (w/v) NH_4NO_3 was added to the furnace before the 50 μL sample aliquot. The drying step consisted of a 100 °C temperature for 35 seconds. Various char programs were investigated, either with a 28 °C/s ramped temperature or an immediate char temperature held for 15 to 20 seconds at several different final temperatures. The use

of slow ramp times during the char step was investigated to remove interferences in seawater due to the high salinity. The atomization temperature used was 2400 °C for 10 seconds and a clean out step at maximum temperature was used for 3 to 4 seconds. The method of standard additions was used in this procedure. The use of ramped char temperature with either 1% NH_4NO_3 or excess NH_4NO_3 greatly reduced the interference of sea salt.

Hydes used 1% (w/v) ascorbic acid to reduce seawater interferences in direct measurements of Cu and eliminate interferences in the direct determination of Co and Mn^{29} . Measurements were made using a Perkin Elmer graphite furnace fitted with tantalum treated tubes purged with Ar at 40 mL/min. Background absorption was compensated for by using deuterium background correction.

No specific char temperatures were recommended but rather a study of char temperature verse peak height for each element was conducted. Char temperatures between 300 and 1500 °C were investigated for times of 20, 40, and 60 seconds. An atomization temperature of 2600 °C for 5 seconds was used for all elements.

The addition of 1% (w/v) ascorbic acid to 20 μL seawater samples increased the analytical sensitivity for Co, Cu, and Mn to approach that observed in a 0.1 M HCl matrix. The interferences occurring in NaCl solution for Co and Mn were eliminated with the use of 1% (w/v) ascorbic acid. In this

work the calibration curves remained linear. The most easily observed effect of the organic acid was that it acted as a surfactant. Seawater without an organic acid dried in the furnace as visible crystals. When the organic acid was added, the surface tension of the sample was reduced and no residue was visible at the end of the drying step. It was suggested that the most likely process to reduce interference in seawater is one that promotes atomization from the oxide rather than the chloride salt of the analyte. A mechanism by which ascorbic acid promotes the conversion of the chloride salt of the analyte to oxide was not discussed.

Of particular interest in the Hydes paper was negative signals observed at the start of the atomization period. This occurred after several analysis cycles when sample volumes larger than 20 μL were used. Condensation of sea salts in cooler portions of the tubes was determined to produce the negative signals at the start of the atomization period. The salts were removed by cleaning the inside of the tube with tissue paper.

Guevremont investigated the use of various organic matrix modifiers for direct GFAAS determination of Cd in seawater³⁰. The modifiers studied were EDTA, citric acid, histidine, lactic acid and aspartic acid. All measurements were made using a Perkin Elmer Model 503 spectrometer equipped with deuterium arc background correction.

Table 6 shows the temperature conditions used for Cd analysis with the different matrix modifiers. The samples were not charred if only slight improvements in the background absorbance was expected. The seawater samples were filtered and stored at 4 °C. The modifiers were weighed directly into the seawater at a concentration of 1 mg/mL. A 20 μ L sample aliquot was used for all analysis. Accumulation of salts from the seawater in the graphite tubes was not a problem but each tube was used for no more than 40 firings. The analysis still required the use of the method of additions to compensate for interferences.

The most effective matrix modifiers were citric acid, lactic acid, and aspartic acid. Direct GFAAS analysis for Cd in seawater was carried out using each modifier. Citric acid was the most promising matrix modifier tested by the authors, yielding the highest sensitivity and the smallest background interferences. These interferences were easily corrected for by using deuterium arc background correction.

Guevremont et al. described a method for the direct determination of Cd in seawater using EDTA as a modifier¹⁵. Measurements were made using a Perkin Elmer Model 503 spectrometer equipped with deuterium arc background correction. It was reported that the addition of EDTA (1 mg/mL) reduced the atomization temperature of Cd far below the volatilization temperature of the other matrix components.

TABLE 6. The temperature parameters for various organic matrix modifiers recommended by Guevermont.

| MATRIX MODIFIER | CHAR TEMPERATURE (°C) | CHAR TIME (s) | ATOMIZATION TEMPERATURE (°C) | ARGON GAS FLOW (instrument units) |
|------------------------|------------------------------|----------------------|-------------------------------------|--|
| EDTA | | | 1000 | 20 |
| citric acid | | | 1000 | 20 |
| histidine | 400 | 10 | 1200 | 10 |
| lactic acid | 550 | 10 | 1100 | 10 |
| aspartic acid | 500 | 10 | 1200 | 0 |

The tetrasodium salt of EDTA was weighed directly into the seawater at a concentration of 1 mg/mL along with the addition of standard concentrations of Cd. Sample aliquots of 20 μ L were used. The Cd atomization was suppressed if the seawater samples were acidified with HNO₃ and required 2.5 mg/mL of EDTA to offset the suppression. No suppressing effect was observed by HCl.

Because of the low atomization temperatures, it was essential to use a char temperature low enough to avoid loss of Cd. A very important point made in this article was that rapid heating rates shifted the analyte signal to the region where co-volatilization with the matrix occurred, thus ramped temperatures were used during the atomization step. A typical heating program for the direct determination of Cd in seawater using EDTA as a matrix modifier is given in Table 7.

The addition of EDTA as a matrix modifier to undiluted seawater in combination with selective volatilization techniques allowed for Cd to be determined by direct GFAAS. Several seawater samples were filtered and acidified to a pH of 2.7 and then analyzed by several methods including 1) GFAAS after separation and concentration with APDC/MIBK, 2) isotope spark dilution spark source mass spectrometry (SSMS) after concentration on a Chelex-100 ion exchange column, and 3) direct GFAAS under the conditions listed in Table 6 using the method of standard additions. An average Cd value of 0.048 ± 0.005 μ g/L was determined using direct GFAAS which was in good

TABLE 7. A typical heating program recommended by Guevremont et al. for the direct determination of Cd in seawater using EDTA.

| STEP | FINAL TEMPERATURE (°C) | RAMP TIME (s) | HOLD TIME (s) | GAS FLOW (mL/min) |
|-------------|-----------------------------------|--------------------------|--------------------------|------------------------------|
| Dry | 90 | 30 | 30 | 200 |
| Char | 250 | 15 | 5 | 200 |
| Atomization | 2500 | 5 | 2 | gas stop @ 3s |

agreement with the results found using solvent extraction of $0.053 \pm 0.005 \mu\text{g/L}$ and by SSMS of $0.063 \pm 0.009 \mu\text{g/L}$. The precision of the determination was $\pm 10\%$ at the $0.05 \mu\text{g/L}$ level. EDTA appears to catalyze or act as a reducing agent to bring about the immediate atomization of Cd at low temperatures. Even with this procedure the method of additions was still required to compensate for signal suppression by the matrix relative to aqueous standards.

Matsusaki et al. proposed the use of tertaammonium EDTA as a matrix modifier for Cr^{31} . They reported that tertaammonium EDTA was a good reagent for the removal of chloride interferences, even when lower charring temperatures are used. Sample aliquots of $5 \mu\text{L}$ were used and samples were adjusted to a pH of 3 with HCl. Some temperatures were given in units of applied voltage between the atomizer terminals and some were given in centigrade.

Several studies were done in conjunction with this report concerning the effect of chlorides on chromium atomic absorption. They included the effect of coexisting cations, the charring temperature, the pH of the sample solution, and the standing time of the sample solution after the addition of chlorides.

In conclusion the only literature that which claimed successful direct determination of trace metals using simple aqueous standards and deuterium background was the Manning and Slavin paper¹⁹. Although the title mentions "Natural Water" the

samples analyzed for this publication were obtained from the Norwalk River, which is a tributary to the Atlantic Ocean. Sample locations were not specified but the assumption was made that the samples had at least a slightly brackish content due to the river's proximity to the Atlantic Ocean. Previous attempts in our lab to use this method for trace metal analysis of local saline water samples had proved unsuccessful.

The focus of this research was to verify the Manning and Slavin methods and study other modifiers that appear to show some promise. Modifiers such as the palladium and magnesium nitrate mixture²⁴, which raise the volatilization temperature of the analyte and the ammonium nitrate¹⁶, which lowers the volatilization temperature of the seawater matrix, show potential for direct determination of trace metals in seawater. Also of interest is the use of EDTA with a ramped atomization temperature¹⁵ and organic acid modifiers^{29,30,32}.

CHAPTER IV

INSTRUMENTATION AND EXPERIMENTAL METHODS

REAGENTS

Reagent grade HCl and HNO₃ (Fisher) were used for cleaning all labware. Trace metal grade HNO₃ and HCl (Fisher) were used for all sample preparation and acid blank calibration solutions. Semiconductor grade deionized water was used with all procedures. This water was produced by first passing laboratory grade deionized water through a particulate filter then through a semiconductor grade deionizing cartridge. A polybutylene tap was connected directly to the deionizing system to avoid contamination that would be encountered by using metal taps.

All calibration standards were derived from serial dilutions of 1000 µg/mL commercial single element standards in 0.5% acid. Standard solutions for As, Co, Cr, Cu, Ni, and Pb were prepared from Aldrich AA standards. The standards for Cd and Mn were prepared from Ricca Chemical Company AA standards. The final standard concentrations used for calibrations, GFAAS detection limits, and federal limits in drinking water are summarized in Table 8.

TABLE 8. GFAAS detection limits, EPA limits in drinking water and concentration used for calibration standards.

| ELEMENT | DETECTION LIMIT ^a ($\mu\text{g/L}$) ^b | FEDERAL LIMIT ($\mu\text{g/L}$) ^c | STANDARDS USED ($\mu\text{g/L}$) |
|-----------------|--|---|---------------------------------------|
| As ^d | 0.5 | 50 | |
| Cd | 0.02 | 10 | 0.25, 0.50, 0.75, 1.0 |
| Co | 0.4 | -- | 10, 20, 30 |
| Cr | 0.08 | 50 | 5.0, 10, 15 |
| Cu | 0.25 | 1000 | 12.5, 25, 50 |
| Mn | 0.6 | 50 ^e | 10, 25, 50 |
| Ni | 0.8 | -- | 10, 25, 50 |
| Pb | 0.15 | 50 | 6.25, 12.5, 25 |

^aReference 27

^bAssumes a 20 μL aliquot

^cU.S. EPA-Federal Register 24 December 1975

^dFailure of As HCL did not allow for completion of the calibration phase.

^eLimits on manganese is not determined by toxicity, but because it stains clothing and ceramic plumbing fixtures.

MATRIX MODIFIERS

A number of different matrix modifiers were used throughout this study. Modifier reagents were obtained at the highest purity when possible. All modifiers were prepared according to the suggestions given in the literature. Many different variations in concentrations and combinations of modifier reagents were tried and specifics will be given in the next chapter. All modifiers were stored in polyethylene bottles except the palladium modifier which was stored in an amber bottle due to its photosensitivity. A list of all reagents used for matrix modification and the manufacturers are given in Table 9.

SALINE WATER SAMPLES

Instant Ocean (Central Scientific Company) was used throughout this study to produce simulated sea salt matrices. Samples were prepared at 10, 20, 30, and 40 parts per thousand (ppt) total salt content in deionized water. The chloride content of the samples was determined by titration with $\text{Hg}_2(\text{NO}_3)_2$.

Samples obtained from several marinas throughout the Hampton Roads area in Virginia were collected by personnel from the Virginia Institute of Marine Science (VIMS). The samples taken from the York River were collected at sights along the Colonial National Historical Parkway in York County, Virginia. The samples from the James River were obtained in

TABLE 9. Manufacturers of the reagents used for matrix modification and their purity.

| MATRIX MODIFIER | MANUFACTURE | MOLECULAR FORMULA | PURITY |
|---|-------------|---|---------|
| ammonium dihydrogen phosphate | Aldrich | $\text{NH}_4\text{H}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$ | 99.999% |
| ammonium nitrate | Aldrich | NH_4NO_3 | 99.999% |
| L-ascorbic acid | Fisher | $\text{C}_6\text{H}_8\text{O}_6$ | |
| citric acid | Baker | $\text{C}_6\text{H}_8\text{O}_7$ | |
| disodium salt dihydrate ethylenediaminetetraacetic acid (disodium EDTA) | Aldrich | $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$ | 99+% |
| diammonium salt hydrate ethylenediaminetetraacetic acid (diammonium EDTA) | Aldrich | $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8(\text{NH}_4)_2 \cdot x\text{H}_2\text{O}$ | 97% |
| magnesium nitrate | Aldrich | $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 99.995% |
| nickel nitrate | Fisher | $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | |
| palladium nitrate | Aldrich | $\text{Pd}(\text{NO}_3)_2$ | |

the vicinity of Newport News Shipbuilding and Drydock, Newport News, Virginia.

The samples were vacuum filtered through a fine texture, acid washed, ashless filter paper. Some samples were stored unacidified for further use. Other samples were preserved with trace metal grade HNO_3 or HCl at a concentration of 0.5% (v/v). Unless specified the samples preserved in 0.5% (v/v) trace metal grade HNO_3 were used for analysis. All samples were kept refrigerated until use.

All samples were titrated for chloride content. The chloride concentration of the natural samples was correlated to the simulated samples to determine the approximate total salt content. The chloride content and relative salinity of these samples are given in Table 10.

INSTRUMENTATION

All GFAAS determinations were made using a Perkin Elmer Model 1100B AAS equipped with an HGA-700 Graphite Furnace and AS-70 Furnace Autosampler. All spectrophotometer, furnace, and auto sampler functions could be set and controlled by an internal microprocessor. The autosampler was used to accurately add the proper amounts of standards, samples and matrix modifiers to the graphite furnace. Background corrections were made using a deuterium arc background correction system.

TABLE 10. Chloride content in parts per thousand (ppt) of simulated seawater samples (SSS) and correlated salinity in ppt of natural samples.

| SAMPLE | CHLORIDES ^a (ppt) | RELATIVE SALINITY (ppt) |
|------------|---------------------------------|----------------------------|
| 0.5% HCl | 2.5 | |
| 10 ppt SSS | 5.9 | |
| 20 ppt SSS | 10.6 | |
| 30 ppt SSS | 15.1 | |
| 40 ppt SSS | 19.7 | |
| HRM #1 | 10.6 | 20 |
| HRM #2 | 10.3 | 20 |
| HYC #3 | 10.5 | 20 |
| York River | 7.3 | 13 |

^aDetermined by titration with $Hg_2(NO_3)_2$.

Both single element and multielement HCLs were used for all determinations. A Perkin Elmer multielement lamp was used for Co, Cu, and Mn analysis. Single element lamps were used for analysis of Cr and Pb (Perkin Elmer) and for As, Cd, and Ni (Fisher). Recommended lamp currents were used in all cases except where the deuterium arc lamp intensity was insufficient to match the gain of the HCL, which predominantly occurs for analyte wavelengths in the visible spectrum. In such cases the current of the HCL was lowered to match the output of the deuterium arc lamp. These adjustments did not effect the outcome of the analysis.

Pyrolytically coated graphite tubes with L'vov platforms (Applied Optics) were used in the graphite furnace. Polyethylene sample cups (Perkin Elmer) were used in the auto sampler for all determinations. Argon gas (Air Products) set at the default flow rate of 300 mL/min was used for all determinations. Temperature programs tailored to each element will be discussed in the next chapter.

OPERATING PROCEDURES

All labware was detergent washed, thoroughly rinsed with semiconductor grade deionized water, rinsed twice with either 2% (v/v) reagent grade HNO₃ or HCl depending on the preservative used, and completed by multiple rinses with semiconductor grade deionized water. Most labware was used immediately after cleaning preceded by multiple rinses with

the standard, modifier, or sample to be contained. Very little if any problems with contamination were encountered due to the thorough cleaning procedure used.

Modifiers for each element were qualified in a very systematic sequence of steps. Temperature programs for selected modifiers were first evaluated to generate reproducible peak profiles from aqueous standards of the analyte element. This generally started with the recommended literature parameters which were fine tuned to optimize the peaks with respect to highest analyte absorption, lowest background absorption, narrowest peak widths, separation of the analyte absorption from background absorption, and reproducibility. All graphite furnace determinations throughout this study were done in triplicate for each change in instrumental parameters and the average of these three determinations was used for all graphs and results. If the three determinations were not reproducible then this data was not used or the parameters were modified until the determinations were reproducible.

Once the temperature programs were optimized for maximum performance with aqueous standards a set of the 0, 10, 20, and 30 ppt simulated sea salt samples was quantitatively spiked with the element of interest and analyzed. This was done to determine whether the set of spiked samples produced comparable absorption profiles throughout the concentration range of sea salts at fixed analyte concentrations as well as

determining if the absorption was comparable to the absorption produced by the simple aqueous standards. The signals were evaluated with respect to increasing background signals and changes in the analyte absorption profiles.

This was achieved by using the auto sampler to add fixed volumes of the simulated sea salt solutions to the standard solutions and matrix modifiers in the graphite furnace. For example when evaluating the use of $\text{Mg}(\text{NO}_3)_2$ as a matrix modifier for the determination of Cr, 15 μL of the simulated sea salt, 5 μL of the most concentrated Cr standard (listed in Table 8), and 5 μL of $\text{Mg}(\text{NO}_3)_2$ were added to the graphite furnace in that specific order. The modifier was always added last so that it would be on top of the other solutions in the graphite furnace and would have a greater chance to mix with the other solutions when drying.

If a modifier fulfilled all of the above requirements, namely that the signal profile was independent of the salt concentration, then natural water samples were spiked in the same fashion. The modifier was again evaluated in two areas. First, reproducible peak profiles along with a reasonable background signal were essential. The second factor was whether the spiked sample gave an absorbance signal comparable to simple aqueous standards or spiked sea salt samples at the same concentration.

