D 01 inia Water Resources Research Center **Bulletin 168** inia Polytechnic Institute and State University .57 0.168 .4 **Helium High Efficiency Microwave Induced Plasma for the Atomic Spectrometric Determination** of Metals and Nonmetals Larry D. Perkins, Curtis B. Motley, Keith A. McCleary, Gary L. Long 1001249822

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Bulletin 168 February 1991

A Helium High Efficiency Microwave Induced Plasma for the Atomic Spectrometric Determination of Metals and Nonmetals

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V.57 This bulletin is published with funds provided in part by the U.S. Geological Survey, Department of the Interior, as authorized by the Water Resources Research Act of 1984. Contents of this publication do not necessarily reflect the views and policies of the

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19.50

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Library of Congress Catalog Number: 90-71338

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3. Acknowledgments

The authors would like to acknowledge the Virginia Water Resources Research Center, the Department of Interior-Bureau of Mines, and BP America Inc. for the financial support of this project. Also to be acknowledged are the Phillips Petroleum Company for the gift of the microwave generator, the Suprex Company for the loan of the Suprex SFC 200A SFC pump, and Keystone Scientific for the gift of the SFC columns. The authors also wish to thank Prof. Charles B. Boss of North Carolina State University, Prof. Larry T. Taylor of Virginia Polytechnic Institute and State University, and Dr. M. Ashraf-Khorassani of the Suprex Corporation for helpful discussions.

The members of the Project Advisory Committee: Edward LeFebvre, Division of Consolidated Lab Services; John Kennedy, Chesapeake Bay Program Office; Rudolf Bieri, VIMS; Wilbur McConico, Richmond Wastewater Treatment Plant; and Robert Rapaport, Proctor & Gamble Company deserve special credit and thanks for providing beneficial suggestions and comments during this research project. The successful completion of this investigation and the relevance of the Virginia Water Resources Research Center's total research program can be partially attributed to the guidance and participation of these knowledgeable and interested members of this project advisory committee.

> Diana L. Weigmann Assistant Director

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4. Abstract

The development and use of a new helium microwave induced plasma for the spectrometric determination of metals and nonmetals in aqueous and organic samples is described. Studies concerning the operation and analytical utility of this plasma are presented. The He plasma is shown to be free from interferences that plague argon-based plasmas in elemental determinations. Limits of detection for metals are below the ng/mL (ppb) level and below the μ g/mL (ppm) level for nonmetals determined with the He plasma. With the use of a desolvation system, a limit of detection of 30 ng/mL can be obtained. A minimum detectable quantity of 50 ng is achieved when this plasma is used as a detector for chromatography.

Keywords: Helium microwave induced plasma

Metals Nonmetals Atomic spectrometric determination

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The development of a detector that is both sensitive and selective for nonmetals (CI, P, N, and S) and metals has been the pursuit of many spectroscopists over the past two decades. While techniques such as the inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) have become commonplace in large analytical laboratories for trace metal determinations, neither of these techniques is able to determine adequately nonmetals in aqueous samples. This limitation is due to the lack of sufficient energy possessed by either analytical discharge. This energy is needed to promote the nonmetal atoms to an excited-state level in order for the process of atomic emission to occur. Of the plasma discharges that are available to the analyst, only a He-based discharge is capable of exciting nonmetal emission.

Resonant cavities, sustained using microwave radiation are capable of igniting and maintaining a He discharge. Unfortunately, the cavity designs that have been available to the analyst require high applied power levels and become unstable when aqueous samples are introduced into them. Nonmetal determinations have been performed with such cavities, but the lack of long-term stability of the plasma prevents the system from being considered as an on-line detector for Cl, P, or S in aqueous samples.

The purpose of this work centers on the development of a new Hebased microwave induced plasma (MIP) for the determination of nonmetals and metals that is well suited to aqueous sample introduction, possesses long term stability, and is suitable for use as an on-line detector for aqueous samples using nebulization or organic samples using supercritical fluid chromatography. The work in this report describes efforts (1) to develop a new MIP system based on He as the support gas using a high-efficiency cavity; (2) to investigate direct aqueous sample introduction as a viable alternative to conventional sample introduction (gaseous) for MIP-AES; (3) to conduct fundamental physical studies of the He plasma; (4) to develop a method that can be applied routinely for the determination of aqueous metals and nonmetals based on atomic emission spectrometry and atomic fluorescence spectrometry; (5) to evaluate the effect of solvent loading on the plasma; and (6) to develop a sensitive and nonmetal-selective detector for supercritical fluid chromatography.

6. Introduction to Microwave Induced Plasmas

The ideal atomic spectrometric source should excite emission from any element in the periodic table, be highly sensitive and stable, possess freedom from both spectral and chemical interferences, accept gaseous, liquid, or solid samples, and be inexpensive and easy to operate. Plasma sources, such as the popular inductively coupled plasma (ICP), fulfill many of these requirements and are thus superior to arc/spark and flame methods of trace analysis [1-6]. When Ar is used as the support gas, these inert gas discharges are characterized by a high temperature, resulting in the sensitive determination of a large number of elements. Within the last 20 years, the microwave-induced plasma (MIP) has evolved as a powerful excitation source, enabling plasmas to be sustained in argon, helium, nitrogen, and air [7-9].

The MIP is essentially a plasma discharge of helium, argon, nitrogen, or air. It is maintained by a plasma-supporting structure (resonant cavity), which is a hollow metal container that allows a standing electromagnetic wave to be established within it or along it. Because the standing wave is at microwave frequencies (usually 2450 MHz), the cavity size is on the order of several centimeters [8].

To generate the standing wave, microwave energy is sent into the cavity by means of a circuit loop, circuit short, or antenna connected to a microwave power supply via a coaxial cable or waveguide. The plasma gas is then passed through the cavity and ionized, with its energy coupled to the gaseous ions to produce the discharge. Transverse electric and magnetic waves enable such a configuration to exist [8].

Aqueous Sample Introduction. Historically, sample introduction into the MIP has been limited to gaseous samples by gas chromatography or gaseous introduction via chemical hydration [7]. Research in the area of introducing aqueous samples directly into the MIP has been limited because the typical Beenakker cavity is not capable of completing the atomization cycle (Figure 1). The atomization cycle includes nebulization, desolvation, vaporization, atomization, and excitation of the analyte. In order to complete this cycle, thus promoting excitation, the MIP must possess a high energy density and a sufficient kinetic temperature to promote the above processes; this does not occur with classical Beenakker cavities. For the MIP to take its place in the area of atomic spectrometry, problems associated with the introduction of liquid samples must be overcome.

One of the most attractive aspects of liquid sample introduction is its relative simplicity and reliability, coupled with the fact that a sample dissolution step is often necessary to produce suitable sampling statistics [10-11].

Direct sample introduction into the MIP thus represents a renaissance

in MIP-AES technology. Literature on the direct introduction of aqueous samples into the MIP has been separated into two areas by researchers: high power and low power [12] (high power MIPs are those maintained above 150 W). Several reviews have appeared on the use of the MIP for atomic spectrometry and have included sample introduction techniques [7-9].

Beenakker et al. [13] introduced aqueous metal samples into the Ar plasma without desolvation at a sample uptake rate of 1.7 mL/min. A 150-W plasma was used to sustain the plasma. Satisfactory AES performance was obtained, but the use of the wet aerosol decreased the sensitivity by a factor of 2 to 10, depending on the element studied.

Hass and Caruso were successful in introducing 0.81 mL/min of aqueous solution into a 500-W plasma for the study of metal ions in synthetic ocean water using a total Ar flow of 450 mL/min. Nebulizers included both concentric and frit. Detection limits were comparable to the ICP. The authors reported severe microwave leakage using their 500-W Ar plasma [14].

In a similar study, Ng and Shen [15] used a 105-115 W Ar plasma to introduce synthetic ocean water at a MAK nebulization uptake rate of 1.4 mL/min. The total Ar flow used in the study was reported at 537 mL/min. Detection limits compared favorably with the work of Beenakker.

In all but one report, reviewed references used Ar as the plasma gas for direct nebulization of aqueous metals. An Ar plasma is easy to ignite and to sustain when compared to He using the typical Beenakker cavity (He has a greater electrical resistivity, heat capacity, and thermal conductivity). However, Beenakker was able to sustain a He plasma while introducing aqueous samples by using a low-flow nebulizer [16]. Unfortunately, the presence of larger droplets degraded signal stability.