The final part of the evaluation consisted of producing a calibration curve and analyzing natural samples with simple

aqueous standards if possible. The graphite furnace programmer in conjunction with the auto sampler was used to produce the calibration curves. Continuing from the previous example, 20 μL of each Cr standard given in Table 8 along with 5 μL of $\text{Mg}(\text{NO}_3)_2$ were added to the graphite furnace to construct the calibration curve. Then 20 μL of the natural sample along with 5 μL of $\text{Mg}(\text{NO}_3)_2$ were added to the graphite furnace and the concentration of Cr in the natural sample was calculated from the calibration curve. Certain analyte metals were below the detection limits in some natural samples, thus they had to be spiked with a known amount of the analyte in order to evaluate the calibration curves. This was accomplished using the auto sampler by adding 5 μL of the most concentrated calibration standard and 15 μL of the natural standard along with 5 μL of the matrix modifier to the graphite furnace. The concentration of this mixture was then determined experimentally using the calibration curve and compared to known concentration to evaluate the performance of the method.

If the literature recommended temperature programs worked, i.e., acceptable background signals and reproducible peak profiles, then they were used, otherwise the temperature programs were optimized for maximum performance. The char step is the most important step in the removal of matrix interferences and thus reducing background absorbance. The higher the char temperature the better possibility of volatilization of the matrix species and reducing background

higher the char temperature the better possibility of volatilization of the matrix species and reducing background interferences before the analyte is atomized and absorption measured. In this study a char temperature 100 °C below the literature recommended char temperature was used as an initial starting point. The temperature was then raised in 100 °C increments until appreciable analyte loss began to occur as indicated by the absorption profile, at which point the next lower char temperature was incorporated into the temperature program. Once a char temperature was established a pre-atomization cool down step to ambient temperature was added to investigate the effects on the absorbance profile. Most of the time the pre-atomization cool down step improved the absorbance profile and was used.

Atomization temperatures were not varied because they did not have much effect on background interference unless the matrix species was being co-volatilized with the analyte species. In these cases ramped atomization temperatures were investigated for separating the volatilization of the matrix from the analyte. Variations on the time of the ramp and the final temperature were tried in order to optimize the absorbance profile and decrease background absorption.

CHAPTER V

RESULTS AND DISCUSSION

DETERMINATION OF Cr, Cu, Mn, AND Ni

The Manning and Slavin¹⁹ procedure was found to be adequate for the determination of Cr, Cu, Mn, and Ni in saline water with only slight modifications. The spectrophotometer settings and the matrix modifiers used were the same as those given in Chapter III, Table 3. Modified furnace programmer settings used in this study are given in Table 11. A ramp time of 30 seconds from ambient temperatures to 250 °C with a hold time of 30 seconds was used for all desolvation steps. A pre-atomization cool down step at 20 °C for 5 seconds was only used if background interferences were reduced or improvements in peak profiles were observed. The primary differences observed with the use of a cool down step were in the overall peak profiles with respect to a lower initial baseline and narrower peak widths. Occasionally the use of this step did not effect the absorption profile or was detrimental to the absorbance profile and was not used. A final clean out step at 2650 °C for 6 seconds was used for all programs. An internal argon gas flow of 300 mL/min was used

TABLE 11. Modified furnace programmer settings used with the Manning and Slavin procedure.

| ELEMENT | CHAR TEMP (°C) | CHAR RAMP TIME (s) | CHAR HOLD TIME (s) | COOL DOWN USED | ATOM TEMP (°C) | ATOM HOLD TIME (s) |
|----------------|---------------------------|-----------------------------------|-----------------------------------|-------------------------------|---------------------------|-----------------------------------|
| Cr | 1600 | 15 | 30 | yes | 2400 | 5 |
| Cu | 1200 | 15 | 30 | no | 2300 | 6 |
| Mn | 1300 | 15 | 30 | no | 2200 | 6 |
| Ni | 1400 | 15 | 30 | yes | 2400 | 10 |

during every step except the atomization step. Absorption readings were initialized at time 0.0 seconds of the atomization step.

The matrix modifier used for Cr, Mn, and Ni was 50 μg of $\text{Mg}(\text{NO}_3)_2$ per 20 μL sample aliquots. The $\text{Mg}(\text{NO}_3)_2$ used was in the hexahydrate form, which was taken into account when the modifier solutions were prepared. The $\text{Mg}(\text{NO}_3)_2$ is thought to act as a charring aid by reduction to the oxide form at temperatures of several hundred degrees, which can trap trace metals that could otherwise be volatilized³².

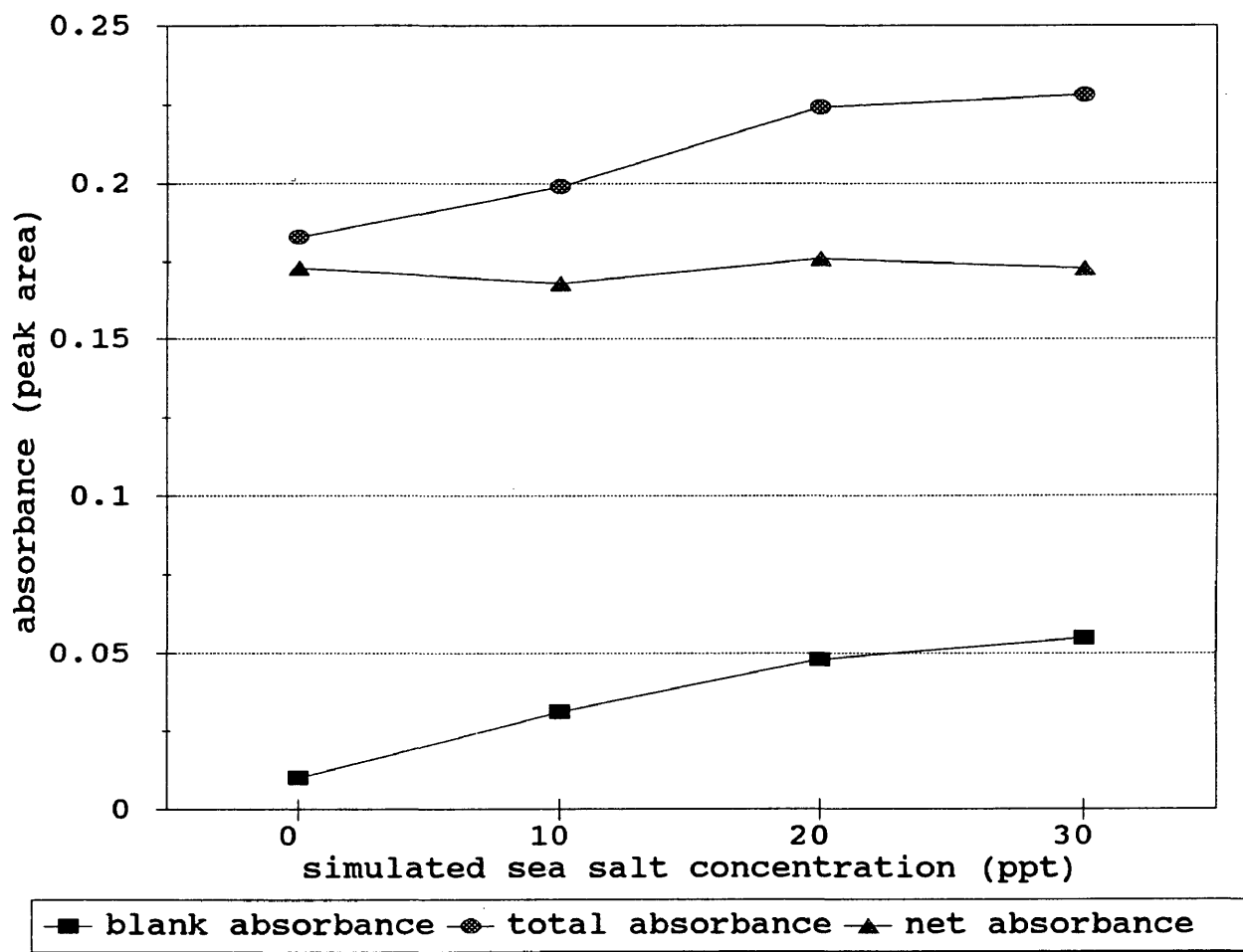
The determination of Mn proved to be successful but produced absorbance profiles with two peaks. An absorbance profile for 20 μL of 2.5 ppb Mn standard in 0.5% HNO_3 using 50 μg of $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier is shown in Figure 10. The dotted line shown in this figure and all subsequent absorption profiles is the background absorption signal, observed from the deuterium arc background correction system, and the solid line is the analyte absorption signal. Both signals are proportioned to fit the full scale, with 0.050 being the minimum and 2.000 being the maximum full scale values set by the instrument. Thus, full scale absorption values for the background and analyte signals, located along the ordinate of the profile, are usually different. The background full scale absorbance value is the value in parentheses, and the analyte full scale absorbance value is the value positioned immediately above the background value.

All of the Mn absorbance profiles followed this two peak pattern regardless of the sample type, temperature program, or amount of modifier, thus the presence of the double peaks was considered to be independent of the sample matrix. These double peaks could be due to "memory" effects or to the element being present as more than one species³³. In our case it is believed that the latter explanation is the reason for the double peaks. Nevertheless, linear absorption curves were obtained from simple aqueous standards and determinations made of Mn in natural saline water samples.

Both the Cr and Ni absorption profiles had substantial noise, as shown in Figure 11 and 12 respectively. The oscillating signal associated with the Cr appears to be electronic in nature, probably due to oscillations in the lamp power. The reasons for these high noise levels are not fully understood, but the absorbance profiles were found to be adequate for quantitative analysis of these metals.

As stated in the operating procedures, one of the requirements for the modifiers was that they produce an absorption signal profile that is independent of the salt concentration in the sample matrix. A graph of the absorbance from 20 μ L of 7.5 ppb Cr vs. increasing salinity concentrations is shown in Figure 13. The blank absorbance is the analyte absorbance observed in the simulated sea salt with no Cr standard added. In this case the blank signal increased with the increasing sea salt concentration due to

FIGURE 13. The absorbance from 20 μL aliquots of 7.5 ppb Cr standards prepared in increasing concentrations of simulated sea salt matrices using 50 μg of $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier.



Cr already present in the sea salt used to make the solutions. The total absorbance is the absorbance due to both the 7.5 ppb Cr standard added and the Cr already present in the simulated sea salt, which increases for the same reasons mentioned previously. The net absorption, which is the difference between the total and blank absorptions, represents the absorption due only to the 7.5 ppb Cr standard. This value should be constant and represented by a horizontal line if the analyte absorbance was independent of the salt concentration. The absorbance vs. salinity profiles for Mn and Ni were observed to be similar using the Manning and Slavin procedure.

Both the Manning and Slavin¹⁹ and the Ediger et al.¹⁶ methods were explored and both performed adequately for the determination of Cu in saline waters. Manning and Slavin recommended the use of no modifier due to the stability and low volatility of Cu. The same revised temperature parameters were used with both methods and are given in Table 11. Ediger et al. recommended 20 μL of 50% NH_4NO_3 per 50 μL sample aliquot. In this investigation 5 μL of 30% NH_4NO_3 per 20 μL sample aliquot was determined to be adequate. Above this concentration no improvement in the absorbance profile occurred and only an increase in background absorption with increasing modifier concentration was observed.

When an excess of an NH_4NO_3 solution is dried with a NaCl solution a mixture of NaNO_3 and NH_4Cl is supposedly formed.

The NH_4NO_3 , NaNO_3 , and NH_4Cl all have boiling points less than 400 °C and are removed by volatilization using a char temperature of 500 °C or above. The boiling point of NaCl is 1413 °C, which makes it very difficult to volatilize during the char step. Unless the analyte metal has a relatively high atomization temperature, loss of analyte will occur during the charring step when trying to volatilize the NaCl .

Graphs of the absorbance for 20 μL of 12.5 ppb Cu vs. increasing salinity concentrations using no modifier and the NH_4NO_3 modifier are given in Figures 14 and 15, respectively. Once again the blank absorbance increased due to the Cu already present in the simulated sea salt. It should be noted that the NH_4NO_3 modifier shows a trend of suppressing the analyte absorption by about 20% as the simulated sea salt concentrations increased to 30 ppt. The use of no modifier showed no trends and produced comparable absorption signals. Thus, the use of no modifier is recommended for the determination of Cu in various concentrations of saline waters using simple aqueous standard for calibration.

The determination of Ni tended to give the most irregular results of all the metals determined using the Manning and Slavin procedure. Applicable absorption profiles were obtained with the exception of the higher than average noise levels as discussed previously. The successful use of no modifier for the determination of Cu prompted the use of

FIGURE 14. The absorbance from 20 μL aliquots of 12.5 ppb Cu standards prepared in increasing concentrations of simulated sea salt matrices with no matrix modifier.

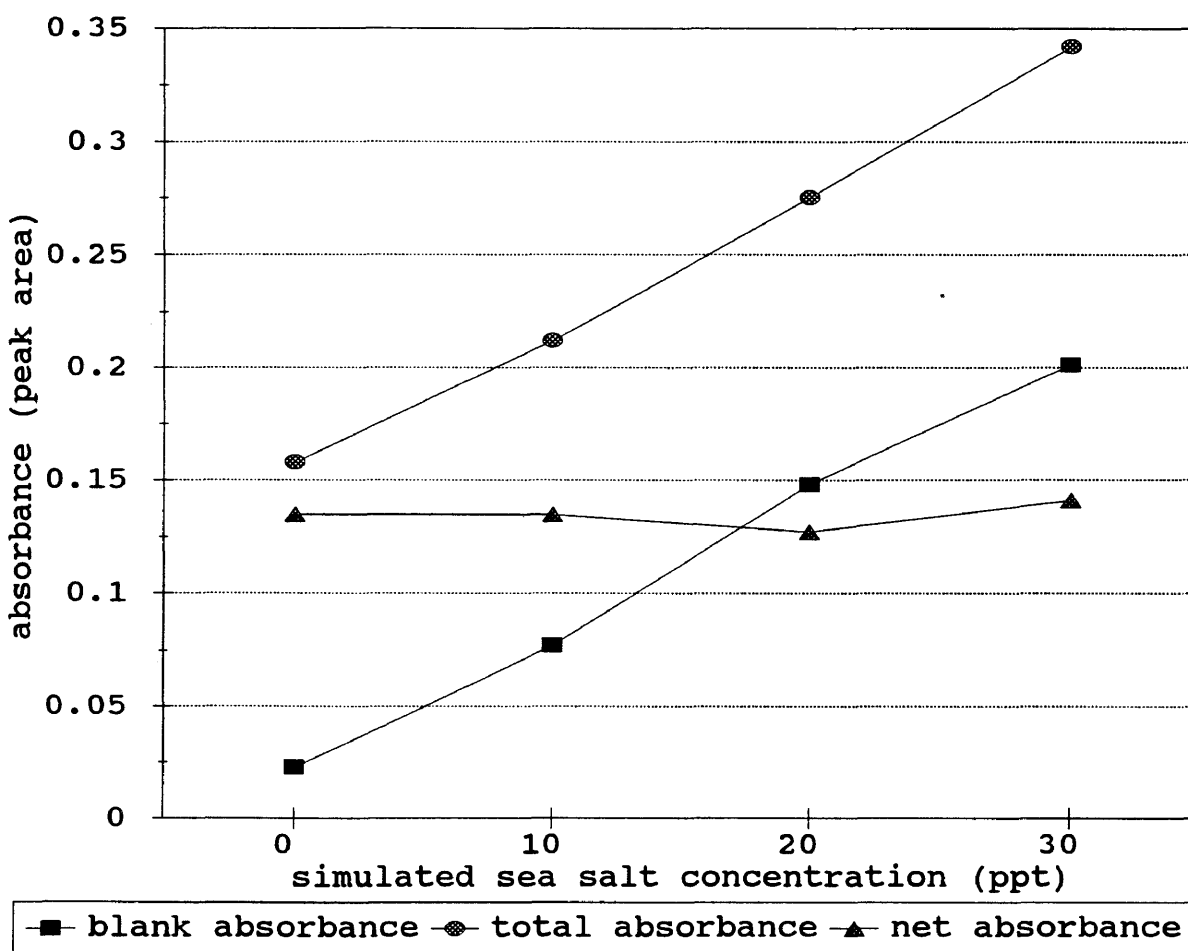
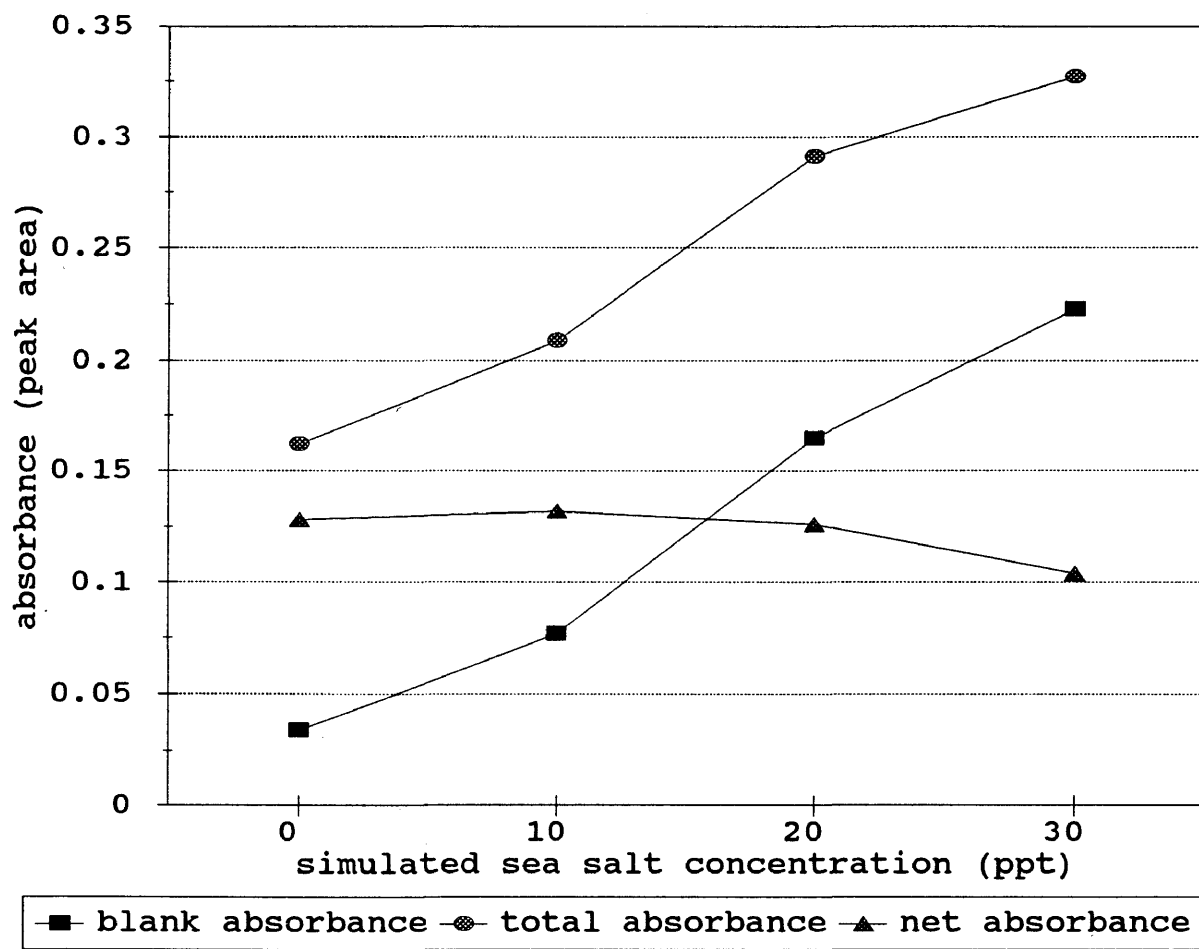


FIGURE 15. The absorbance from 20 μL aliquots of 12.5 ppb Cu standards prepared in increasing concentrations of simulated sea salt matrices using 1500 μg of NH_4NO_3 as the matrix modifier.



the same procedure for Ni to determine if the erratic results were due to the modifier. The same irregularities were experienced for the determination of Ni using no modifier. Plots of the absorbance from 20 μL of 25 ppb Ni vs. increasing salinity concentrations for the $\text{Mg}(\text{NO}_3)_2$ matrix modifier and no modifier are shown in Figures 16 and 17, respectively. The data did not show any trends but fluctuated within a reasonable range. All of the runs were repeated using both procedures and the same results were again obtained, which lead to the conclusion that the erratic results were possibly due to lamp fluctuations, although this was never determined to be the case and time did not allow for further investigation.

The low volatility of Cr, Cu, Mn, and Ni relative to the salt matrix easily allowed for direct determination of these elements with the appropriate matrix modifiers. Table 12 gives typical statistical data for fluctuations obtained in the net absorption signals of these elements over the 0 to 30 ppt simulated sea salt ranges. The relative deviation of Mn appears to be high due to the high concentration of Mn that was present in the simulated sea salt. A relatively small concentration of Mn was required to spike the sea salt samples to prevent the total absorption from exceeding a linear absorption range. The net effect is shown in Figure 18, in which the net absorbance of approximately 0.080 is appreciably less than those for the other elements. The reasons for the

FIGURE 16. The absorbance from 20 μL aliquots of 25 ppb Ni standards prepared in increasing concentrations of simulated sea salt matrices using 50 μg of $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier.

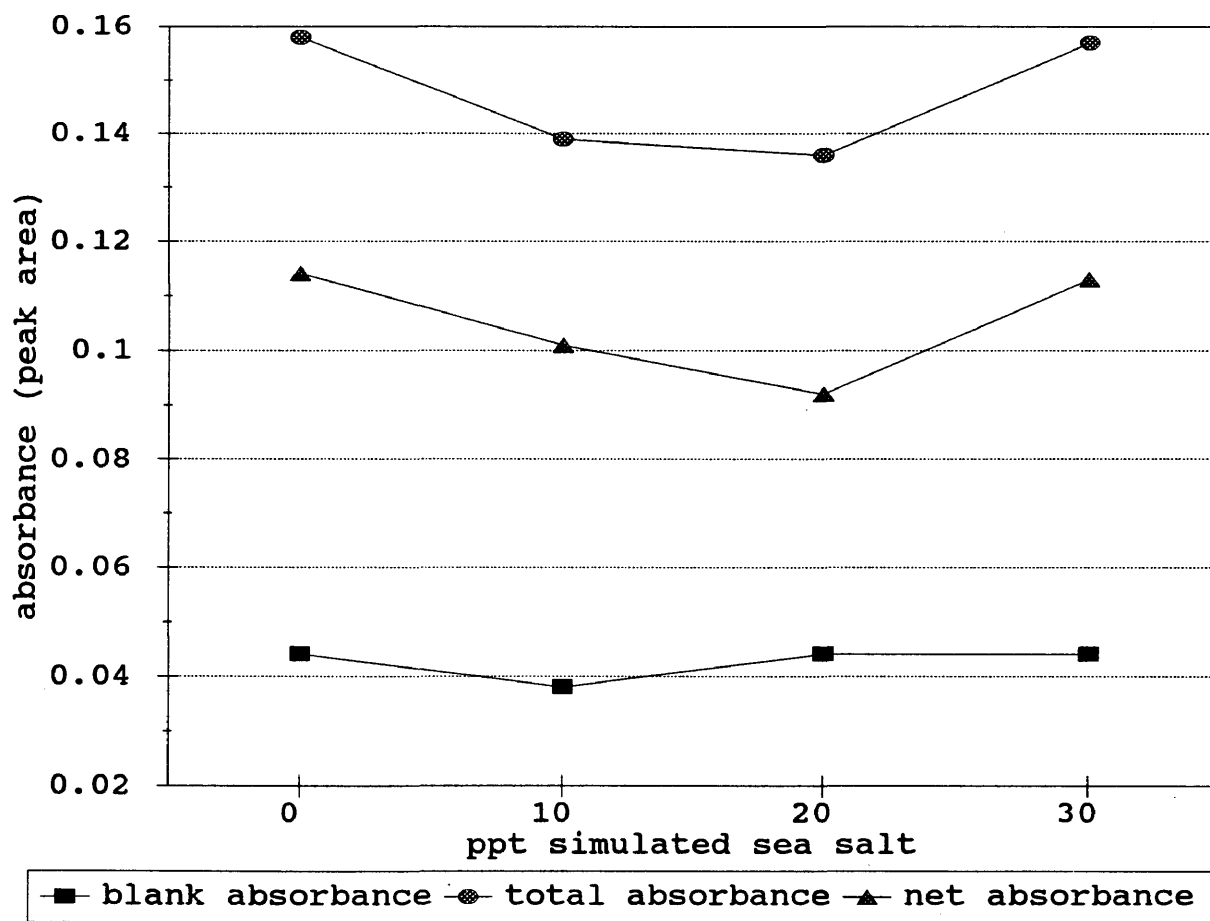


FIGURE 17. The absorbance from 20 μL aliquots of 25 ppb Ni standards prepared in increasing concentrations of simulated sea salt matrices with no modifier.

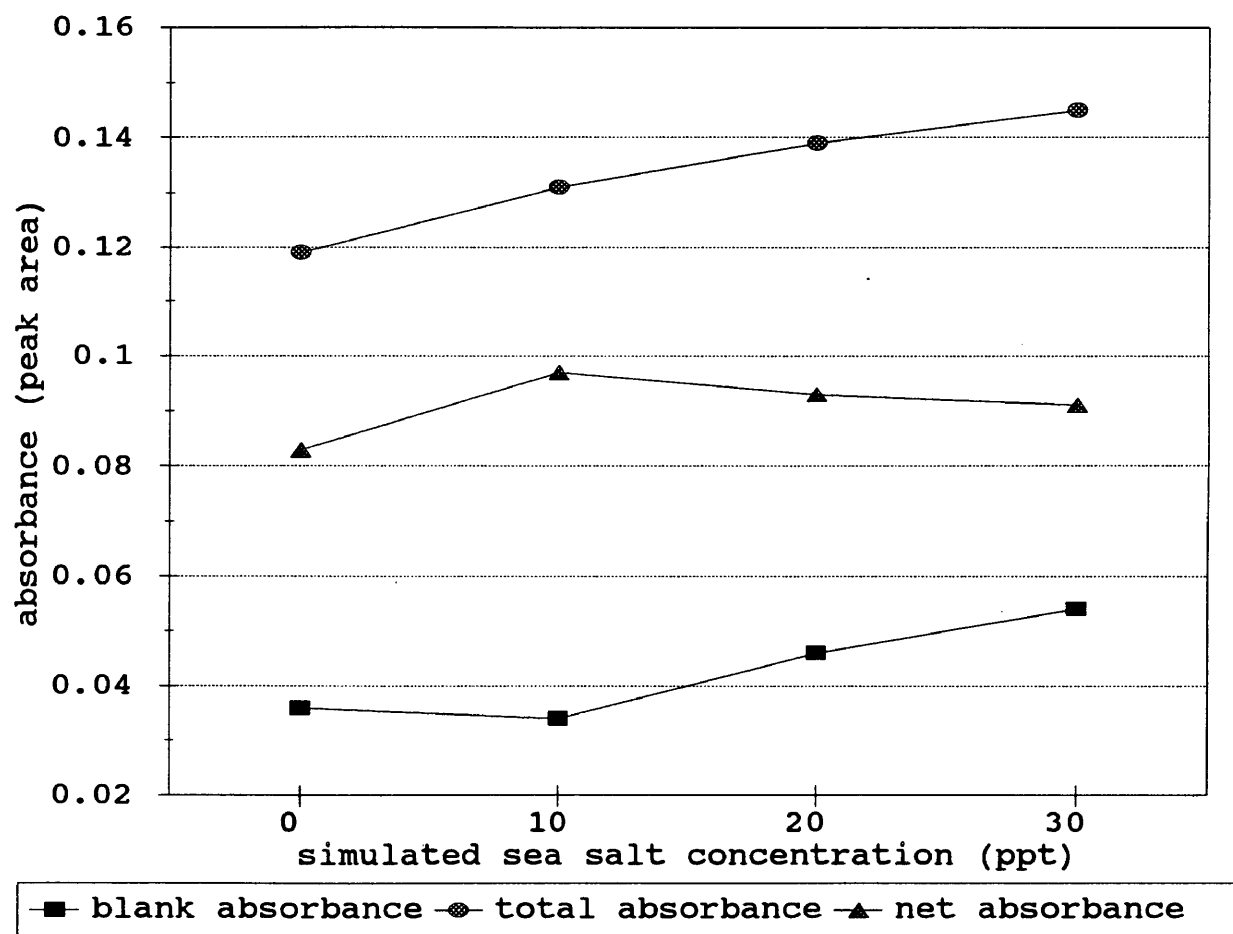
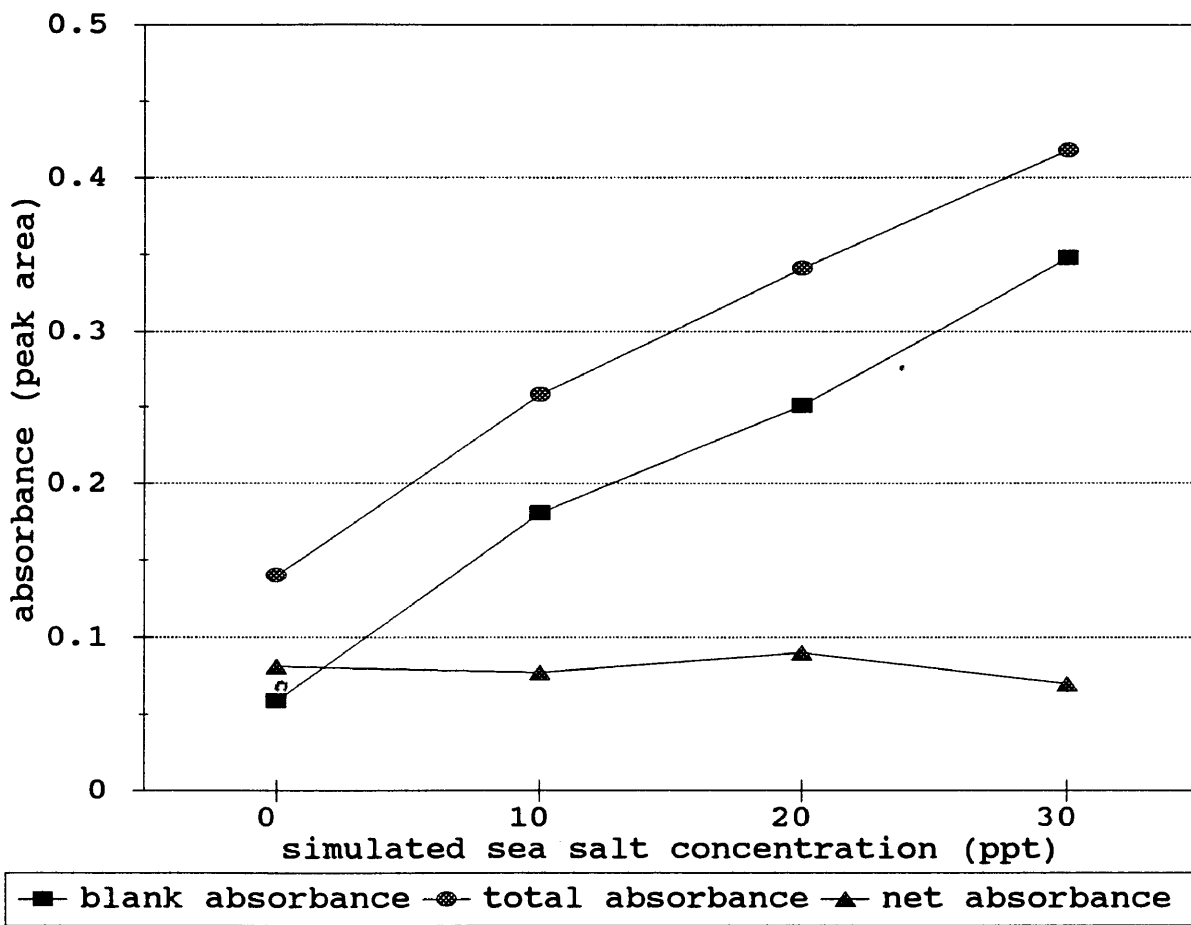


TABLE 12. Descriptive statistical data for the net absorbance signals.

| ELEMENT | CONC. (ppb) ^a | MODIFIER USED | MEAN NET ABSORBANCE | RANGE | STANDARD DEVIATION | RELATIVE DEVIATION |
|---------|-----------------------------|-----------------------------------|------------------------|-------|-----------------------|-----------------------|
| Cr | 7.50 | Mg(NO ₃) ₂ | 0.173 | 0.008 | 0.003 | 1.2% |
| Cu | 12.5 | none | 0.135 | 0.014 | 0.006 | 4.4% |
| Cu | 12.5 | NH ₄ NO ₃ | 0.123 | 0.028 | 0.013 | 11% |
| Mn | 2.50 | Mg(NO ₃) ₂ | 0.080 | 0.020 | 0.008 | 10% |
| Ni | 25.0 | Mg(NO ₃) ₂ | 0.105 | 0.022 | 0.010 | 9.5% |
| Ni | 25.0 | none | 0.091 | 0.014 | 0.006 | 6.6% |

^aAssumes a 20 μL aliquot.

FIGURE 18. The absorbance from 20 μL aliquots of 2.5 ppb Mn standards prepared in increasing concentrations of simulated sea salt matrices using 50 μg of $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier.