The ability to sustain a He plasma while introducing aqueous samples is of great importance for the following reasons: (1) the background continuum in the He plasma is about an order of magnitude weaker than that of Ar [17]; (2) He has greater optical transparency at shorter wavelengths than Ar [17]; and (3) the high excitation energies of a He plasma enable the production of analyte emission from states having energies in excess of 16 eV [18]. Simply stated, He has a higher excitation energy than Ar, which allows for the detection of every element on the periodic table. In addition, there are fewer He lines to produce potential spectral interferences.

Supercritical Fluid Introduction. A chromatographic technique that has gained popularity in the analytical community in the past few years is supercritical fluid chromatography (SFC). This technique requires that a gas such as CO_2 be elevated to its supercritical state and used as a

mobile phase in chromatography. A great advantage of this technique over gas chromatography and liquid chromatography is the ability of SFC to separate compounds containing highly polar functional groups. For instance, SFC can be used to determine the concentrations of halogenated pesticides in aqueous samples. It also can be used in many applications where derivatization is not possible due to sample complexity, steric hindrance, or other reasons. However, these types of compounds often require the addition of polar organic solvents (modifying agents).

Although the technique of SFC gives the analyst a new ability to separate polar nonmetal-containing compounds, the detectors first applied to SFC were not well suited for this separation technique. The criteria for a chromatographic detector are that the method used be selective and unaffected by the introduction of the supercritical fluid into the detector. Flame ionization detectors [19-24] were studied first but failed both criteria. They were not very selective to the nonmetal species separated and were not able to be used when modifying agents were employed.

A portion of this work has been directed toward the examination of the He HEMIP as an element-selective detector for nonmetals. The He HEMIP is able to fulfill both criteria for an SFC detector. Unlike the flame-based detectors, the He plasma tolerates the use of modifiers. The He plasma also is unaffected by the introduction of CO_2 into the discharge. Ar-based plasmas experience a degradation in the excitation temperature and the electron number density when CO_2 is added to the plasma [25]. Most importantly, the He plasma is able to promote the nonmetal atoms in the discharge to an excited state in order that atomic emission may occur. The He HEMIP is selective to nonmetals (CI, P, and S) as well as metals.

7. Experimental Considerations

The experimental conditions listed in this section pertain to two individual microwave plasma setups. One MIP was configured for the determination of aqueous samples while the second was configured as an element-specific detector for supercritical fluid chromatography (SFC).

Reagents. All chemicals used were analytical reagent grade. Water was distilled and deionized. Stock solutions of all aqueous metals were purchased as 1000 ppm (Buck Scientific, Inc.) or prepared following standard procedures [26]. Iron for organic solvent determinations was prepared by dissolving ferrocene in xylenes to obtain a 1000-ppm solution. Volumetric dilutions of these solutions were performed to obtain desired concentrations.

The plasma gas used was Airco analytical-grade He. Carbon dioxide for the mobile phase of the SFC was purchased as chromatographic grade (Scott Specialty Gases, PA) with a He headspace of 1500 psi and dip tube [27,32]. All samples were prefiltered via 0.5 μ m teflon filters (Fisher Scientific, NC).

AES & AFS Optical System. The atomic emission and atomic fluorescence systems used in this work are shown in Figures 2 and 3, respectively. Table 1 lists all optical, electrical, and gas handling equipment, along with their manufacturers.

Emission from the plasma was focused onto the entrance slit of the monochromator (0.25-m monochromator for AFS and AES of metals; 0.35-m monochromator for nonmetal determinations) using a f/3 lens for one-to-one imaging. Current signals from the photomultiplier tube were converted to voltage using a current-to-voltage converter, in order to make the final signal compatible with the input of the analog-to-digital converter (ADALAB, Pittsburgh, PA) on the Apple *l*/e computer.

Two different viewing geometries were used for collection of data with the He-HEMIP (Figure 4). Studies of metal atomic emission and atomic fluorescence were conducted with the plasma in the radial position (side-on), unless otherwise stated. An axial observation position (endon) was used for all nonmetal studies.

To use the emission lines below 190 nm, the monochromator and optical path must be evacuated and purged with an inert gas. The laboratoryconstructed purge system is shown in Figure 5. The purge system consists of Pyrex glass and rubber o-rings connected to an aluminum plate attached to the entrance slits of the monochromator. Ar was used as the purge gas.

SFC Optical System. The atomic emission data obtained for this work was performed in the radial or axial mode. These two modes are shown

in Figures 6 and 7, respectively. Table 2 lists all of the optical, electrical, and gas handling equipment with their manufacturers for SFC-MIP-AES.

Emission from the plasma was focused onto the entrance slit of a 0.25m monochromator using a f/3 suprasil lens to obtain one-to-one imaging. Current signals resulting from analyte emission were collected using a R955 Hamamatsu PMT and converted to voltage via a PTI MOD 01-512 model current-to-voltage converter. The resulting voltage was sent to a strip chart recorder.

Two different geometries of viewing were employed for collection of data with the SFC-HEMIP system (Figures 6 and 7). Unless otherwise stated, experiments with gas were carried out in the axial mode.

SFC Instrumentation. The CO₂ was prefiltered through a 0.5- μ m stainless steel frit filter prior to the filling of the 200-mL capacity SFC pump (Suprex SFC/200A). DeltaBond phenyl and DeltaBond cyano columns (Keystone Scientific, PA) used in these studies had an inner diameter of 1 mm and were 10 cm long with 5- μ m particles.

Injections were performed with a high-performance chromatography Rheodyne Model 7250 valve (Cotati, CA) equipped with a 0.5- μ L injection rotor. To eliminate band broadening at the injector point, the head of the column was placed as close as possible to the injection rotor. All injections were performed in a splitless manner. The entire injection apparatus was mounted outside the oven to allow injections to be made at room temperature.

To detect elements at atmospheric pressure, a tapered restrictor was employed [29]. The restrictor was fashioned in-house and pulled from 50- μ m fused silica to an orifice approximately 10 μ m. The restrictor was inserted into the plasma torch through a septum and placed either 1 cm directly below the plasma plume (Figure 8) or inserted into the sidearm of the torch (Figure 9).

Microwave Cavity. The microwave cavity chosen for this work is diagrammed in Figure 10. The design is a modified version of that described by Boss, Matus, and Riddle [30]. Modifications included a change in size and reconstruction of the probe translation stage. The cylindrical cavity was machined from a 0.78-in-thick sheet of oxygen-free high conductivity copper (OFHC). The internal diameter and depth of the cavity were fixed at 89.1 mm and 10 mm, respectively. A 6-mm diameter quartz rod extended into the cavity from the side wall. Movement of the generator frequency, 2.45 GHz. A brass tuning rod extended into the cavity from the side wall opposite the quartz rod. This brass tuning rod was initially employed for frequency tuning. However, it was determined later that the brass rod was ineffective in tuning the cavity and it was removed. A removable cavity lid was machined from a 0.197-in OFHC sheet. An 8-mm hole was drilled into the center of the lid to facilitate insertion of the plasma discharge tube. A 5 X 40 mm radial slot was milled along the coordinate axes of the circular lid. This allowed lateral movement of the capacitive antenna coupling probe.

The capacitive antenna coupling probe was used for proper coupling between the generator and the load (plasma). The capacitance of the probe was adjusted by varying the surface area at the end of the probe. Coupling was further adjusted by sliding the probe along the radial face of the cavity to match the capacitive and inductive coupling power to the impedance of the generator.

Antenna probes were fashioned from UG 58 A/U type N coaxial connectors, as described by Boss [30,31]. A 10-gauge copper wire was soldered to the center post of the N connector. A 16-mm diameter metal disk was soldered to the end of the copper wire. Sheet metal shims were used to set the probe penetration depth at 96%. The probe translation mechanism was constructed from brass.

Microwave Torch. A centered plasma was produced using a tangential torch similar to those currently employed in ICP-AES [32]. The torch used in all studies consisted of two concentric quartz tubes (see Figure 11). For all experiments, the He flow was introduced tangentially into the outer tube along with the analyte aerosol from the nebulizer. This method of introduction allowed a homogeneous mixture to form between the aerosol and plasma gas before ignition. The plasma uniformly filled the discharge tube and extended beyond the face plate of the cavity. Initially, aqueous samples were to be introduced through the center tube; however, the back pressure created by the small center tube made this impossible. Because of the back pressure problem, the center tube was constricted using sealed tygon tubing to prevent leakage of the He plasma gas.

Plasma Ignition and Operation. In operation, the He-HEMIP is selfigniting. On those occasions when the plasma did not ignite, the following procedure was employed. The circular probe was placed near the center of the cavity. The plasma gas was allowed to flow (1-2 L/min) through the side inlet of the torch. Microwave power was applied to the cavity, up to 150 W maximum. The quartz tuning rod was adjusted to obtain a minimum reflected power. The plasma was ignited with a small tungsten wire attached to a rubber policeman; inductive heating of the wire caused a seeding of the He gas. If the plasma did not ignite, the probe was moved toward the walls of the cavity, and the above process was repeated. Once the plasma ignited, the reflected power was minimized by adjustments of the antenna probe and quartz rod. The flow was reduced to 1 L/min to sustain the plasma by the nebulizer alone. Aqueous Sample Introduction. Sample solutions were introduced into the plasma with a typical ICP-AES pneumatic nebulizer/Scott spray chamber system. The optimum operational parameters used for all studies involving aqueous sample introduction are shown in Table 3. A diagram of the sample introduction system is shown in Figure 12. The nebulizer, while operated at a flow rate of 1 L/min of He gas, the aspirated sample solution at a rate of 0.46 mL/min. The resulting aerosol passed through the spray chamber enroute to the He-HEMIP. All liquid sample introduction was conducted without the use of a desolvation chamber, except for the determination of CI (see Chapter 6).

The desolvation system is shown in Figure 13 and was a modified version of that used by Galante et al. [33]. The system consisted of a heated Pyrex tube to dry the aerosol and a 6-in-long condenser with a spiral condensing tube (1 cm i.d. X 28 cm long) to remove much of the water vapor. The desolvation tube was wrapped in heating tape to maintain a tube temperature of 150°C. The wrapped tube was then encased in an insulating outer Pyrex tube (2 in i.d.), which also served to hold the heating tape in place. The condenser was maintained at a constant temperature of -10° C by a refrigerated circulating bath. A solution of automotive antifreeze (50% v/v) was used as the coolant.

The entire desolvation system was connected by 12/5 ball joints for experimental simplicity. A 25-mL conical flask was used for waste collection.

Cooled Spray Chamber Introduction. A cooled spray chamber and condenser system was fabricated to examine the effect of solvent loading on the microwave plasma. The system is illustrated in Figure 14. A cooling unit maintained the temperature of the system at 0.1° C using a 50% v/v mixture of ethylene glycol in water.

SFC Sample Introduction. Samples were introduced into the plasma one of three ways: (1) aqueous nebulization, (2) supercritical fluid effluent through the central portion of the microwave torch, or (3) supercritical fluid effluent through the sidearm of the microwave torch. The operational parameters for the SFC studies are listed in Table 4.

Sample introduction via supercritical fluid effluent through the central portion of the microwave torch was done with the tapered restrictor (8 mm I.D.) positioned in the central tube of the torch and placed approximately 1 cm below the plasma plume (Figure 8). This arrangement proved to be somewhat troublesome, since the restrictor would occasionally "freeze" when the CO_2 decompressed, thus causing detector "spiking." More importantly, great caution had to be exercised to prevent the plasma from arcing back on the restrictor. If arcing had occurred, the result would have been fusion of the tip. In other work Hieftje et al. [33] also noted the fusion phenomenon to occur. In addition, this central arrangement required approximately twice the Ar flow (as compared to sidearm introduction) to maintain a centered plasma within the torch.

The final sample introduction method placed the restrictor in the sidearm of the torch where the effluent gas was premixed with the plasma support gas (Figure 9). This arrangement did not result in restrictor "freezing," because the plasma gas flow was at a right angle (Figure 15) to the restrictor tip thus preventing the nucleation of CO_2 as it decompressed. Arcing by the plasma did not occur, eliminating the possibility of the restrictor being fused. An additional benefit of this type of introduction was the premixing of the effluent with the plasma gas prior to encountering the plasma discharge. This mixing permitted the plasma gas flow rate to be reduced, resulting in a more stable plasma discharge.

Plasma Behaviors and Features. Using the He-HEMIP, the He plasma was stable over all operating periods used to gather data. The time periods varied from 30 min to 10 hours of plasma operation. Further tuning was not needed during these time periods. The temperature of the cavity did not exceed 35°C.

After ignition, the tangentially formed plasma appeared red in color. The afterglow was colored blue. Once aqueous samples were introduced, the intensity of the red color increased. When organic solvents were aspirated, a large greenish-blue afterglow formed, apparently resulting from the combustion of organic species.

Limits of Detection. The limits of detection, C_L , all were calculated in accordance with IUPAC guidelines [34-36]. The limit of detection is defined as a value twice the standard deviation of the noise level divided by analytical sensitivity. The standard deviation of the noise was calculated from 20 consecutive background readings. The analytical sensitivities were calculated from the working curves of the element, which spanned at least three orders of concentrative magnitude. The k value used for all calculations was 2 rather than 3. This lower k value was used only for comparative purposes with the existing literature.

Minimal Detectable Quantity. The term minimal detectable quantity (MDQ) is related to the smallest detectable sample that can be read above the noise level at an 80 percent confidence level. For chromatography it has been almost universally, yet arbitrarily, decided that the smallest readable response above noise should be a factor of two. One method [37] of calculating the MDQ is defined by dividing the sensitivity into twice the noise level. The equation for calculating the MDQ is: MDQ = 2*N/S, where N is the noise level and S is the sensitivity.

Data Presentation. The data presented in this report are shown as background-corrected values. For AES and AFS profiles, the background signal was subtracted by the computer from the analyte signals. Working curve and inter-element effect plots were similarly treated.

Data sets for temperature and electron number density studies represent an average of at least five repeated experiments.

Data Collection of Chromatograms. The chromatograms in the radial mode and slightly off center for the axial mode. The radial mode allowed improved selectivity [38] due to a more stable plasma viewing zone, while the axial mode allowed greater sensitivity. The sample chromatograms were collected with the use of a strip chart recorder.

Electronic Excitation Temperature. The electronic excitation temperature of the He-HEMIP was determined from the spectral emission intensities of He and Fe as thermometric species [39]. A Fe solution of 1000 ppm was introduced into the plasma, and the relative intensities of the Fe atom lines in the spectral region of 370-390 nm were mea ured. He atom lines in the region of 380-502 nm also were measured. The excitation temperature was determined from the following equation [40]:

$$\ln ((I_{pq}/g_p)/(A_{pq} v_{pq})) = E_p/(kT)$$

where Ipq = measured relative intensity

g_p = statistical weight of the upper state

A_{pq} = transition probability

v_{pq} = frequency of the pq transition

E_p = energy of the upper state

k = Boltzmann constant

T = electronic excitation temperature

A plot of In $((I_{pq}/g_p)/(A_{pq} v_{pq}))$ vs. E_p yields a straight line with a slope inversely proportional to the excitation temperature [-1/(kT)]. Constants for all Fe and He lines used for temperature measurements are listed in Tables 5 and 6, respectively.

Ionization Temperature. The spatial ionization temperature, T_{ion} , was determined from the relative emission intensities of the Cd atom (228.8 nm) and Cd ion (226.5 nm) lines using the same position and resolution as the measurements for the excitation temperature and was calculated using the following Saha-Eggert relationship [40]:

 $(I_{i}/I_{a}) = \frac{4.83^{*}10^{15}}{n_{e}} (g_{p}A_{pq}/\lambda_{pq})_{i} (\lambda_{pq}/g_{p}A_{pq})_{a} (\lambda_{pq}/g_{p}A_{pq})_{a} (\lambda_{pq}/g_{p}A_{pq})_{a}$

where I_i = intensity of the ion line

l_a = intensity of the atom line

g_p = statistical weight of the upper transition

A_{pq} = transition probability of the upper transition

 λ_{pq} = wavelength

ne- = electron number density

T = ionization temperature

E_i = ionization energy of the species

 E_p = excitation energy of the upper transition

The Saha equation can be combined with the Boltzmann equation to relate intensities of line emission from the two charged species. While this equation has no exact solution for T, it can be solved numerically using a computer program written in BASIC for this work.

Electron Number Density. Three methods were used for the determination of the electron number density in the He-HEMIP:

- measurement of the Stark broadening of the H-beta Balmer line as described by Griem [41],
- the He line method also described by Griem [41], and
- the Saha-Eggert relationship method [40].