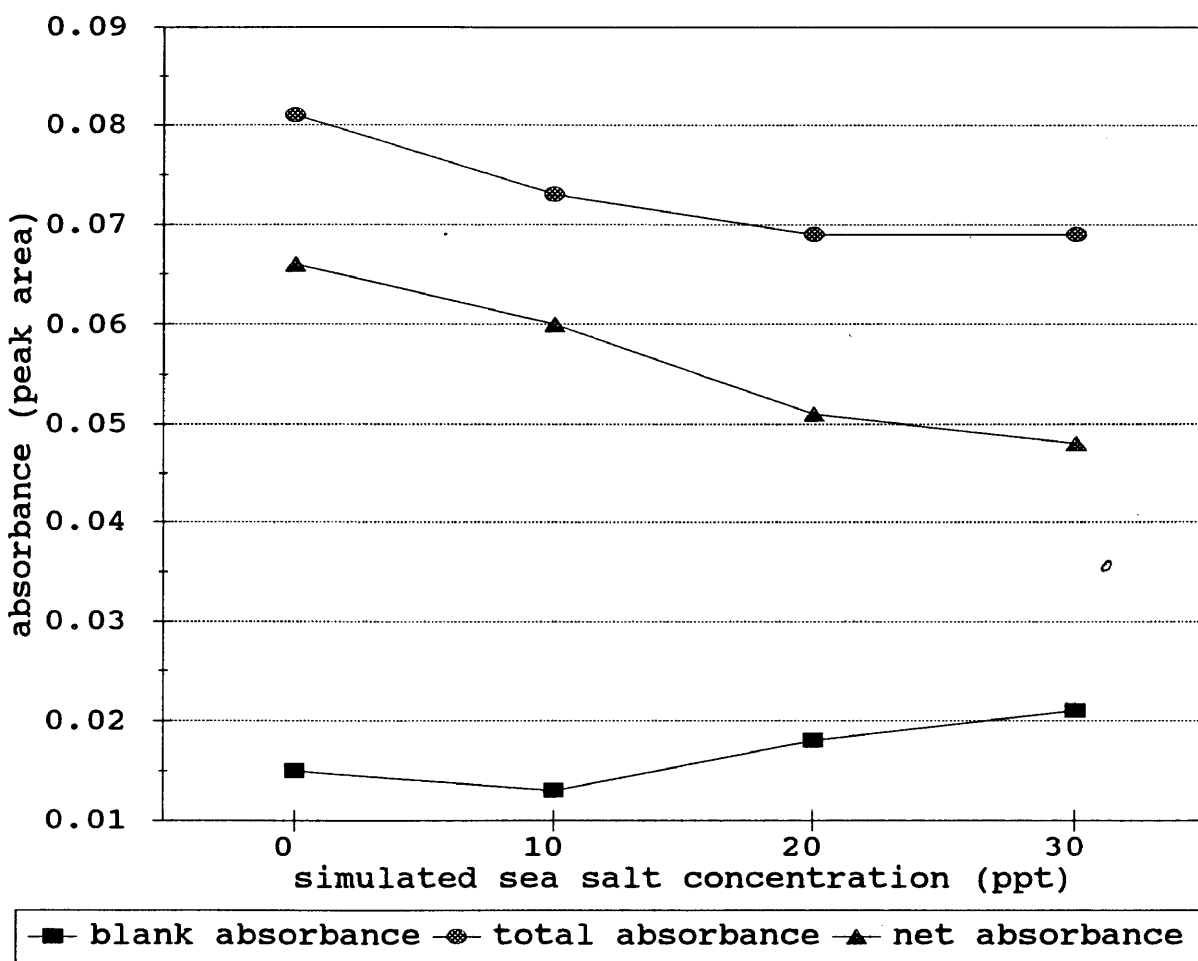
high relative deviation of Cu with NH_4NO_3 and Ni with $\text{Mg}(\text{NO}_3)_2$ was discussed previously. The low ranges and relative deviations in the absorption values implied that the suggested methods greatly reduced background interferences allowing for quantitative analysis of these elements using simple aqueous standards for calibration.

DETERMINATION OF Co

The procedures recommended by Manning and Slavin¹⁹ using $\text{Mg}(\text{NO}_3)_2$ as the modifier for the determination of Co did not prove successful. Although a usable absorption profile could be obtained, the signal profile was suppressed with the increasing salt concentration as shown in Figure 19. The net absorption dropped about 30% going from deionized water to a 30 ppt simulated sea salt matrix with a relative deviation in the net absorption was 14%. Thus, the ability to use simple aqueous standards to construct calibration curves for the determination of Co in salt matrices would be non-quantitative and no analysis for Co was completed using $\text{Mg}(\text{NO}_3)_2$ as the modifier.

The ascorbic acid matrix modifier proposed by Hades²⁹ worked well for the direct determination of Co in saline water samples using simple aqueous standards. A 5 μL aliquot of 4% ascorbic acid was added to 20 μL sample volumes. The temperature program used consisted of a drying step ramped for 30 seconds from ambient temperatures to 250 °C and a charring

FIGURE 19. The absorbance from 20 μL aliquots of 7.5 ppb Co standards prepared in increasing concentrations of simulated sea salt matrices using 50 μg of $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier.



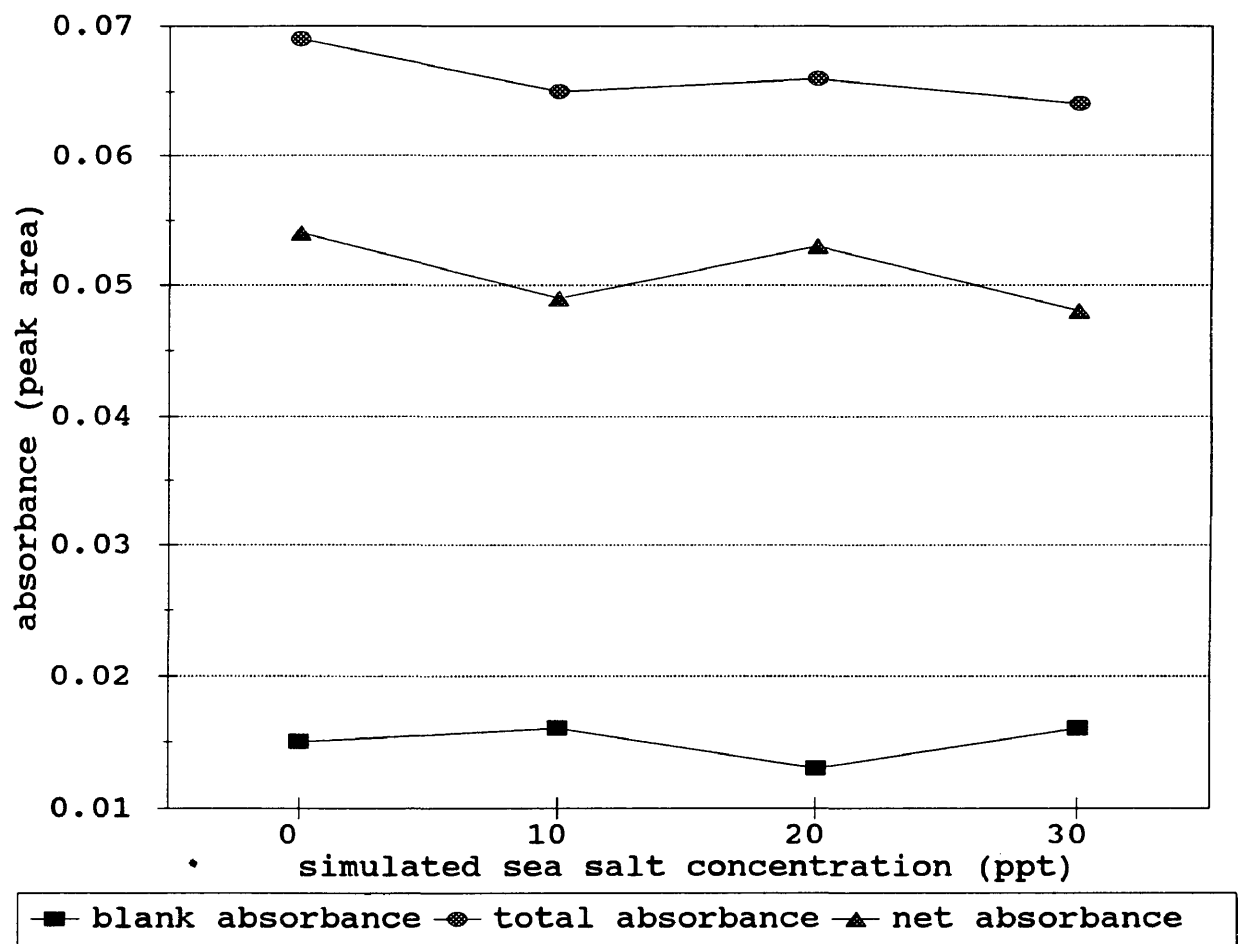
temperature ramped for 15 second to 1400 °C. Both steps were held constant for 30 seconds. A pre-atomization cool down step was used. An atomization temperature of 2500 °C was held for 5 seconds and followed by a clean out step. The use of ascorbic acid produced absorbance signals for Co that were independent of the salt concentrations as shown in Figure 20. The relative deviation in the Co net absorption over the span of the simulated sea salt concentrations was 5.9%.

It is not fully understood how ascorbic acid performs as a matrix modifier but some suggestions are given in the Hades²⁹ paper. It was reported that the most likely process to reduce interference in seawater is one that promotes atomization from the oxide rather than the chloride salt of the analyte. A mechanism by which ascorbic acid promotes the conversion of the chloride salt of the analyte to the oxide was not discussed.

DETERMINATION OF As

Only initial screenings were done for the determination of As in saline waters using both the Manning and Slavin¹⁹ and Schlemmer and Welz²⁴ procedures. Manning and Slavin proposed the use of nickel and Schlemmer and Welz proposed the use of palladium and magnesium nitrates as modifiers for As. The use of the palladium and magnesium nitrates showed more promise than the Ni for the determination of As in natural water

FIGURE 20. The absorbance from 20 μL aliquots of 7.5 ppb Co standards prepared in increasing concentrations of simulated sea salt matrices using 200 μg of ascorbic acid as the matrix modifier.



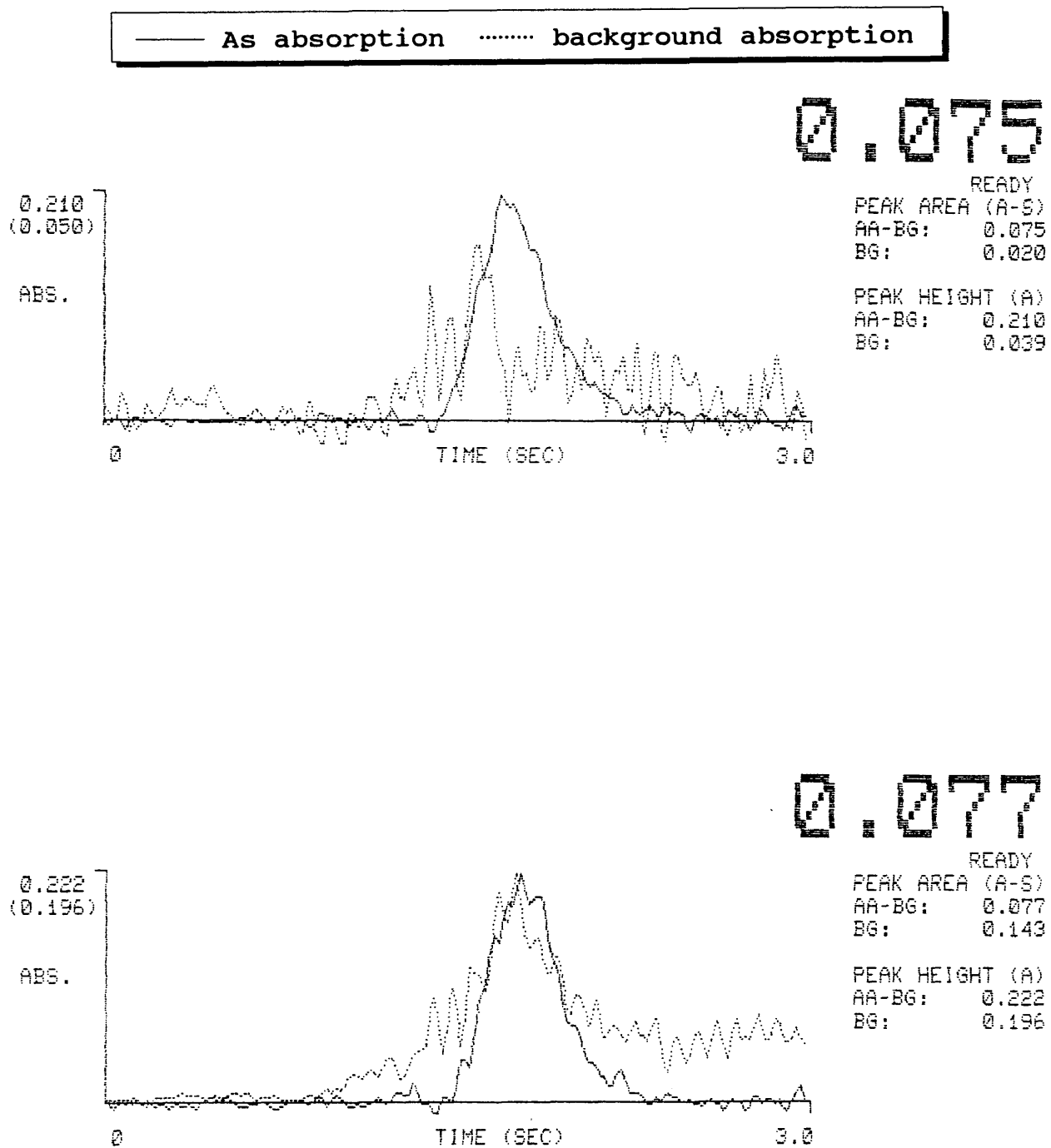
samples during these initial studies, which were curtailed due to failure of the hollow cathode lamp.

The Manning and Slavin matrix modifier for As was 20 μg of Ni per 20 μL sample aliquots in the form of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 2% HNO_3 . Most commercial sources of $\text{Ni}(\text{NO}_3)_2$ are hydrated with six waters of hydration, which was taken into account when the recommended amounts were added to the solutions. This modifier can also be produced by gently heating the appropriate amount of pure Ni metal in 20% HNO_3 until completely dissolved. It is believed that the Ni stabilizes the As by converting the As to a much less volatile Ni-As compound during the charring step²³.

The Schlemmer and Welz modifier consisted of 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 15 μg of $\text{Pd}(\text{NO}_3)_2$ per 10 μL of modifier solution. The modifier was prepared by dissolving 3.25 g of palladium nitrate and 0.173 g of magnesium nitrate hexahydrate in 100 ml of 2% trace metal grade HNO_3 . The solution was then mixed and stored in an amber glass bottle to prevent the photodecomposition of the palladium compound.

Comparisons of a simple aqueous As standard absorbance profile and a spiked York River water absorbance profile are shown in Figure 21. The top profile is 15 μL of deionized water blank containing 0.5% HNO_3 spiked with 5 μL of 75 ppb As using a 5 μL aliquot of the palladium and magnesium nitrate modifier. Although 10 μL is the recommended modifier volume,

FIGURE 21. An example of the absorbance profiles obtained with the Schlemmer and Welz modifier for the determination of As. The top absorbance profile is from 15 μL of deionized water spiked with 5 μL of 75 ppb As using the palladium and magnesium nitrate modifier. The bottom absorbance profile is the same except the deionized water was replaced with York River water.



5 μL proved to be adequate for the determination of As in the York River water. The bottom profile is the same except that 15 μL of deionized water blank containing 0.5% HNO_3 was replaced with 15 μL of the York River water preserved in 0.5% HNO_3 . The temperature program used to obtain the absorbance profiles in Figure 21 consisted of a 250 °C drying temperature ramped for 30 second and held constant for 30 second, a 1500 °C charring temperature ramped for 15 second and held constant for 30 second. An atomization temperature of 2500 °C was held for 6 seconds followed by a clean out step.

The only significant difference in the absorption profiles was the increase in background absorbance from the salt matrix. Thus, it would appear that the modifier combination of palladium and magnesium nitrates would be well suited toward As determinations in natural saline waters using simple aqueous standards for calibration.

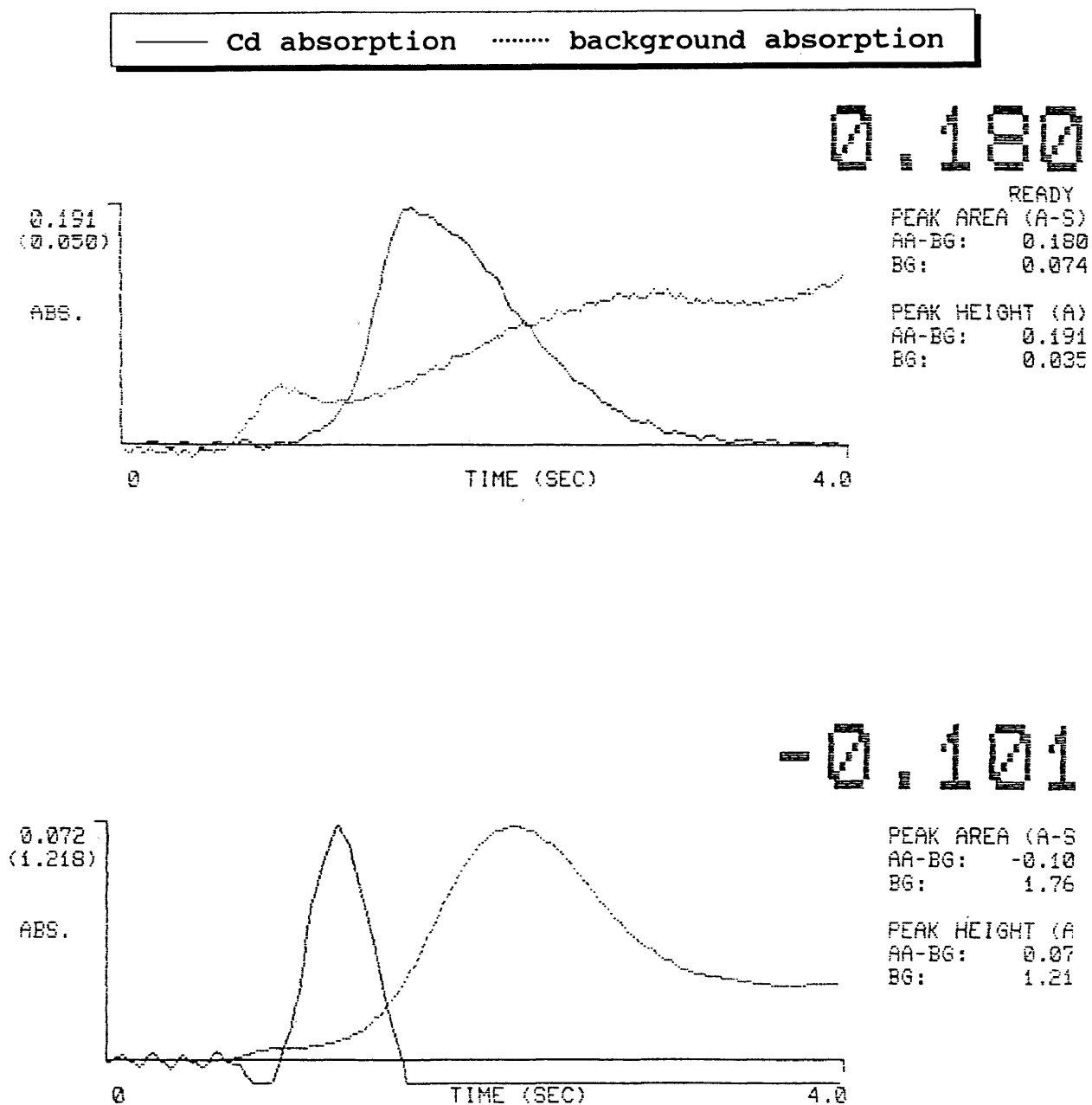
The mixture of palladium and magnesium nitrates is believed to stabilize certain elements to allow the use of substantially higher char and atomization temperatures. The mechanism of the stabilization has not been investigated in detail but it is believed that the palladium forms an alloy with the analyte which allows for increased atomization temperatures²⁴.