The determination of the electron number density by full width at half height (FWHH) of the Stark broadening of the H-beta Balmer line (486.1 nm) tends to be the most common method. This line offers several particular advantages [39,41]:

- The range of half widths anticipated (approximately 1.0 to 5.0 A) and the relative intensities are large enough to allow accurate measurements at various observation heights in the plasma.
- Extensive Stark data are available for complete line profiles encompassing a broad range of electron number density values and temperatures.
- Stark broadening is strongly influenced by an electric field, making it a sensitive measurement.
- The line is relatively temperature-independent, with little variation over tens of thousands of degrees.
- It is relatively free from spectral interferences by plasma components.
- Greater accuracy is generally associated with Stark calculations for the H beta line than for other atomic H lines [41].

After deconvolution of the line profile to account for instrumental, collisional, and Doppler broadening, the electron number density can be related to the FWHH by the foillowiung equation

 $n_e = C(n_e, T)(\lambda_s)^{3/2}$

where $C(n_{\text{e}},T)$ is a function of electron density and temperature, and

 λ_s = FWHH of the hydrogen beta line.

C(n_e,T) values are tabulated in Griem's book for different values of electron temperature and electron number density [41].

Experimentally, a spectral scan of the H beta line at 486.1 nm is all that is necessary for the electron number density determination. Broadening from the effects mentioned above is ordinarily small and is usually neglected. Calculations were performed using a BASIC computer program.

The He atom 388.9 nm line also was employed for the effective electron number density determination. Experimentally, this method follows that of the hydrogen-beta measurement. In contrast to the considerable amount of experimental data for H lines, there is very little laboratory material available for Stark-broadened lines from He, the next oneelectron sequence [41]. However, in view of the successes with sources in the case of H lines, this should not be considered a drawback.

The electron number density also can be determined from the Saha-Eggert ionization relationship [40]. This method requires the determination of the relative emission line intensities from successive ionization stages, generally for the neutral atoms and ionized species. When these intensities are combined with the known equilibrium relationships among the emission spectra, temperatures, and the Saha-Eggart expression, the electron number density can be obtained. Electron densities so obtained are dependent upon the assumption that the plasma is in local thermal equilibrium, which may not be the case.

Two elements with neutral atom ionization potentials, Cd and Ca, were selected for atom/ion emission line intensity measurements. These elements were selected primarily for the following reasons:

- availability of transition probability data for atom and ion lines,
- closely matched excitation energies for the atom and ion pairs so that the exponential temperature effect would be minimized,
- freedom from spectral interferences,
- freedom from physical and chemical interferences, and
- wavelength proximity so that the necessity of calibrating the detector response with respect to the wavelength could be circumvented [29,40].

The wavelengths and their excitation energies, statistical weights, and transition probability data are given in Table 7.

8. Physical Measurements of the He HEMIP

Measurements of physical parameters play an important role in the development of any atomization source for spectrometric analysis. These measurements provide the information necessary for the determination of plasma properties such as electron number densities, particle energies, distribution temperatures, and gas-flow dynamics. In turn, these properties are used as a basis for describing fundamental processes or mechanisms related to interactions between analyte species (atoms, ions, and molecules) and plasma species (electrons, atoms, ions, and molecules).

In the strictest sense, a temperature may only be defined for systems in thermodynamic equilibrium, TE. The existence of such a state implies the fulfillment of several criteria [42]:

- The velocity distribution function of all particles behaves according to Maxwell's equations.
- The excited states are populated according to the Boltzmann distribution.
- The distribution of the atom-ion equilibria behaves according to the Saha-Eggert relationship.
- The distribution of molecules and their dissociation products behaves according to the mass action law of Guldberg and Wagge.
- The distribution of electromagnetic radiation in the plasma must be in agreement with Planck's law.

Simply stated, a system is in TE if it can be described by a single temperature. Temperature in this sense is a descriptive term that relates the magnitude of each type of energy associated with the plasma. In an atomic gas, one recognizes several temperatures [42]:

- electron temperature, which is determined by the kinetic energy of electrons
- gas temperature, which is defined by the kinetic energy of neutral atoms
- excitation temperature, which describes the populations of the various energy levels
- ionization temperature, which governs ionization equilibria

Summarizing, in an atomic gas one recognizes translation, excitation, and ionization temperatures. In molecular gases, temperatures assigned to dissociation equilibria and to rotational and vibrational states of the molecules should be added. In a plasma discharge, the numerical differences among the temperatures depend mainly on the strength of the applied electric field (E) and on the gas pressure (P) (specifically on the ratio P/E). At reduced pressure and/or in a strong electric field, the electron temperature is high, whereas the gas temperature is low. As the electric field is attenuated and/or the pressure is raised, the electron temperature decreases and the gas temperature rises. All temperatures become equal when the system has reached a state of thermal equilibrium.

Unfortunately, no laboratory plasma exists in a state of complete thermal equilibrium [39], because only the radiation field in a blackbody source follows Planck's distribution. The flame or plasma cannot be described by Planck's function because it is often transparent over large wavelength regions. Thus, radiation equilibria may only exist in the central portion of the flame or plasma source and at the wavelength center of strong resonance lines. This lack of radiative equilibrium produces a depopulation of the upper energy levels with respect to the lower ones, because the atoms and molecules are de-excited by emission of radiation and inelastic collisions. Therefore de-excitation, since self absorption is relatively small, occurs only by inelastic collisions. Nonetheless, the extent of this depopulation effect is small for plasma collisional induced transitions, and they are more frequent than radiative ones.

In cases for which the Planck function is not valid, all other relationships can remain locally valid. Plasmas satisfying these other relations at any spatial point, and at any instance in time, are said to be in local thermal equilibrium (LTE). Generally, laboratory plasmas and flames are described qualitatively and quantitatively in terms of their deviation from LTE. At atmospheric pressure, LTE would be expected to prevail in flames and plasmas because of their high particle density and collision frequency.

To evaluate whether a plasma is in LTE or non-LTE, the most important criteria are temperature and electron number density measurements. These measurements can provide the spectroscopist with insight on the reaction mechanisms occurring in the plasma. The experimental values of temperature and electron number density are directly related to the extent of departure from LTE and are extremely helpful in characterizing the volumes of different species for analyte excitation.

In this chapter, diagnostic studies of the He-HEMIP are presented. Diagnostic measurements included excitation temperatures with the use of aqueous and organic nebulized thermometric species, electron number densities, and ionization temperatures for the plasma.

Experimental

The He-HEMIP was viewed in the radial mode for all measurements reported in this chapter, unless otherwise stated. A 1.0-mm circular aperture was positioned in front of the entrance slits of the monoch-

romator upon which the radiation from the He-HEMIP was focused. A 25- μ m slit width was used, providing a spectral bandpass of 1.5 A, unless otherwise stated. The He-HEMIP was translated in the X, Y, and/or Z direction via translation stages (Newport Research Corporation).

All reported data are background subtracted. Data sets for temperature and electron number density studies represent an average of at least five repeated experiments. Abel inversions were not used for radial spatial information.

Results and Discussion

Excitation Temperature. The excitation temperatures were determined using several thermometric species (He with and without water, aqueous Fe, and organic Fe) and are tabulated in Table 8. The temperatures varied from 5100 K (organic Fe nebulization) to 6100 K (radiance of He lines). It is interesting to note that the excitation temperature with the nebulization of water alone into the plasma, and the introduction of Fe as the thermometric species into the plasma, resulted in values that were not statistically different. The random error for the estimation of the excitation temperatures is less than 90 K. The decrease in the excitation temperature for organic nebulization into the plasma, although not experimentally confirmed, can be attributed to the absorption of energy by molecular species (C2, CN, CO, etc.) from the plasma. This type of phenomenon was also found to occur in the ICP, in which the temperature was lower for an organic aerosol than for an aqueous aerosol at a fixed power and observation height [42]. According to Blades, the molecular carbon species adsorb energy from the plasma and affect the thermal conductivity of the plasma during the process of dissociation. It should be noted that this effect of lowering the excitation temperature by the nebulization of organic liquids into the He-HEMIP is smaller than that found for a 1.75-kW ICP, where a reduction in the excitation temperature by the nebulization of organics was found to be approximately 1500 K [31].

A comparison of the excitation temperature of the He-HEMIP used for this work and that of other plasma sources is shown in Table 9. The results of this comparison show that the excitation temperature of the He-HEMIP is higher. This increased excitation temperature is an indication of the robustness of the He-HEMIP and is also an indication that this plasma source may be closer to LTE than any other previously tested microwave cavity.

Ionization Temperature. Spatially integrated intensities of the Cd emission atom (228.8 nm) and Cd ion (226.5 nm) lines were measured for the determination of the ionization temperature. Results of the ion/atom line ratios were tabulated and substituted into the Saha-Eggert relationship and T_{ion} calculated using an iterative process. T_{ion} as deter-

mined by the Saha-Eggert equation was 6200 K.

Electron Number Density. Figure 16 depicts the electron number density (ne-)profile across the face of the cavity, with and without direct nebulization of water at 0.46 mL/min, as determined by the half width from the broadening of the H-beta Balmer line at 486.1 nm. These number density determinations are at best an approximation because of the resolution of the monochromator employed. However, these relative values are useful in illustrating an ne- trend with the introduction of samples into the plasma. The electron number density profile was demonstrated to be essentially flat with increases at 0.5mm-1mm without the nebulization of water. With the introduction of water by nebulization, the number density profile continues to increase above 0.5 mm, and peaks at 1 mm. This increase in the number density with water nebulization may be the result of the ionization of H and O species in the plasma. Since the ionization energies of H and O are about 2 eV below those of Ar, their degree of ionization at 6000 K would be expected to be about 5 times higher than that of Ar; thus an increase in the electron density would be expected when water is present [43-45].

Although the plasma visually appeared symmetrical, the number density profile suggested that the plasma is asymmetrical. This asymmetry is attributed to errors in the flow pattern of the laboratory-constructed torch, which may have been creating a hot spot in the plasma. To confirm this hypothesis, plots of analyte emission vs. observation heights for a variety of elements were constructed. In Figure 17, a representative plasma emission profile is shown. In this profile, the existence of a maxima in relative emission intensity was observed at 0.5mm-1.0 mm in the plasma. This observation was the same as observed with the electron number density profile, suggesting the creation of a hot spot in the plasma.

The average n^{e-} using the helium line at 388.7 nm was determined to be 1.4×10^{14} e⁻/cc and 2.5×10^{15} e⁻/cc employing the Saha-Eggart relationship.

Summary

The He high efficiency MIP approaches local thermal equilibrium (LTE). Evidence of this is based on the fact that the excitation temperature is approximately equal (within statistical error) to that of the ionization temperature. Unfortunately, without the knowledge of plasma gas temperatures, electron temperatures, and accurate electron number densities, the existence of LTE cannot be conclusively confirmed or rejected. The temperatures determined in this work and the ability to aspirate organic samples directly into the He-HEMIP suggest that this source is the most robust of the MIPs used in the analytical community to date.

9. Determination of Aqueous Metals by MIP-AES and MIP-AFS

Over the past ten years, few reports have appeared on the use of direct nebulization of aqueous samples for the determination of metals and nonmetals in the H microwave induced plasma (MIP) [46-48]. One of the reasons for this exiguity of studies with direct nebulization into the He MIP is that the original Beenakker cavity does not afford sufficient desolvation and excitation of liquid samples. However, direct nebulization of metal and nonmetal solutions into the helium plasma has been achieved using the Caruso type "two-stub internally tuned" cavity [49]. In several reports employing this design, applied power levels from 500 W to several kilowatts and plasma gas flow rates of up to 50 L/min were required to sustain an analytically useful discharge [39, 40, 42]. Detection limits employing UV-visible lines were obtained at and below 1 ppm.

The use of large power levels and gas flow rates clearly diminishes the low power advantages of the MIP (i.e., simplicity, versatility, and low cost). Furthermore, the use of high power levels requires cooling (due to excessive heating of the cavity) and the utilization of special discharge tubes at the expense of increased background emission, microwave leakage, and cost.

This chapter focuses on the use of a He high efficiency microwave induced plasma (He-HEMIP) for the determination of metals using direct nebulization of aqueous samples. The cavity was a modification of the Beenakker design by Matus et al. and operated at a power transfer efficiency of 95% [30,31]. In previous work with this cavity using Ar as the plasma gas, Long and Perkins were able to sustain a centered and stable discharge with direct nebulization of aqueous samples at 36 W of power and 1 L/min gas flow [51]. The system also has been characterized for AES and AFS studies using Ar as the plasma gas [52]. Furthermore, the HEMIP tends to be more amenable to the introduction of directly nebulized aqueous and organic solutions, than are the Beenakker cavities introduced to date [50, 53].

Metal species were determined in the UV-visible region using atomic emission and atomic fluorescence spectrometry. No desolvation apparatus was employed. Measurements of excitation temperatures, electron number densities, detection limits for AES and AFS, interelement effects, linear ranges, plasma profiles, and sample uptake studies are discussed.

Experimental

A 25- μ m slit width providing a spectral band pass of 1.5 A was used unless otherwise stated. All operational conditions used were described in Chapter 3. Studies of metal atomic emission and atomic fluorescence were conducted with the plasma in the radial position (side-on), unless otherwise stated.

Results and Discussion

Effect of Sample Uptake Rate. Due to changes in solution viscosities, the effect of sample uptake rate on atomic spectrometric signals is a very important parameter in system optimization. The effect of varying the aqueous solution uptake rate on the Ca (II) emission signal at 393.6 nm is shown in Figure 18 for a 50 ppm solution. The sample uptake rate was controlled by a peristaltic pump (Cole Palmer, Chicago, IL).

Little variation in the emission signal appeared at a solution uptake rate of 0.17 mL/min up to 0.60 mL/min. Above 0.60 mL/min the signal rises by 17% and levels off between 0.80 mL/min and 1.0 mL/min. An analysis of these data suggests that there is no advantage in the use of a peristaltic pump to control the natural uptake rate of this system.

Organic Nebulization. It was determined in this work that the He HEMIP can operate continuously during direct nebulization of organic samples. Solutions of up to 1000 ppm ferrocene in xylene were aspirated directly into the plasma. Carbon deposits on the torch wall were minimal and did not disturb the plasma. The ability of the plasma to support organic nebulization at 0.46 mL/min without the extinction of the discharge by the organic aerosol indicates the He HEMIP's robustness (other MIP sources that have been used for chromatographic detection must be vented, cooled, or heated to prevent the extinguishing of the plasma discharge) [54].

Profiles. Figure 19 depicts intensity profile for AES using the optimized conditions outlined in Chapter 3 and a 6 mm i.d. discharge tube. For all AES studies of metal determinations, the optimum height was 2-3 mm above the top of the cavity. The optimum observation height for AFS measurements shifted to 8 mm above the top of the cavity. This shift in the AFS maximum intensity above that of the AES observation zone is consistent with earlier studies performed with the Ar HEMIP [52]. In this higher region of the plasma, there exists a decrease in plasma flicker and spectral background. In addition, the analyte species have experienced a longer residence time, resulting in a more complete molecular dissociation of the original species.

Linearity. The linearity ranges obtained for metal determinations using MIP-AES (radial mode) typically span four to five orders of concentrative magnitude. However, linear ranges for AFS span five and one-half orders of magnitude.

Limits of Detection. The limits of detection for metals using the He HEMIP are listed in Tables 10 and 11. These values were obtained for
AES and AFS using direct sample introduction via a Meinhard nebulizer and were calculated according to the IUPAC guidelines [36]. It should be noted that a k value of 2 was used instead of the prescribed value of 3. This substitution was done so that the experimental detection limits could be compared to the existing limits of detection for MIP and ICP systems.

The superior atomization characteristics of the He HEMIP are compared to the Ar HEMIP in Table 10. In the first column of this table, the detection limits of the MIP are shown for metal determinations using Ar and He as the plasma gas. The Ar data are from previous research with this cavity [51]. In all cases, except for Na, the use of He resulted in a substantial decrease (factor of 8 to 100) in the detection limit value. This trend was also observed for AFS data (Table 11), where the use of He for hollow cathode lamp (HCL) MIP-AFS resulted in a decrease in the detection limit from a factor of 4 up to 50. It should be noted that the current He HEMIP limits of detection are not statistically different from that published for HCL-ICP-AFS [55].

Inter-element Effects. The effect of the presence of an easily ionized element (EIE) on the Ca (I) atomic emission and fluorescence signal at 422.7 nm is shown in Figures 20 and 21. Using the conditions outlined in Chapter 3 and a 10-ppm solution, no discernible effect of the Na interferent was observed to occur for AFS. However, a slight enhancement was observed for AES while introducing a 1000-ppm solution of the interferent. The EIE effect in this He HEMIP was significantly less than that observed using the Ar HEMIP, where an increase in signal of 300% was observed for AES and 100% for AFS with a 1000-ppm Na solution.