DETERMINATION OF Cd

An example of absorbance profiles obtained with the Manning and Slavin¹⁹ method for the determination of Cd are shown in Figure 22. The top profile is 15 μL of deionized water blank containing 0.5% HNO_3 spiked with 5 μL of 5 ppb Cd using a 5 μL aliquot of matrix modifier containing 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 200 μg of $\text{NH}_4\text{H}_2\text{PO}_4$. The bottom profile is the same except that the deionized water was replaced with 15 μL of York River water preserved in 0.5% HNO_3 . The temperature program used to obtain the absorbance profiles consisted of a 200 °C drying temperature ramped for 30 second and held constant for 15 seconds, and a 900 °C charring temperature ramped for 15 seconds and held constant for 30 seconds. A pre-atomization cool down step to 20 °C was used. An atomization temperature of 1500 °C was held for 6 seconds followed by a clean out step.

The background interference was too great for the deuterium arc background correction system used and when the background was subtracted from the total absorbance a negative net signal was produced by the microprocessor. The problem appeared to be the inability to sufficiently separate the volatilization of the matrix species from the analyte atoms using these modifiers and temperature programs, which is a factor inherent of the similar volatilization temperatures of the Cd and this matrix. Many different

FIGURE 22. An example of the absorbance profiles obtained with the Manning and Slavin method for the determination of Cd. The top absorbance profile is from 15 μL of deionized water spiked with 5 μL of 5 ppb Cd using a 5 μL aliquot of the $\text{Mg}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ matrix modifier. The bottom absorbance profile is the same except the deionized water was replaced with York River water.

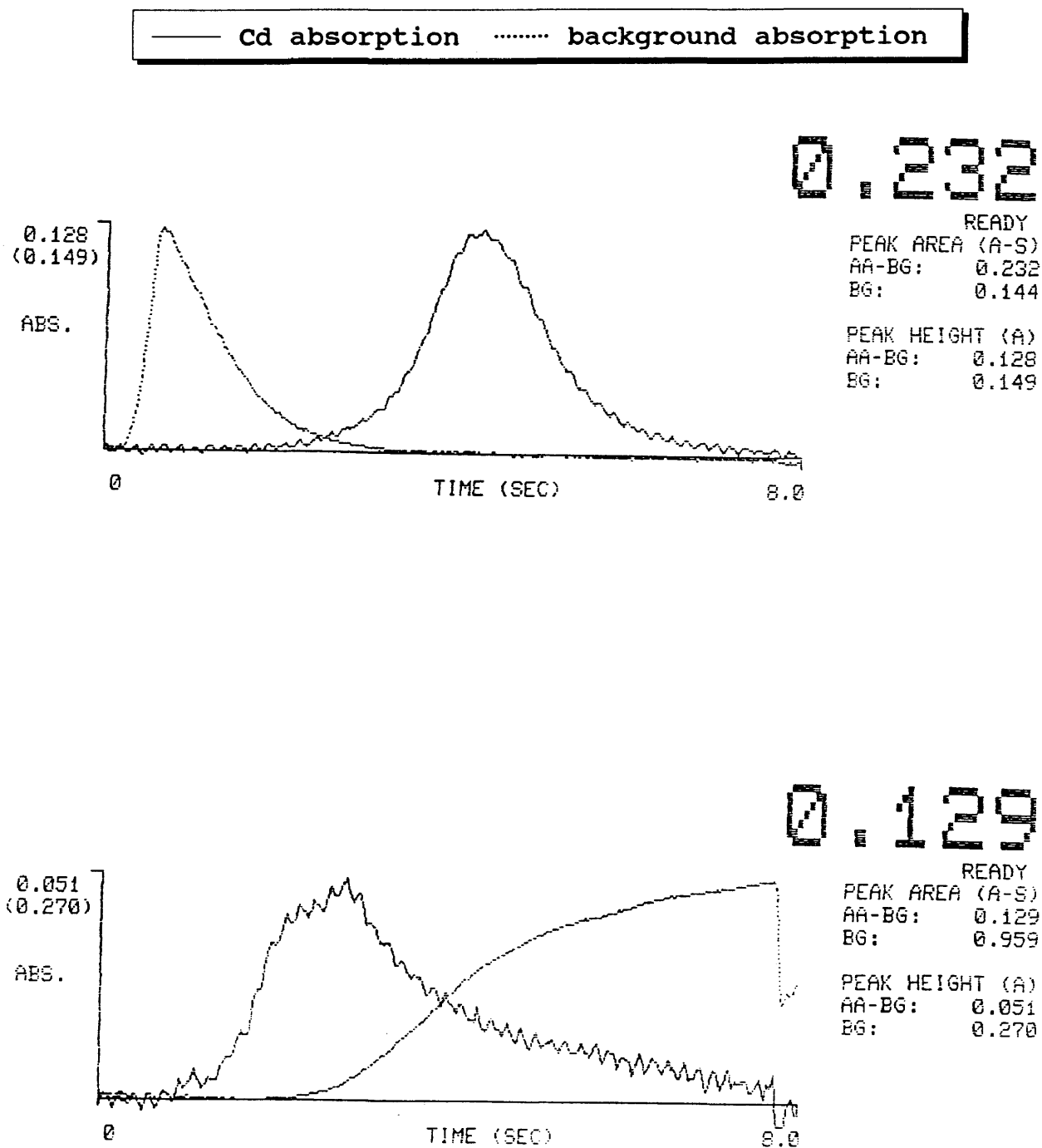


variations in the Manning and Slavin temperature program were tried for the determination of Cd in natural waters with no success. Also different concentrations of the combination of $\text{Mg}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ matrix modifiers were explored with no successful improvement of the absorption profiles.

The Guevremont³⁰ method was tried next using citric acid as the matrix modifier. An example of absorbance profiles obtained with the Guevremont method are shown in Figure 23. The top profile is 15 μL of deionized water blank containing 0.5% HNO_3 spiked with 5 μL of 5 ppb Cd using a 5 μL aliquot of 10 mg/mL citric acid as the matrix modifier. The bottom profile is the same except that the deionized water blank containing 0.5% HNO_3 was replaced with 15 μL of the York River water preserved in 0.5% HNO_3 . The temperature program used to obtain the absorbance profiles in Figure 23 consisted of a 140 °C drying temperature ramped for 15 seconds and held constant for 30 seconds with no char step or pre-atomization cool down step. The atomization temperature was 1000 °C held for 8 seconds followed by a clean out step.

There are several factors worth noting when comparing these profiles. A 50% loss of analyte absorption signal occurred in the natural water matrix as compared to the deionized water blank. Thus, simple aqueous standards could not be used to construct a quantitative calibration curve using citric acid as the matrix modifier. The background is more than six times as great in the natural water sample and

FIGURE 23. An example of the absorbance profiles obtained with the Guevremont method for the determination of Cd. The top absorbance profile is from 15 μL of deionized water spiked with 5 μL of 5 ppb Cd standard using 50 μg of citric acid as the matrix modifier. The bottom absorbance profile is the same except the deionized water was replaced with York River water.

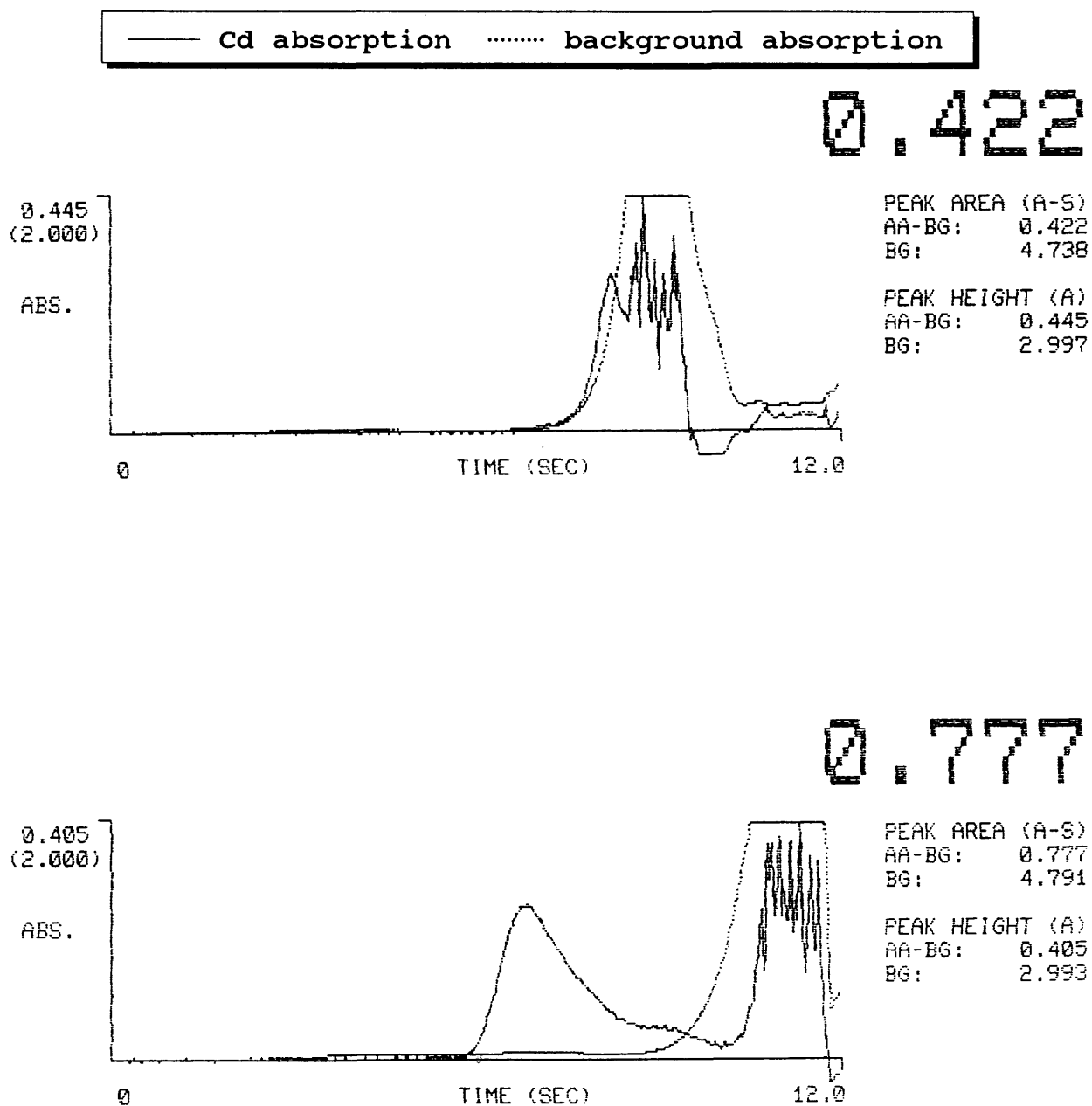


is very close to the recommended limit of one absorption-second for the deuterium arc background correction system. The absorption profiles were also very different in that the Cd signal appeared earlier in the natural water sample, was spread out over a larger span of time, and was very noisy as compared to the deionized water sample.

Other matrix modifiers that have been suggested are the tetrasodium salt of EDTA by Guevremont et al.¹⁵ for the direct GFAAS determination of Cd in sea water and tetraammonium salt of EDTA by Matsusaki et al.³¹ for the removal of chloride interferences in the determination of Cr. The use of these modifiers for the determination of Cd in saline waters appeared to have some promise. Due to limited resources only the disodium and the diammonium salts of EDTA were available for this study.

Absorption profiles for 15 μL of the York River water preserved in 0.5% HCl spiked with 5 μL of 5 ppb Cd using a 10 μL aliquot of 10 mg/mL EDTA as the matrix modifier are shown in Figure 24. The temperature program consisted of a 90 °C drying temperature ramped for 15 seconds and held for 30 seconds. The charring temperature was 250 °C ramped for 15 seconds and held for 5 seconds with no cool down step. The final atomization temperature in the top profile was 1900 °C ramped for 7 seconds and held constant for 5 seconds

FIGURE 24. An example of the absorbance profiles obtained using EDTA as the matrix modifier for the determination of Cd. The bottom profile used a relatively longer ramped atomization time than the top profile.

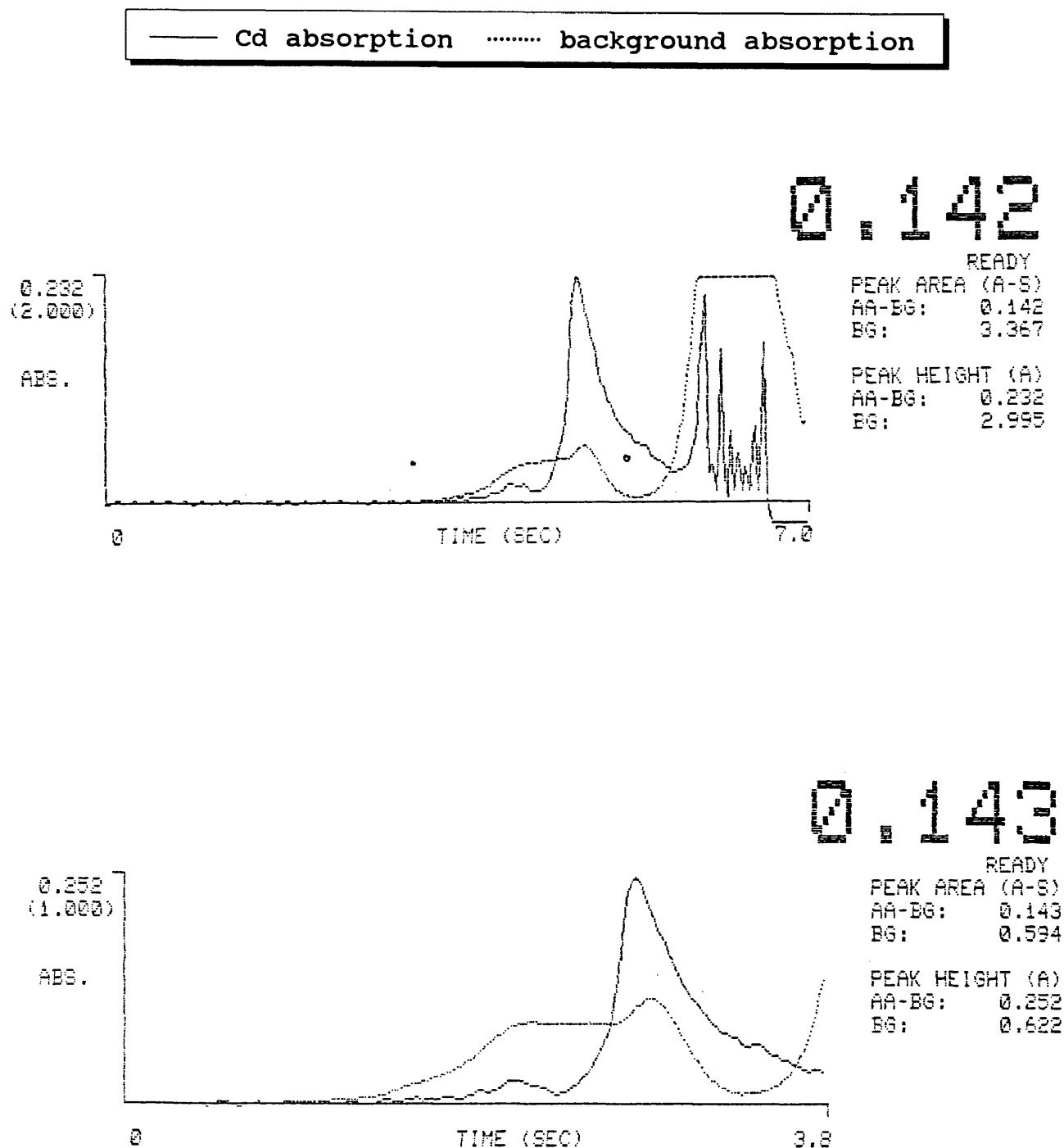


while the bottom profile used a 10 second ramp time to 1900 °C held constant for 2 seconds.