Importantly, as shown in Figures 22 and 23, the classical phosphate interference was not observed for AES or AFS. This suggests that the He HEMIP is a robust atom cell that is able efficiently to cause complete dissociation of gaseous refractory molecules into free vapor phase atoms.

Summary

In this work, the advantages of using He versus Ar as the plasma gas for the high efficiency MIP with direct aqueous sample introduction for metal determination by AES and AFS have been demonstrated. Not only were detection limits superior to that of Ar HEMIP, but the values obtained for He HEMIP-AFS were equivalent to those of HCL-ICP-AFS. The robustness of the He HEMIP over the Ar HEMIP has been shown by the larger excitation temperatures, electron number densities, and freedom from inter-element effects.

10. Determination of Nonmetals by MIP-AES

Several well known methods exist for the determination of nonmetals in aqueous solution. These methods are gravimetric, titrimetric, and electrochemical (i.e., potentiometric titration and ion selective electrodes).

Gravimetric methods for the determination of Cl, Br, I, S, F, and P have been extensively studied [56]. Cl, Br, and I are determined by precipitation of their silver salts: AgCl, AgBr, and Agl, respectively. The S in sulfides, sulfites, thiosulfates, and tetrathionates is determined by oxidizing the S to $SO_4^{2^-}$ and then precipitating BaSO₄. F is often determined by precipitation as CaF_2 . and PbCIF. $PO_4^{3^-}$ is determined by precipitation as MgNH₄PO₄· 6H₂O [57].

With proper technique and utmost care, gravimetric determinations have great accuracy. For example, if the analyte of interest is a major constituent (>1% of the sample), accuracy of a few parts per thousand can be expected if the sample is not too complex. If the analyte is present in minor or trace levels (<1%), a gravimetric method is not generally employed [57].

In general, gravimetric methods are not specific and are time consuming [58]. Moreover, potential problems of coprecipitation, postprecipitation, improper technique, or incomplete reaction may lead to significant decreases in accuracy.

Titration methods are considerably more rapid than gravimetric methods because no lengthy drying (and/or ignition) and weighing steps are required.

Perhaps the most classical of all titrations is the determination of Cl with a standard solution of AgNO₃. [59]. Br, I, and $SO_4^{2^-}$ can also be determined with greater accuracy than is possible using gravimetric methods. Limitations of this method include the lack of suitable indicators, interferences from species that react with the titrant, and/or poor technique [56]. As with gravimetric methods, titrimetry is not well suited for ultratrace analysis [56].

The method of potentiometric titrimetry offers a number of advantages. Perhaps the primary advantage of potentiometric titrations is that (with the addition of classical titration procedures) they generally offer a large increase in accuracy and precision; \pm 0.1% levels are not uncommon [56]. Potentiometric end-point detection is applicable to Cl, Br, and I. There are, however, certain disadvantages to potentiometric titrations: the increase in analysis time and operator attention required and the difficulties associated with the preparation, standardization, and storage of standard titrant solutions [59].

lon-selective electrodes are especially useful for the determination of Cl, S₂, Br, I, and F in aqueous solution [60]. The working range is quite large, generally from four to six orders of magnitude. Electrodes function well in colored or turbid samples. Analysis times are reasonably short, with equilibrium being reached in less than 1 min., but in some cases, usually in very dilute solutions, slow electrode response may require 15 min. to an hour for equilibrium. The equipment is simple and inexpensive. The method is nondestructive. The greatest disadvantage of ion-selective electrodes is that they are subject to rather large numbers of interferences. Ion-selective electrodes are not ultratrace level sensors; some electrodes are good down to only about 10^{-4} M and are not usable around 10^{-6} M.

While it is clear from the above discussion that no universally sensitive and selective detection system exists for the determination of trace halogens, plasma atomic spectrometry shows great promise in this area. However, few reports concerning the application of this technique have appeared.

Direct analyses of nonmetals in solution have been performed by observing spectral lines in the vacuum UV region of the spectrum with the inductively coupled plasma (ICP) [61]. While detection limits appeared promising (1, 3, and 10 ppm for I, Br, and Cl) operation in the vacuum UV spectral region imposes constraints that may not be overcome easily. Vacuum monochromators and nonabsorbing optics must be used in all spectral determinations. Detection limits in the near infrared region were considerably greater, at 2000, 100, and 500 ppm for F, Cl, and Br [61].

Michlewicz and Carnahan directly nebulized nonmetal halidecontaining solutions into a high power (500 W) He MIP [47,48]. They used emission lines in the UV-visible spectral region and reported detection limits of 2 ppm for Cl, 60 ppm for Br, and 7 ppm for I [48]. However, the plasma required a modified resonant cavity, a specialized torch design (lifetime less than 0.7 hour), 17-21 L/min of He, and an air coolant flow rate of 19-25 L/min. Moreover, an ultrasonic nebulizer and a desolvation system were needed to minimize the water loading of the plasma to achieve detection limits of 0.4 ppm for Cl, 3 ppm for Br, and 0.8 ppm for I. Their plasma also suffered from considerable matrix interferences, despite its high operating power.

In this chapter, the high efficiency helium microwave induced plasma (He-HEMIP) is explored for the determination of nonmetals in aqueous solution. The He-HEMIP is more easily tuned and more resistant to solvent loading than are conventional Beenakker-type cavities. Moreover, the He-HEMIP operates at low power and at a low gas consumption rate, thus producing lower overall background radiation, less microwave leakage, and a longer residence time for the analyte in the optical path.

Experimental

All organic solvents were spectral grade. A list of the solvents used for nonmetal analysis is shown in Table 12. Aqueous standards were prepared using the procedure outlined in Chapter 3. Operational parameters and equipment were the same as out lined in Chapter 3.

Results

Wavelength Calibration. The selection of the sensitive spectral lines for organic vapor nonmetal determinations was achieved using the apparatus shown in Figure 24. The device termed "wavelength calibrator" was a modification of that used by Barnett and Kirkbright [62]. Modifications of the apparatus of Barnett and Kirkbright included changes in apparatus size and experimental procedure. The flask used in this study was 25 mL rather than 10 mL. With tap A open and taps B and C closed, the plasma was ignited by insertion of a tungsten wire into the discharge tube. After ignition of the plasma, tap A was closed and taps B and C were opened to purge the 25 mL conical flask with the He gas plus the organic nonmetal vapor of interest. The system was allowed to equilibrate for approximately five min. prior to data collection.

Carbon Transitions Observed in the He-HEMIP. Table 13 is a listing of the atomic C transitions observed in the spectral region 190-500 nm. Energy levels and wavelengths were obtained from Reference 63 and transitions were from References 64-66.

The most intense MIP excited C(I) line that was observed occurred at 247.86 nm. A wavelength scan of the two most intense lines observed, which included the 247.86 nm atom line, is shown in Figure 25.

Fluorine Transitions Observed in the He-HEMIP. Table 14 summarizes the prominent F emission lines observed, along with upper state energies for the wavelength region studied. The energies and wavelengths were obtained from Reference 48. Figures 26 and 27 indicate the origins of the more important lines listed in Table 14 [63,67]. A number of known transitions originating from term multiplicities >1 produced a group of F emission lines close in wavelength (i.e., 677.39, 679.55, 683.42, 685.56 (the strongest line), 687.02, 690.24, and 690.98).

Most of the major transitions with upper states greater than or equal to 18.5 were observed as predicted from atomic diagrams. Grotrian diagrams indicate that no F(I) lines can occur between 100 nm and 350 nm [67].

The most intense F(I) line observed in this study was the 685.6 nm line, which originates from the $3s^4P_{(5/2)}-3P^4D^0_{(7/2)}$ transition.

The principal reasons for loss of signal response at long wavelengths are the decrease in resolution of the grating of the 0.35-m monochromator and the decrease in the signal response of the photomultiplier tube. Therefore, further studies in the near-IR region were abandoned.

Chlorine, Bromine, Phosphorus, and Iodine Observed Transitions in the He-HEMIP. The most intense CI, P, I, and Br atomic emission lines in the spectral region 200-800 nm, along with their transitions, are listed in Table 15. An abbreviated scan of the region for CI is shown in Figure 28.