There are several features that should be noted about the absorption profiles in Figure 24. A closer look at the top profile reveals that the Cd peak can be seen occurring immediately before and during the sample matrix absorption, which and consequently reduces the net absorption signal due to the excessive background signal. Supposedly the EDTA reduced the volatilization temperature of the Cd but in this case did not allow for separation from the volatilization of the matrix species. A longer ramped atomization temperature delayed the volatilization of the matrix just long enough to allow for the atomization of the Cd before the matrix as shown in the bottom absorption profile. Also worth noting is the exceptionally high background absorption in both profiles, which also gets delayed by using a ramped atomization temperature. The rather noisy signal following the Cd absorption is thought to be due to light scattering from particulate material in the sample matrix.

With some fine tuning of the times, an absorbance profile of the Cd with a relatively low background signal could be obtained utilizing selective volatilization techniques and precise delay and read times as shown in Figure 25. Both of these absorption profiles were obtained in the same manner as those shown in Figure 24 except that a cool down step was used and the atomization temperature was

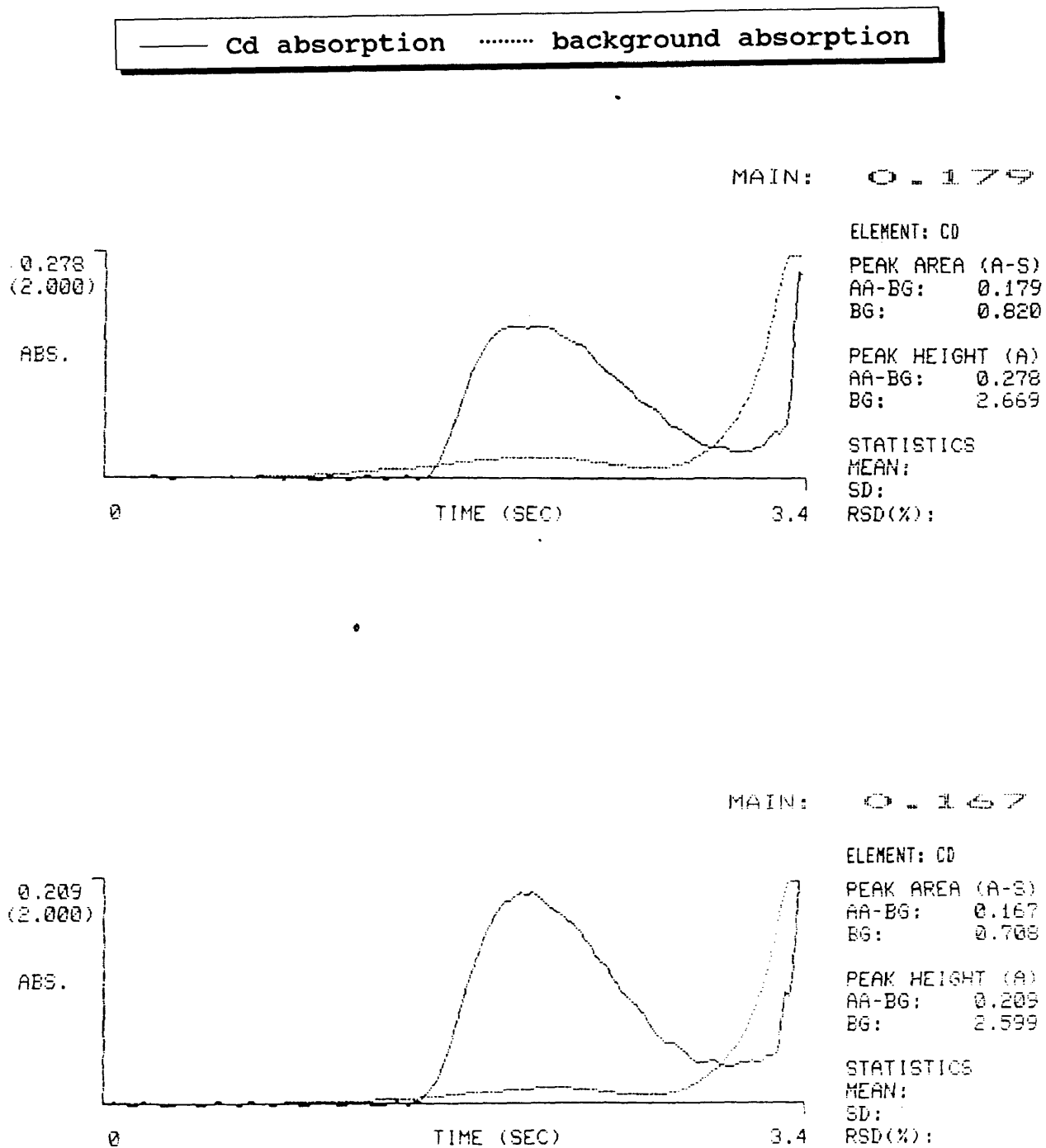
FIGURE 25. An example of the absorbance profiles obtained using EDTA as the matrix modifier for the determination of Cd. The bottom profile illustrates how the high background absorption of the top profile can be lowered by using precise delay and read times with the same temperature program. Both absorption profiles were produced from identical samples.



2500 °C ramped for 5 seconds and held for 2 seconds. In the bottom profile the absorption read was delayed for 2 seconds into the atomization step and lasted 3.8 seconds. These times were carefully selected in order to avoid the matrix signal. These times can vary, the ones given above worked best with the recommended sample volumes and a new graphite tube. As the graphite tube ages, the sample can take longer to atomize due to a build up of salts on the graphite tube which lowers the rate of heat transfer.

Both the diammonium and disodium salt of EDTA produced usable peak profiles as shown in Figure 26. Both of these absorption profiles are for 15 μL of 20 ppt simulated sea salt preserved in 0.5% HCl and spiked with 5 μL of 5 ppb Cd. A 5 μL aliquot of 10 mg/mL diammonium salt of EDTA was used as a matrix modifier for the top profile and a 5 μL aliquot of 10 mg/mL disodium salt of EDTA was used as a matrix modifier for the bottom profile. The temperature program was identical to that used in the previous determination except a read delay time of 2 seconds and a read time of 3.4 seconds was used with this temperature program. The diammonium salt produced a slightly larger absorption signal for the same Cd concentration, but this determination was performed using a newer graphite tube. The slight reduction in sensitivity for the disodium salt of EDTA was probably due to the use of an older graphite tube. Also samples preserved in both HNO_3 and

FIGURE 26. An example of the absorbance profiles obtained using EDTA as the matrix modifier for the determination of Cd. The diammonium salt was used for the top profile and the disodium salt was used for the bottom profile. Both absorption profiles were produced using identical samples and temperature profiles.

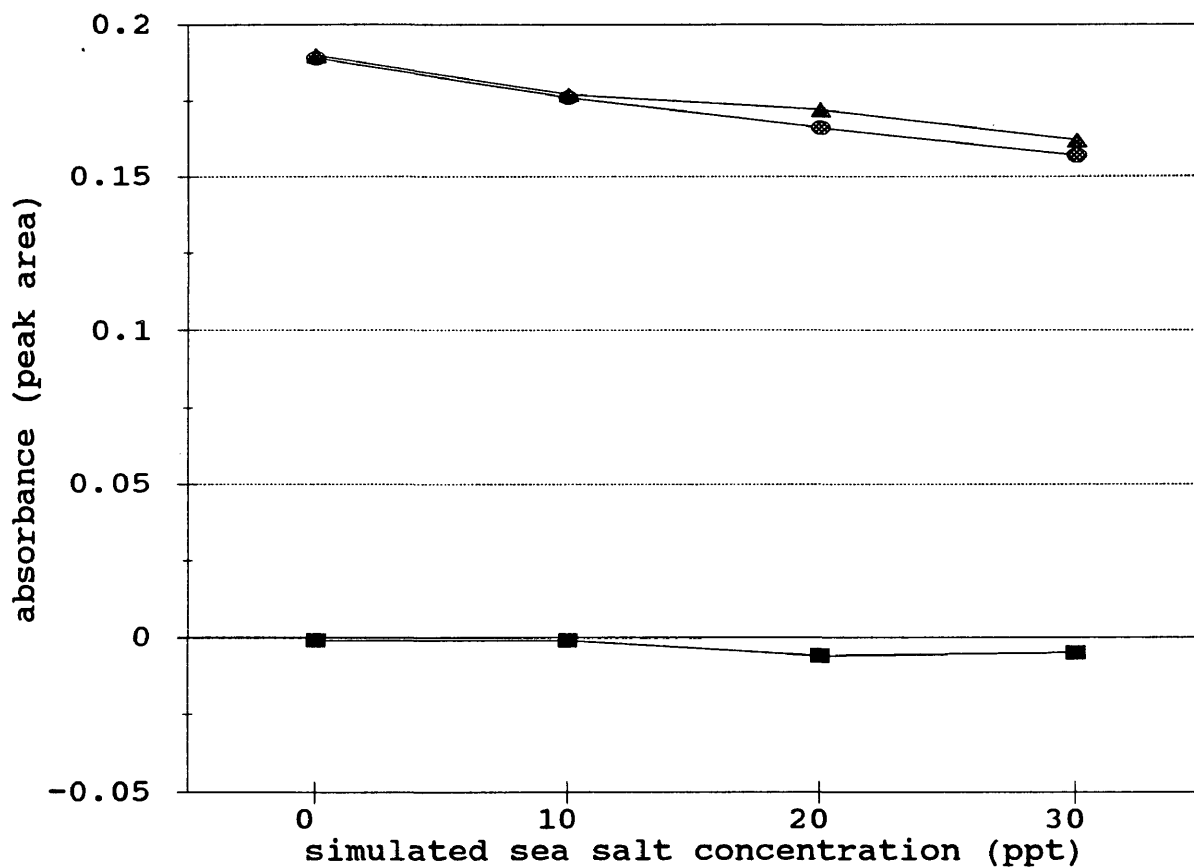


HCl were used but the samples preserved in HCl produced a more symmetrical peak profile.

A graph of the absorbance for 20 μL of 1.25 ppb Cd vs. increasing salinity concentrations is given in Figures 27 and 28. The disodium salt of EDTA was used as the modifier for the determinations in Figure 27 and the diammonium salt of EDTA is used as the modifier in Figure 28. The signal profiles were suppressed with the increasing salt concentrations, with a net drop of 13% in the net absorbance going from deionized water to a 30 ppt simulated sea salt matrix using the disodium salt of EDTA as the modifier and a 23% drop in the net absorbance using the diammonium salt of EDTA as the modifier.

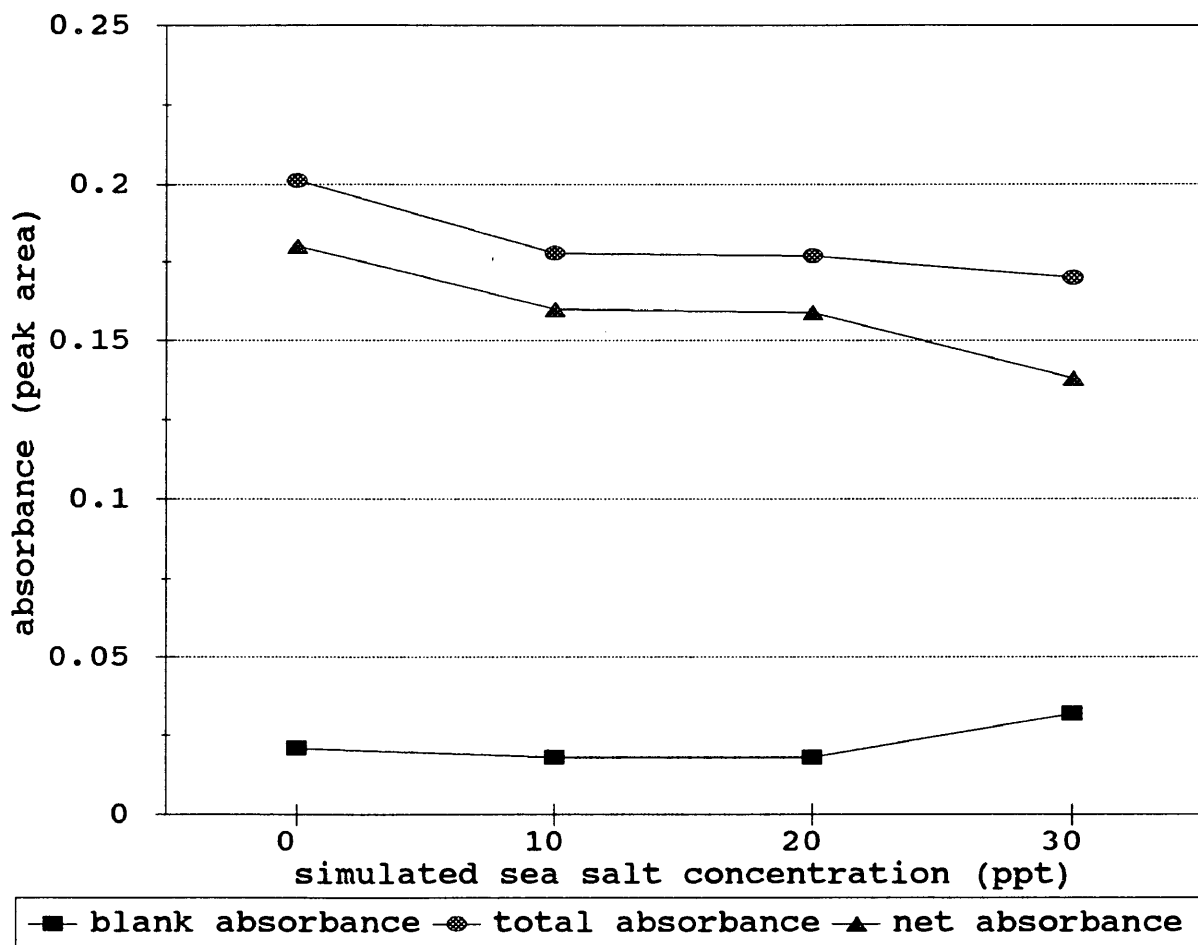
The lower signal suppression and better peak profiles obtained using the disodium salt of EDTA with HCl as a preservative suggested that this combination would perform best for the determination of Cd in natural waters. The signal suppression could be avoided by constructing a calibration curve with standards made up in a simulated sea salt matrix at concentrations comparable to the sample being analyzed within a variation of ± 5 ppt. This would correlate to a $\pm 3\%$ error in concentration due to the signal suppression within a ± 5 ppt error in the matrix matching. Constructing a calibration curve in this manner avoided the use of the method of additions which as stated before can be very tedious and time consuming.

FIGURE 27. The absorbance of 20 μL aliquots of 1.25 ppb Cd standards prepared in increasing concentrations of simulated sea salt matrices with 50 μg of the disodium salt of EDTA as the matrix modifier.



■ blank absorbance ● total absorbance ▲ net absorbance

FIGURE 28. The absorbance of 20 μL aliquots of 1.25 ppb Cd standards prepared in increasing concentrations of simulated sea salt matrices with 50 μg of the diammonium salt of EDTA as the matrix modifier.

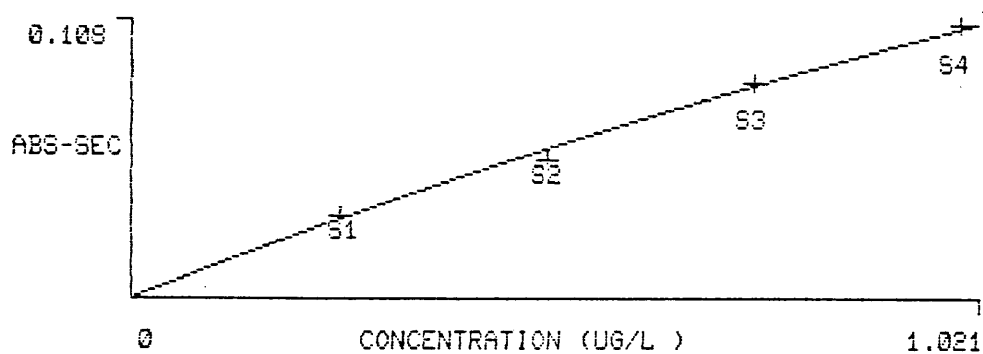


In our study of Cd a calibration curve was constructed using 20 μL aliquots of 0.25, 0.50, 0.75, 1.00 ppb Cd standards prepared in 20 ppt simulated sea salt. The standards were chosen at such a low level because the sensitivity of the GFAAS for Cd is very high and no Cd was expected in the natural water samples. The simulated sea salt concentration of 20 ppt was chosen because of the similarity to the Hampton Roads Marina samples (see Chapter IV, Table 10).

The standards were prepared using a 1.00 mL micro burette to add increasing concentrations of a 100 ppb Cd standard to 100 mL volumetric flasks and diluting to volume with 20 ppt simulated sea salt solution preserved in 0.5% HCl. Three natural samples spiked with 0.50 ppb Cd were also prepared in the same manner. A 20 mg/mL solution of the disodium salt of EDTA was prepared and used as the matrix modifier.