The most intense CI(I), Br(I), I(I), and P(I) lines observed were at 479.45 nm, 470.49 nm, 206.23 nm, and 213.54 nm, respectively. These lines originated from the

 $4s^{5}S^{0}_{(2)}-4p^{5}P_{3}$ transition for CI(I) $5s^{5}S^{0}_{(2)}-5p^{5}P_{3}$ transition for Br(I) $5p^{5}{}^{2}P^{0}_{(1/2)}-6s^{2}P_{(1/2)}$ transition for I(I) $3p^{3}{}^{2}D_{0}{}^{(3/2)}-4s^{2}P_{(3/2)}$ transition for P(I).

Sulfur Observed Transitions. S scans were obtained with and without a purge system, as described in Chapter 3. Table 16 lists the atomic lines observed from 170-500 nm.

The most sensitive MIP excited atomic S emission line was observed at 180.7 nm (Ar-purged environment). The 217.1 nm line also proved to be sensitive when compared to other S lines observed in a nonpurged environment. Because of the complexity of the Ar-purged system, the 217.1 nm line may be of particular importance for the determination of S via direct nebulization.

Determination of Aqueous Nonmetals by Direct Nebulization. Nonmetal detection limits for aqueous samples are listed in Table 17, and the results of the He-HEMIP values are compared to data from Michlewicz and Carnahan (47, 48) using a 21 L/min He MIP and an applied power of 500 W. In addition, a MAK pneumatic nebulizer was employed by Michlewicz and Carnahan (47, 48). In terms of droplet size distributions, the MAK produces a much smaller droplet size distribution than does the Meinhard nebulizer used in this work [68,69]. Because droplet sizes affect the desolvation and vaporization times of the analyte and the solvent loading, smaller droplet sizes should result in decreased detection limits. In the case of the He-HEMIP, the detection limits are significantly lower than that reported for the high power MIP Carnahan cavity and MAK nebulizer. With the desolvation apparatus shown in Figure 13, the detection limit for chlorine using the He-HEMIP was determined to be 30 ppb.

Also reported in Table 17 are detection limits for S and P using the He-HEMIP. These detection limit values for S and P are the first

reported for He MIP-AES with the use of direct nebulization without desolvation and a Beenakker modified cavity.

Determination of Nonmetals in NBS Simulated Rain Water. The ability of the MIP to selectively and accurately determine nonmetals in complex aqueous samples is shown in Table 18. It should be noted that the chloride detection values provided by NBS were not certified.

Summary

It has been established that the simple and inexpensive atmospheric He-HEMIP system described can be used for qualitative and quantitative determinations of halogens with high selectivity and sensitivity. This technique shows great promise for the direct determination of nonmetals in aqueous and organic solutions. All of the emission lines used in this study arose from nonresonant transitions and should be reasonably immune to self-absorption.

11. Effect of Solvent Loading

As suggested in the previous chapter, the presence of water vapor in the plasma gas results in a degradation of the analytical sensitivity of the plasma. This effect, denoted as solvent loading, occurs when an excessive amount of water vapor is contained in the plasma gas prior to introduction into the plasma discharge. The water vapor is thought to impede the plasma formation process and absorb plasma energy. The analyte, therefore, is subjected to a less energetic discharge under these conditions. The effect of solvent loading on the operating characteristics of Ar plasmas has been the subject of much study [48,70].

A method to remove the water vapor from the plasma without removing the analyte uses a cooled spray chamber and condenser (see figure 14). By lowering the temperature of the system, less evaporation of water from the pneumatically generated droplets will occur. The reduction of the evaporation process should reduce the mass of water vapor in the plasma gas and result in a more energetic plasma discharge, thereby enhancing the analytical sensitivity of refractory metals and nonmetals.

The subject of this chapter is an investigation of the effect of solvent loading on a HEMIP. A cooled spray chamber/condenser system was used to control the temperature of the analyte aerosol. Parameters studied were sample transport efficiency, excitation temperature, electron number density, emission signal profiles, and limits of detection.

Experimental

The cooled spray chamber/condenser system for the HEMIP is described in Chapter 3 and shown in Figure 14. The temperature range studied was 0-40°C. For the laser scattering experiments a 0.5-mW He-Ne laser was focused onto the aerosol stream that exited the plasma torch. A plasma discharge was not ignited for the aerosol scattering experiments. The laser light (632.8 nm) scattered by the droplets was collected at a right angle to the laser beam by the 0.35-m scanning emission monochromator of the AES setup. The plasma used for the excitation temperature, electron number density, emission profiles, and limits of detection was Ar. The applied power level to the plasma was 70 W with 0 W being reflected. The Ar gas flow was approximately 0.85 L/min.

Results and Discussion

Effect of Cooling System on Sample Transport. The effect of the cooled temperature spray chamber/condenser system on the sample transport process was monitored by measuring the sample uptake rate of the nebulizer and by measuring the scatter intensity of the droplets as a function of spray chamber/condenser temperature. The effect of temperature on the uptake rate of the Meinhard pneumatic nebulizer is

shown in Figure 29. At room temperature (20°C) the nebulizer normally draws analyte solution at a rate of 1.6 mL/min using a nebulizer pressure of 40 psi. The difference in the uptake rates at lower temperatures was not statistically different from room temperature flows. However, at the 40°C temperature a significant difference was seen, in which the rate decreased to 1.4 mL/min. Based upon mass of analyte entering the plasma (as defined from the flow), the use of higher temperatures should result in a reduced analyte signal.

The effect of temperature on the combined size and number of droplets entering the plasma can be assessed through the use of laser scattering measurements. The intensity of the scattered laser light is related to the mean particle size and relative number of aerosol particles generated. In these experiments, no attempt was made to employ scattering theory to determine the size of the analyte droplets. Rather, the intensity signal was used as a measure to determine the combined number of aerosol droplets that would be introduced into the plasma discharge. A plot of scatter intensity vs. system temperature is shown in Figure 30. Differences in the data from 10°C to 30°C were not statistically significant. At the extremes of 0°C and 40°C a decrease in the scatter signal was seen. The smaller decrease at 0°C was most likely a result of the lower uptake rate. The greater decrease at 40°C was also a result of a lower uptake rate. More importantly, this decrease may be attributed to an increase in the evaporation of the aqueous droplets. The droplets generated by the pneumatic nebulizer have an approximate residence time of 5 s in the cooling system. At 40°C significant evaporation should occur. This evaporation would reduce the mean droplet diameter, resulting in a decreased scatter signal, and contributing a higher fraction of solvent vapor to the plasma discharge. Hence, the effect of solvent loading should be diminished at temperatures in the 0°C range.

Excitation Temperature. The excitation temperature for the 70-W Ar plasma was determined using the Fe slope method [39,40] for the various cooling system temperatures in order to assess the effect of solvent loading on the plasma. The plasma excitation temperature calculated for each spray chamber/condenser temperature is plotted in Figure 31. Generally, a decrease in excitation temperature was noted for an increase in spray chamber temperature. The data obtained at 20°C and 30°C were not statistically different. However, the data for 0°C and 40°C were different. Solvent loading was shown to diminish the available plasma energy to the analyte by yielding the lowest temperature of 4000K. The reduction of the mass of water vapor in the plasma gas yielded the highest temperature of 4700K with the use of 0°C for the cooling temperature.

Electron Number Density. The effect of solvent loading on the electron number density (n_e -) was also investigated for these temperature ranges of the spray chamber/condenser system. A plot of n_e -, determined using the method of Griem [41], vs. spray chamber temperature

is shown in Figure 32 for the Ar plasma. The trends observed in the excitation temperature plot are obvious in this figure. The use of a 40°C system temperature caused a significant decrease in n_{e^-} over the 10°C-30°C temperatures due to solvent loading. The highest n_{e^-} value was obtained for 0°C where solvent loading of the plasma was the least.

Emission Profiles. The effect of solvent loading on the analytical emission signals can be shown by constructing emission profiles (signal vs. observation height) for the various spray chamber/condenser temperatures. These profiles from a 100-ppm aqueous Mg solution are illustrated in Figure 33 for temperatures from 0°C to 40°C. The emission units are in mV while the zero position of the observation height was flush with the surface of the cavity. The use of higher spray chamber/condenser temperature resulted in a decreased emission signal at all observation positions. At 40°C the profile was barely discernible from the background emission for the 100-ppm Mg solution. This decrease may be attributed to the effect of solvent loading.