A linear calibration curve was developed using the GFAAS autosampler and the microprocessor as shown in Figure 29. The calibration curve was constructed using 20 μL aliquots of the Cd standards with 5 μL of the 20 mg/mL solution of the disodium salt of EDTA as the matrix modifier. There was some question as to which concentration of modifier (the 10 or 20 mg/mL solution) was sufficient based on observations that as the graphite tube aged a higher concentration of the matrix modifier was needed to adequately

FIGURE 29. Calibration curve used for the determination of Cd in natural water samples. The calibration curve was constructed using 20 μL aliquots of 0.25, 0.50, 0.75, 1.00 ppb Cd standards prepared in a 20 ppt simulated sea salt matrix. The disodium salt of EDTA was used as the matrix modifier.



separate the Cd absorption peak from the matrix absorption interferences. In this case the higher amount was used for constructing the calibration curve and performing the subsequent determinations.

Two sets consisting of three natural samples both preserved in 0.5% HCl were analyzed. The first set was not spiked and the second was spiked with Cd as mentioned above. The results of these analyses are given in Table 13. The mean value obtained with the spiked samples was 0.49 ppb, which was in excellent agreement with the 0.50 ppb actual concentration, implying that matrix matching of the standards could provide an acceptable technique for the quantitative analysis of Cd in saline water samples even with only a marginal reduction of interferences by the modifier.

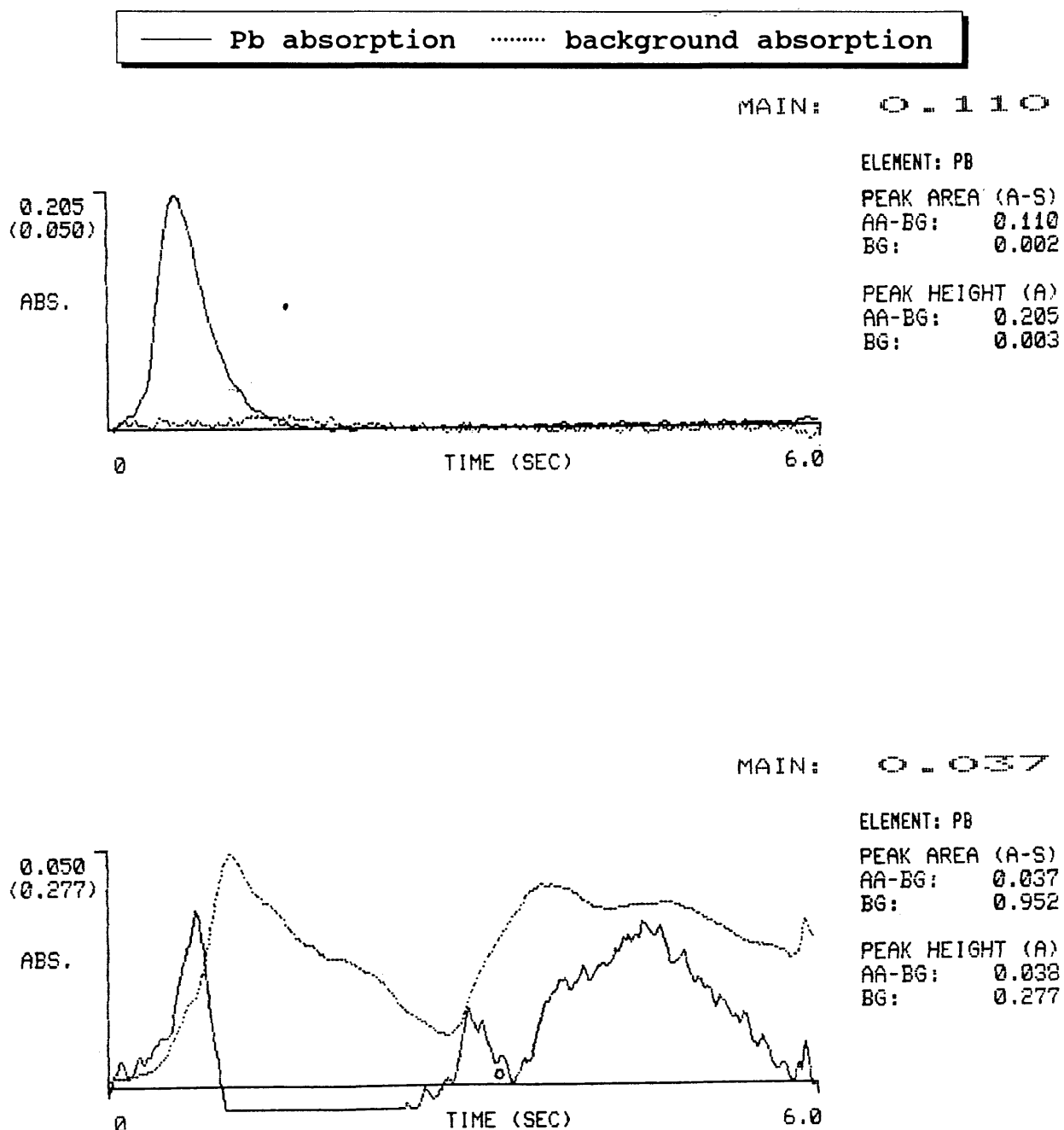
DETERMINATION OF Pb

An example of absorbance profiles obtained with the Manning and Slavin method for the determination of Pb are shown in Figure 30. The top profile is 15 μL of a 0.5% HNO_3 deionized water blank spiked with 5 μL of 100 ppb Pb using a 5 μL aliquot of matrix modifier containing 2 μg of $\text{Mg}(\text{NO}_3)_2$ and 10 μg of $\text{NH}_4\text{H}_2\text{PO}_4$. The bottom profile is the same except that the deionized water was replaced with 15 μL of 10 ppt simulated sea salt preserved in 0.5% HNO_3 . The temperature program used to obtain the absorbance profiles consisted of

TABLE 13. Results of the Cd analysis using the disodium salt of EDTA as the matrix modifier and standards prepared in 20 ppt simulated sea salt matrix.

| LOCATION | CONCENTRATION OF Cd ($\mu\text{g/L}$) | |
|----------|---|------------------------|
| | UNSPIKED SAMPLES | SPIKED WITH 0.5 ppb Cd |
| HRM #1 | 0.01 | 0.48 |
| HRM #2 | -0.02 | 0.44 |
| HYC #3 | -0.03 | 0.55 |

FIGURE 30. An example of the absorbance profiles obtained with the Manning and Slavin method for the determination of Pb. The top absorbance profile is from 15 μL of deionized water spiked with 5 μL of 100 ppb Pb using a 5 μL aliquot of the $\text{Mg}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ matrix modifier. The bottom absorbance profile is the same except the deionized water was replaced with 10 ppt simulated sea salt.



a 250 °C drying temperature ramped for 30 seconds and held constant for 15 seconds and a 1000 °C charring temperature ramped for 15 seconds and held constant for 30 seconds. A pre-atomization cool down step not was used. An atomization temperature of 1800 °C was held for 6 seconds followed by a clean out step.

The salt matrix, even at the 10 ppt simulated sea salt concentration, produced interferences too great for the deuterium arc background correction system to manage. The net signal produced by the microprocessor for the deionized water blank spiked with 5 μL of 100 ppb Pb standard was more than three times greater than the highly irregular signal produced by the same standard in 10 ppt simulated sea salt. The problem appeared to be the inability to sufficiently separate the volatilization of the matrix species from the analyte atoms using these modifiers and temperature programs, which is a factor inherent of the similar volatilization temperatures of the Pb and this matrix. Many different variations in the Manning and Slavin temperature program were tried for the determination of Pb in natural waters with no success. Different concentrations of combinations of $\text{Mg}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ matrix modifiers were also explored with no successful improvement of the absorption profiles.

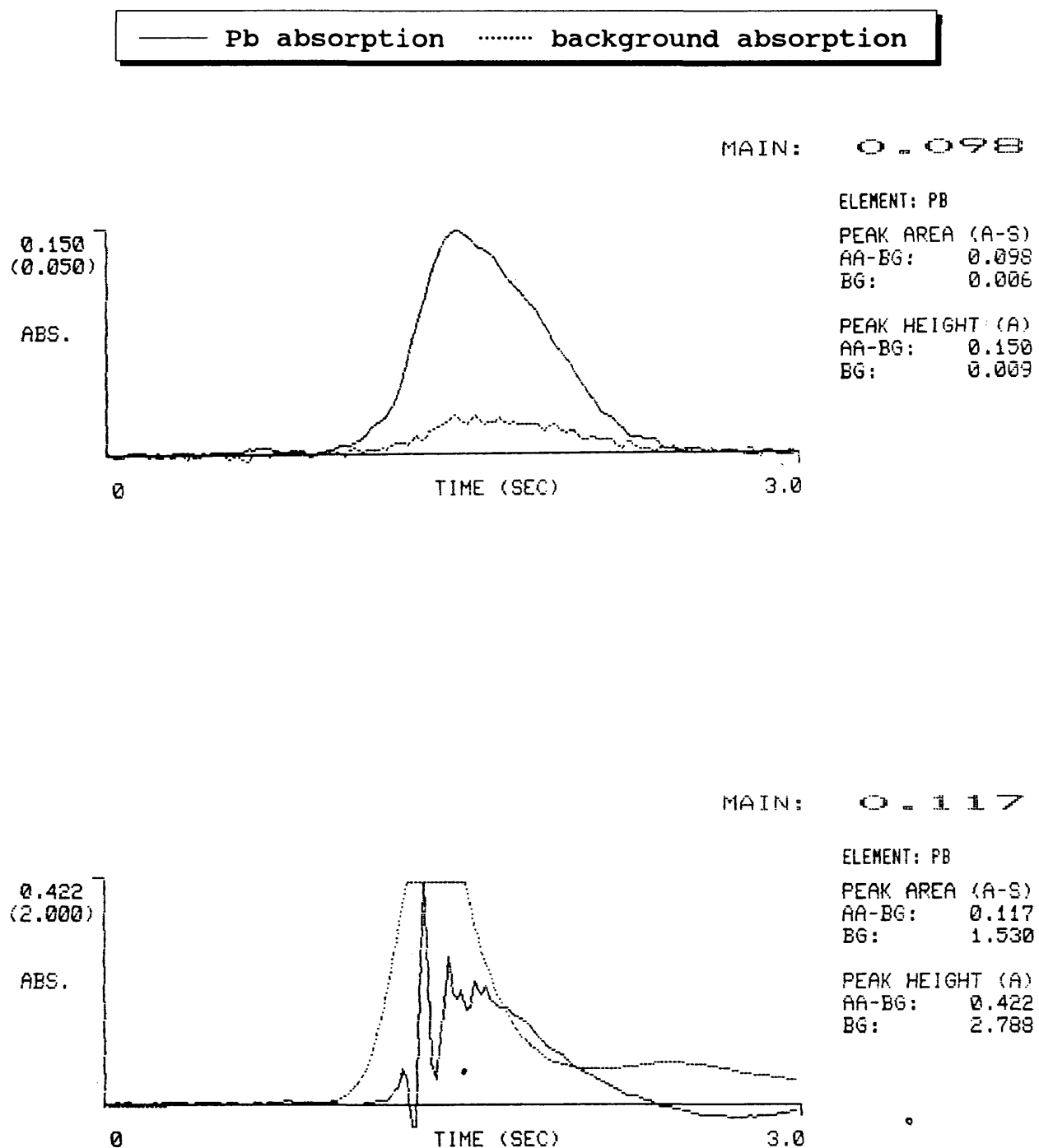
The EDTA modifiers successfully used for the determination of Cd were investigated in concentrations ranging from 5 μL of 10 mg/mL to 10 μL of 20 mg/mL of EDTA.

Various temperature programs were explored using these modifiers including the ramped atomization temperature step that was effective for the determination of Cd in saline waters. Nothing resembling a usable absorption profile was obtained for the determination of Pb in saline waters using these modifiers.

The Schlemmer and Welz²⁴ method was also tried using a mixture of palladium and magnesium nitrates as the modifier. An example of absorbance profiles obtained with the Schlemmer and Welz modifier are shown in Figure 31. The top profile is 15 μL of 0.5% HNO_3 deionized water blank spiked with 5 μL of 100 ppb Pb using 10 μL of the modifier solution containing 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 15 μg of $\text{Pd}(\text{NO}_3)_2$. The bottom profile is the same except that the deionized water blank was replaced with 15 μL of 20 ppt simulated sea salt preserved in 0.5% HNO_3 . The temperature program used to obtain the absorbance profiles in Figure 26 was the same as given previously.

There are several factors worth noting when comparing these profiles. The background absorption signal produced by the 20 ppt simulated sea salt matrix was more than 250 times greater than the deionized water sample background and was well beyond the maximum expanded scale of the microprocessor (2.000 absorbance-second units). Although the signals are within 20% of each other the Pb profile in the 20 ppt simulated sea salt matrix was so irregular that there is no certainty of what absorbance was being measured. Ramped

FIGURE 31. An example of the absorbance profiles obtained with the Schlemmer and Welz modifier for the determination of Pb. The top absorbance profile is from 15 μL of deionized water spiked with 5 μL of 100 ppb Pb using a 5 μL aliquot of the palladium and magnesium nitrate matrix modifier. The bottom absorbance profile is the same except the deionized water was replaced with 20 ppt simulated sea salt.



atomization temperatures were investigated for the separation of the broad band absorption from the analyte absorption with no success. Both peaks did appear in the same time frame, thus the Pb peak could be overshadowed by the broad band absorption exhibited by the salt matrix.

The use of the NH_4NO_3 matrix modifier with the mixture of palladium and magnesium nitrates was explored in an attempt to remove the interferences during the char step. The NaNO_3 and NH_4Cl that can be formed and the excess NH_4NO_3 could supposedly be removed by volatilization using the previously mentioned temperature program with a 1000 °C charring temperature. The Pb could be stabilized by the mixture of palladium and magnesium nitrates to allow for the use of a 1000 °C char temperature which is high for Pb relative to the recommended char temperature of 700 °C.

An example of the absorption profiles obtained with this combination of modifiers is shown in Figure 32. The top profile is 15 μL of 0.5% HNO_3 deionized water blank spiked with 5 μL of 100 ppb Pb using 10 μL of the modifier solution containing 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 15 μg of $\text{Pd}(\text{NO}_3)_2$ and 10 μL of 30% NH_4NO_3 solution. The bottom profile is the same except that the deionized water blank was replaced with 15 μL of 30 ppt simulated sea salt preserved in 0.5% HNO_3 . The temperature program used to obtain the absorbance profiles in

Figure 32 was the same program given previously except that a pre-atomization cool down step was added.

One interesting observation about the use of the palladium, magnesium, and ammonium nitrate modifier combination is that a more symmetrical and narrower absorption curve was produced in the presence of a salt matrix. The reason for this enhancement is unknown at this time, although it would appear that components in the sample matrix actually act as modifiers as well, by enhancing the Pb absorption profile. Nevertheless, the background corrected absorption signals were very comparable.

This approach worked well in producing a signal profile that was relatively independent of the salt concentration. A graph of the absorbance for 20 μL of 25 ppb Pb vs. increasing salinity concentrations is given in Figure 33. The combination of 10 μL of the solution containing 10 μg of $\text{Mg}(\text{NO}_3)_2$ and 15 μg of $\text{Pd}(\text{NO}_3)_2$ and 10 μL of 30% NH_4NO_3 solution were used as the modifier for the determinations. The signal profile was slightly suppressed with the increasing salt concentration with a net absorption drop of about 10% going from deionized water to a 30 ppt simulated sea salt matrix with a relative deviation of 4.5% using this combination of matrix modifiers.

A linear calibration curve was developed using the GFAAS autosampler and the microprocessor as shown in Figure 34. The calibration curve was constructed using 20 μL aliquots of

FIGURE 32. An example of the absorbance profiles obtained with the palladium, magnesium, and ammonium nitrate modifier combination for the determination of Pb. The top absorbance profile is from 15 μL of deionized water spiked with 5 μL of 100 ppb Pb using this matrix modifier combination. The bottom absorbance profile is the same except the deionized water was replaced with 30 ppt simulated sea salt.

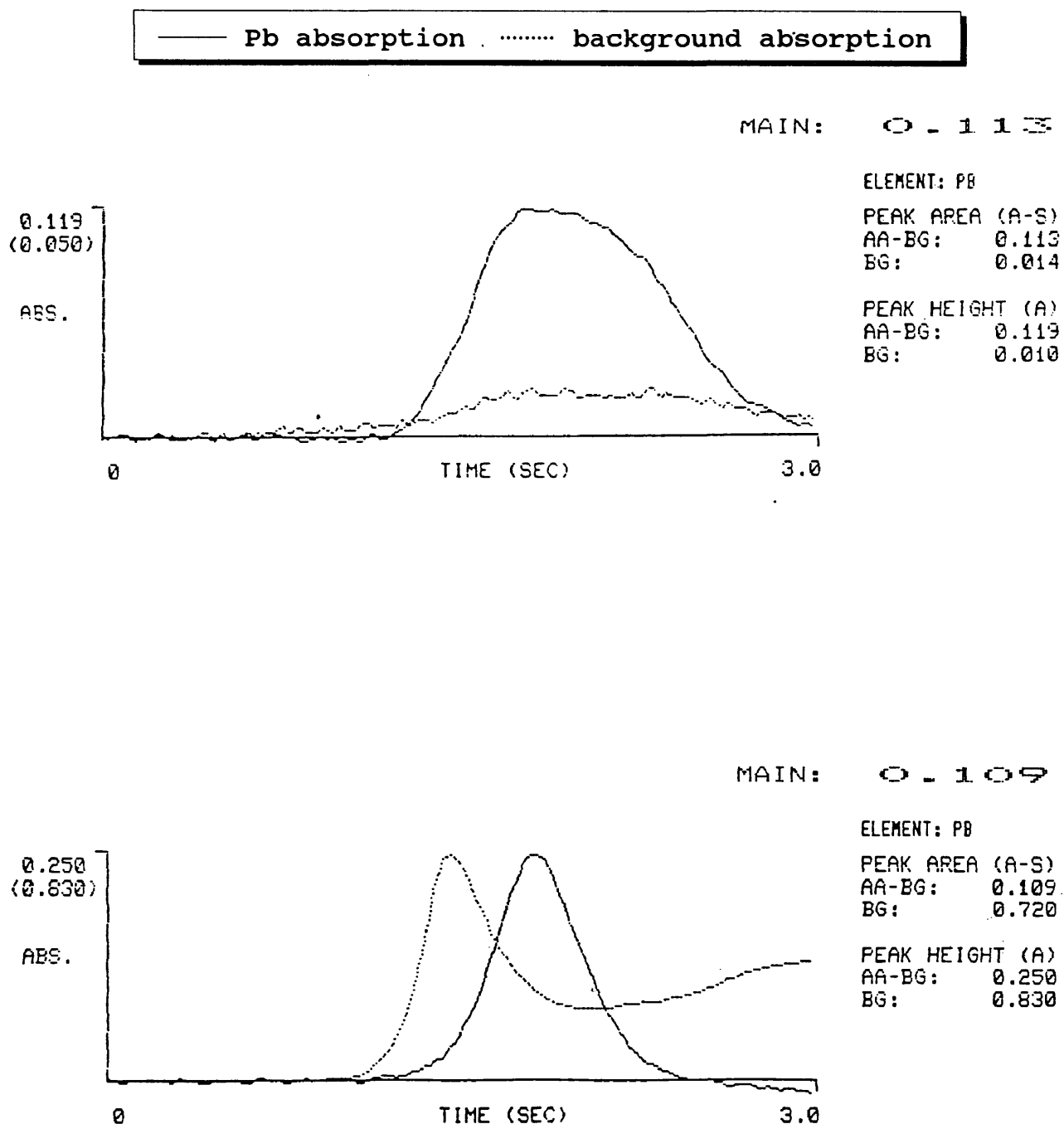


FIGURE 33. The absorbance of 20 μL aliquots of 25 ppb Pb standards prepared in increasing concentrations of simulated sea salt matrices with 10 μg of $\text{Mg}(\text{NO}_3)_2$, 15 μg of $\text{Pd}(\text{NO}_3)_2$, and 3000 μg of NH_4NO_3 as the matrix modifier.

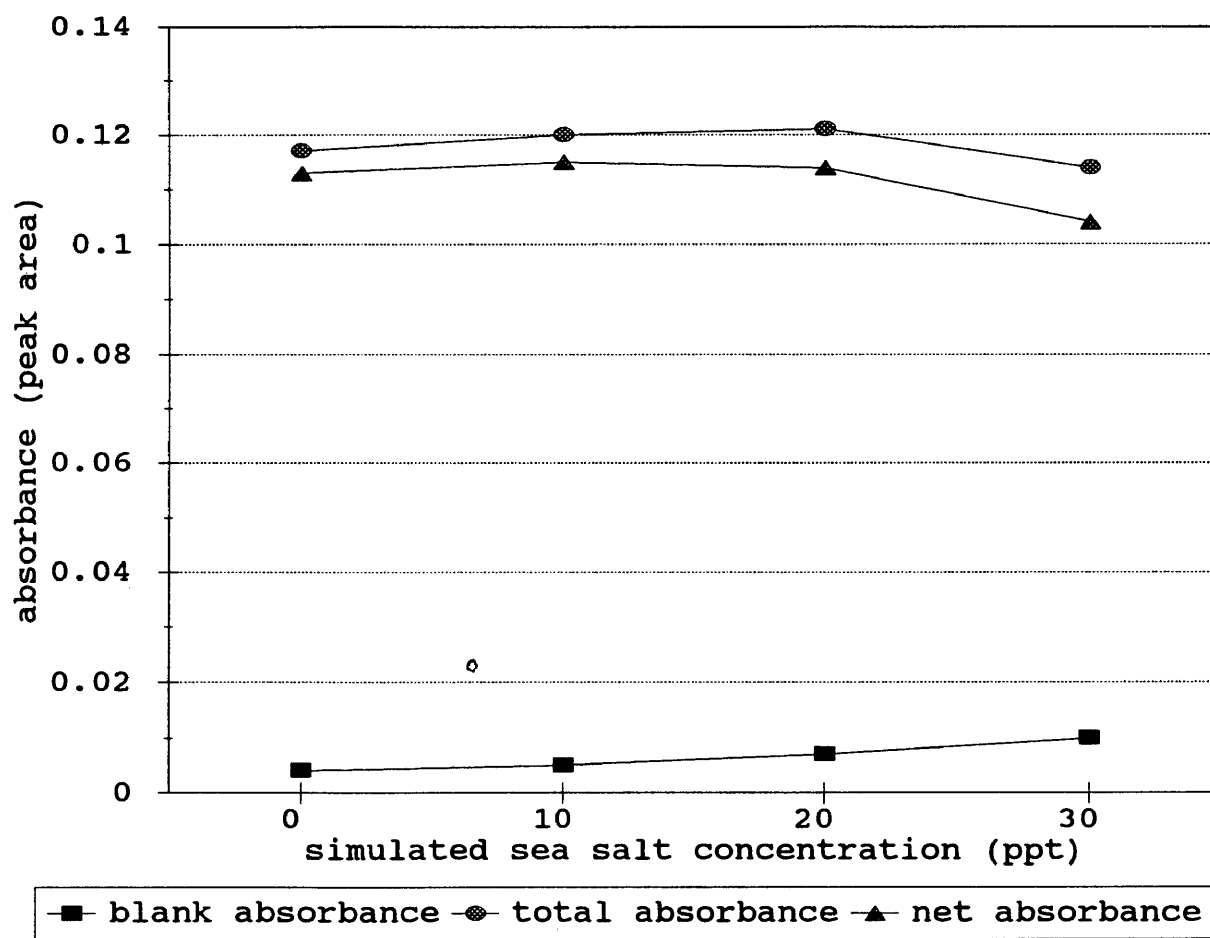
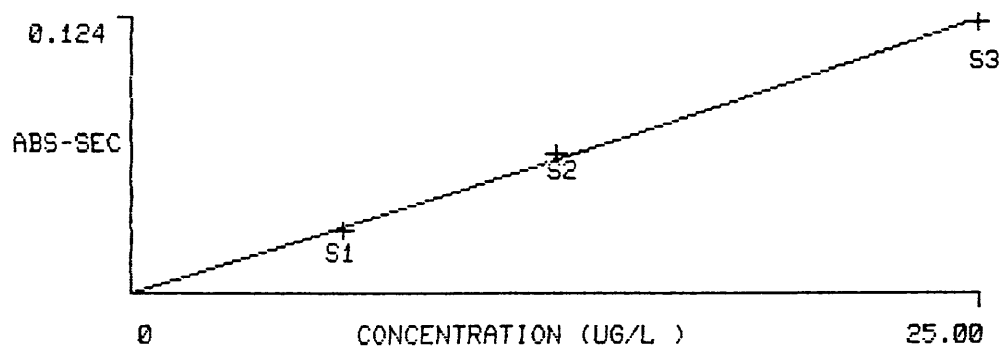


FIGURE 34. Calibration curve developed for the determination of Pb. The combination of palladium, magnesium, and ammonium nitrates was used as the matrix modifier.



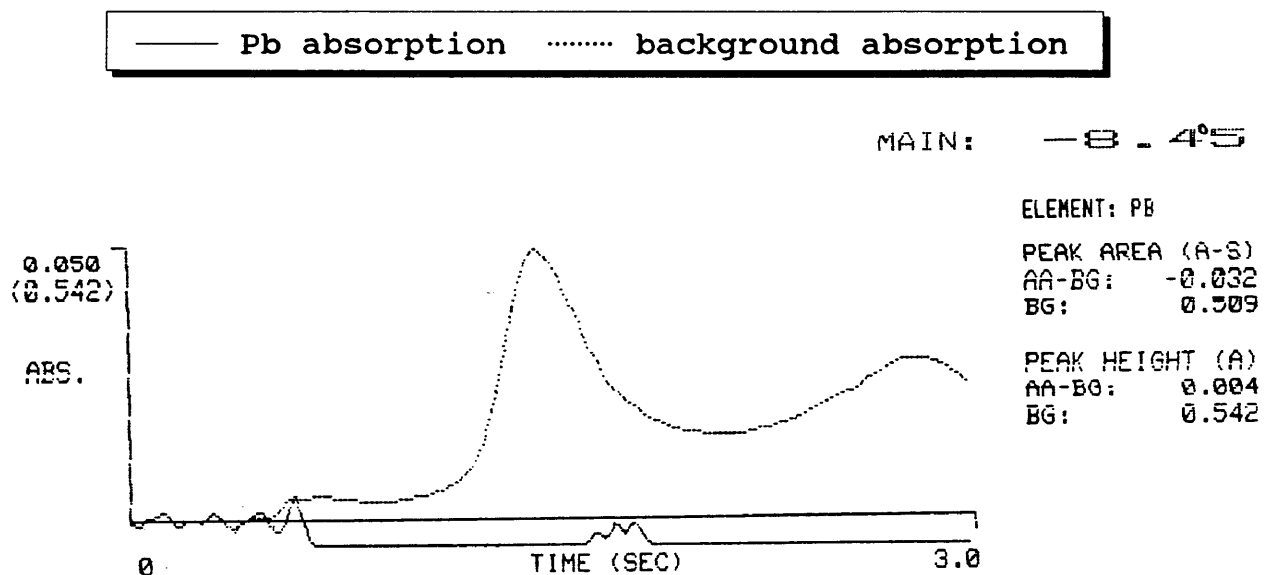
6.25, 12.5, and 25.0 ppb Pb standards prepared in 0.5% HNO₃ with the same aliquots of modifiers as given previously. It has been observed that this combination of modifiers rapidly degrades the graphite tube, which will be discussed later in this chapter.

This procedure produced excellent absorption profiles for Pb when used with simulated sea salt but when tried with natural samples the absorption profiles appeared as those shown in Figure 35. A possible explanation for this behavior is that the natural water sample may have an organic/biological component in the matrix that is not present in the fabricated sea salt matrix, which was prepared from dried simulated sea salt. Light scattering may become a problem due to incomplete atomization of an organic matrix which can form carbonaceous particles and lead to substantial background absorbance. More research is needed to determine why these disparities exist with this combination of modifiers for natural water samples.

GRAPHITE TUBE DEGRADATION

Direct determination for trace metals in saline water by GFAAS was shown to be feasible but the useful lifetime of the graphite tubes was shortened to varying degrees. All saline water determinations eventually effected the sensitivity of the graphite tubes after continued use, but the use of NH₄NO₃ as a matrix modifier proved to be extremely harsh on the

FIGURE 35. An example of the absorbance profile obtained with the palladium magnesium and ammonium nitrate modifier combination for the determination of Pb in a natural water sample. The absorbance profile is from 15 μL of HRM #1 water sample using this matrix modifier combination.



tubes. There are two possible reasons for the rapid decline in the sensitivity of the tubes when using NH_4NO_3 as a matrix modifier. During the charring steps the salts visibly produced a white puff of smoke that issued from the injection hole of the graphite tubes. This salt vapor can also condense in the cooler portions of the tubes and cover a progressively larger area as more salts condense. These white deposits were quite visible on the inner surface of the graphite tubes. The corrosion of the tube by halogen containing compounds may also occur if they are not completely removed either with the temperature cycle or the cleaning procedure that follows.

The condensation of salts throughout the tube probably effects the heat transfer rate and delays the atomization of the analyte. Once atomized the analyte could then condense on portions of the tube covered with salts due to the lower temperatures in these portions of the tube causing both chemical and spectral interferences. This factor was reversible to a certain extent by soaking the tubes in a 25% HCl or HNO_3 solution for several hours, followed by multiple rinses with semiconductor grade deionized water and drying in an oven. Prior to reuse the tubes were again preconditioned using the recommended procedure by Perkin Elmer.

The tubes were always good for one day of continuous use with NH_4NO_3 as a matrix modifier and the rapid decrease in sensitivity was not directly related to the number of firings

but rather the amount of time that lapsed between uses. After a day of heavy use with the NH_4NO_3 modifier the tubes had to be cleaned or they could not be used the following day due to losses in sensitivity and changes in the absorption/time profiles, i.e., the peaks required a longer time to appear and were wider. The tubes worked fine at the end of a day of continuous use with NH_4NO_3 but after sitting over night the tubes were found to be useless the next morning until cleaned as previously mentioned. There is no solid data on how many times a tube can be rejuvenated since this was discovered late into the study, but tubes have been cleaned up to six times and have performed adequately.

The degradation of graphite tubes caused much anxiety during most of the study. Substantial time was required investigating the loss in sensitivity of the tubes and changes in absorption profiles. Other causes were investigated because of the belief that the tube degradation could not occur that quickly. Nevertheless, the useful lifetime of the graphite tubes could be extended substantially to allow for the use of GFAAS for the direct determination of trace metals in saline water samples.

RESULTS OF NATURAL WATER ANALYSIS

The results of the analysis of randomly chosen natural water samples from various locations throughout southeastern Virginia are given in Table 14. The Cr, Cu, Mn, and Ni were

determined using the Manning and Slavin modifiers. The Co was determined using the Hades modifier and Cd was determined using the Guevremont et al. modifier. All determinations were accomplished using procedures developed in this study.

The results for this study are higher than expected when compared to the results of the Kingston et al.³⁴ study. The water for the Kingston et al. study was obtained during high tide at the Virginia Institute of Marine Science (VIMS), Gloucester Point, Virginia on the Chesapeake Bay. The samples were collected 100 meters offshore from VIMS with a permanently placed submersible pump and plastic tubing. The analyses were done using a separation and perconcentration method and the determinations made with GFAAS.

The water for this study was obtained directly offshore or at various marina and shipyard locations in southeastern Virginia. The higher levels obtained are not believed to be from contamination problems that occurred during this study because the absorbancies of the blanks were acceptably low. The higher values are probably due to the sample locations, (coastal waters as opposed to open bodies of water) or metal sources close to the sample locations, (metal ship hulls or industrial sources).

TABLE 14. The results of trace metal analysis in natural samples from various locations throughout southeastern Virginia. Limits of detection for the current study and typical trace metal concentrations from the Chesapeake Bay are given for comparison.

| LOCATION | CONCENTRATION ($\mu\text{g/L}$) | | | | | |
|---------------------------------|-----------------------------------|-----------------|------|------|------|------|
| | Co | Cd | Cr | Cu | Mn | Ni |
| HRM #1 | | ND ^a | | 26 | 11 | 1.5 |
| HRM #2 | 17 | ND | 4.3 | 12 | 10 | ND |
| HYC #3 | 14 | ND | 1.8 | 7.3 | 10 | |
| York River | | | | 16 | | 2.0 |
| James River | 1.4 | | 2.0 | | | |
| Chesapeake Bay ^b | <0.01 | 0.05 | | 2.0 | 2.0 | 1.2 |
| Limit of Detection ^c | 0.61 | 0.025 | 0.25 | 0.43 | 0.15 | 0.57 |

^aND = none detected

^bReference 34

^cConcentration required to produce 0.005 absorption units.

CHAPTER VI

CONCLUSIONS AND FUTURE RESEARCH

CONCLUSIONS

Direct determination of As, Co, Cr, Cu, Mn, and Ni in saline water by GFAAS using simple aqueous standards and analysis of Cd using a matrix matching technique was shown to be feasible in this study. These methods provide an improved way of determining trace metals in saline waters as compared with methods currently being utilized. Further refinements of these procedures and confirmation of the accuracy of the proposed methods are needed. The direct determination of Pb in saline water by GFAAS using simple aqueous standards needs further development but modifiers investigated in this study showed potential and demand more investigation.

SUGGESTIONS FOR FURTHER RESEARCH

The accuracy of the proposed methods could be augmented by the determination of trace elements in standard seawater reference materials available from several sources (i.e., National Research Council of Canada, Ottawa, Canada). The trace metal concentrations may not be high enough for direct

analysis of some of the elements by GFAAS, but the samples could be spiked with small but known amounts of the analyte for comparisons of matrices.

Further exploration of the type and concentration of the acid used to preserve the samples is also needed. Different acids can have varying effects on the peak profiles, implying that they not only act as a preservative but also as a matrix modifier by enhancing the peak profile as seen with the determination of Cd using EDTA as the matrix modifier. There is also not much agreement in the literature on what concentration of acid is appropriate as the preservative for the determination of trace metals in saline waters, which is another area that should be investigated for the same reasons as mentioned.

There are other modifiers which exist that could be investigated. Lanthanum compounds³⁵, such as LaCl_3 or $\text{La}(\text{NO}_3)_2$ have been mentioned in the literature as modifiers for the determination of Pb, but we did not have the time to investigate their use. Also recommended in the literature is the use of tantalum³⁶ as a coating for tubes used in the determination of Pb. Another area that could be investigated is the use of other chelating agents as modifiers.

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VITA

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