At lower temperatures a large enhancement of the signal was noted. This large increase in signal is attributed to the plasma discharge being able to vaporize and excite the analyte more effectively in the absence of significant water vapor in the plasma. A second feature in this profile that should be noted is a shifting of the emission maximum to higher observation heights for lower spray chamber/condenser temperatures. This increase is attributed to a reduction in the evaporation process in which larger droplets are maintained in the spray chamber/condenser system at the lower temperatures. Because analyte desolvation and vaporization are related to droplet diameter, the larger droplets should result in an emission maximum later in the plasma. Similar trends were observed for Na, Ca, and Co.

Limits of Detection. The effect of solvent loading on the Ar plasma also may be observed by displaying the limit of detection as a function of spray chamber/condenser temperature. These values (using k=3) are shown in Figure 34. Because the limit of detection value is a ratio of noise to signal, an increase in the observed signal will correspond to a lower limit of detection. If the noise increases, however, for a certain temperature range, the limit of detection also will increase.

The elements studied in this experiment were aqueous solutions of Co, Mg, Ca, and Na and were chosen because of their differing refractory natures. The effect of solvent loading on the Co (a refractory element) limit of detection is clearly seen in Figure 34. The value dropped from 17 ppm at 20°C to a sub-ppm value at 0°C. The use of temperatures above 20°C so greatly diminished the signal that a limit of detection was not reported. The decrease in the limit of detection can be attributed to an increase in the energy of the plasma discharge due to the removal of the water vapor from the plasma. A similar effect is shown for Mg (a refractory element) in which a factor of 10 decrease occurred

in the detection limits as the temperature was dropped from 20°C to 0°C. Ca, a mild refractory element, exhibited a small dependency on the spray chamber/condenser temperature. However, a significant deviation from the limit obtained at 0°C only occurred at temperatures above 30°C. The limit of detection for Na did not significantly change with the temperature of the spray chamber/condenser system. This lack of change may be explained by the fact that Na is not a refractory element and is quite easy to vaporize and promote to an excited state. Although the plasma energy decreases at higher spray chamber/condenser temperatures, the plasma possessed sufficient energy to vaporize and excite Na.

Summary

Solvent loading has a marked effect on the excitation temperature, electron number density, and analytical sensitivity of a HEMIP. By cooling (O to 10°C) the pneumatically generated aerosol the effect of solvent loading is reduced. Limits of detection are greatly reduced (by two orders of magnitude) for refractory compounds by cooling the aerosol prior to introduction into the plasma discharge. Therefore, the pursuit of heated spray chamber and condenser systems for nonmetal determinations should be modified to investigation of a cooled spray chamber/ condenser system.

12. Examination of a HEMIP as an Element Selective Detection for SFC

In this chapter, the coupling of the He-HEMIP to a packed column SFC will be described. The effect of the introduction of supercritical CO_2 on the plasma excitation temperature, electron number density, plasma geometry, and cavity coupling will be reported. For nonmetal species, the selection of emission lines used will be noted. Studies of the effect of plasma gas flow rates, plasma position, and applied power will be discussed. MDQ values for S, P, and Cl will be presented. The effect of plasma flow rates and pressure programming on these values also will be presented.

Experimental

Apparatus. The equipment and methods used are described in Chapter 3 and illustrated in Figures 8-10.

Viewing Geometry. Traditionally, the most sensitive spectral emission from an Ar MIP is found using radial (side-on) (Figure 6) viewing of the plasma. This mode is employed because the predominant analyte emission occurs outside the cavity in the plasma tail when using Ar as the plasma. Radial viewing also offers improved selectivity [38], because both vertical and lateral profiles of the plasma tail are possible, allowing spatial resolution of various analyte species (i.e., nonrefractory vs. refractory).

However, when He is employed as the plasma the axial mode (end-on) (Figure 7) is preferred. It should be noted that the He discharge is considerably smaller than that of the Ar discharge in the HEMIP cavity and a luminous plasma tail is not observed to extend outside of the cavity. Also, this mode offers improved analytical sensitivity [38], which is necessary for the detection of nonmetals and halogens. Further, the axial mode for He is used because the plasma is optically transparent in the radial mode. This mode affords improved sensitivity because the cross-section of the plasma discharge monitored offers a greater density of excited state analytes. Therefore, the axial mode was employed for this study.

Results and Discussion

Effects of CO₂ on Excitation Temperature. Although the exact effects of C species on atomic spectrometric signals have not been entirely determined among atomic spectroscopists, it has been noted that the combustion and decomposition products of C-containing species (acetylene, propane, and CO₂) absorb plasma energy [25,42,71] and thus result in diminished atomic emission signals of the analyte in Ar plasmas. This effect of organic species on the plasma temperature of the He HEMIP is shown in Table 19. The plasma excitation temperature, determined using the slope method with aqueous Fe [39], is shown

with the introduction of 0 mL/min, 70 mL/min, and 120 mL/min of CO₂ into the plasma. These flow rates represented CO₂ flows of 0%, 7%, and 12%, respectively. With the introduction of CO₂, the plasma temperature was noted to drop by 250 K. Since the error in these measurements was 3%, this difference was not statistically significant. Unlike the Ar plasma, in which the excitation temperature dropped 30% with the introduction of CO₂ [72], the He plasma appeared to be relatively unaffected by the gas; it may function as a more precise elemental plasma detector than an Ar-based system.

Effects of CO₂ on Electron Number Density. Although the exact excitation mechanism for atomic emission spectroscopy in MIPs is not unanimously agreed upon, the electron number density is helpful in making predictions of the performance of the plasma under different analytical conditions. In this study, the measured electron number density for a He plasma was calculated to be 5×10^{14} 1. e⁻/cc (Table 20). It should be noted that this value did not change with the addition of CO₂, whereas the number density fell by a factor of 10 for an Ar-HEMIP under similar conditions [71]. These data suggest that the He plasma contains enough energy to maintain its robustness even when organic gases are added.

The Effect of CO2 on Plasma Geometry. Although the plasma discharge of the Ar-HEMIP did not show evidence of constriction with the addition of CO₂ [73], the plasma discharge of the He-HEMIP did constrict in size upon the addition of CO₂ to the plasma. When operated with He only or with the addition of nebulized aqueous samples, the plasma discharge filled the plasma torch. This diameter is approximately 5 mm. When the CO₂ was introduced into the plasma, the constriction occurred. Figure 35, a lateral profile of the plasma (monitored with time), shows the observed plasma emission background (set at the CI emission line of 479.5 nm) with the addition of CO_2 to the plasma gas and the observed chlorine emission with the addition of CO₂. These plots illustrate that the plasma was no longer 5 mm wide but was constricted to approximately 1 mm in width with the addition of CO2. Therefore, there was approximately 2.5 mm annular distance, dictated by the torch dimensions, about the plasma where the gas (CO2 and analyte) would not be subjected to the discharge and would fail to undergo analytical atomic emission.

Cavity Coupling. The coupling of the cavity to the generator plays an important role in power transfer efficiency [30] and ultimately in the analytical performance of the MIP. Figure 36 demonstrates the effect of the cavity not being critically coupled over all pressures of a SFC pressure ramp. These observations were made using a P emission line. To the left of the plot the background emission level started to increase at 150 atm and continued to increase until approximately 270 atm, where (due to the increased mass of CO_2 being introduced into the plasma) the cavity was no longer critically coupled. At this point (270 atm) the back-

ground emission level greatly decreased due to a power loss to the cavity and continued until the pressure ramp terminated at 350 atm. A reflected power of 10 W was measured when the cavity was no longer critically coupled.

In Figure 37, the pressure ramp was run again with the cavity being adjusted to achieve critical coupling at 350 atm. Under these conditions the background emission level continued to increase as the pressure ramp increased. The reflected power remained below 1 W during the course of the pressure ramp. The increase in molecular background emission was due to an increase in the mass flow of CO_2 into the He plasma as the pressure was increased.

Line Selectivity. A CI headspace generator, Figure 24, was used to provide a constant source of analyte to the plasma for line selection. Figure 38 shows a scan from 477 nm to 486 nm that contained three CI lines. These lines were 479.5 nm (A), 481.0 nm (B), and 481.9 nm (C). The data illustrate that the line at 479.5 nm was the most intense line; it was selected for all CI measurements. A similar procedure was followed for determining the visible emission lines for P and S.

Effects of Plasma Flow Rate on the Signal-to-Noise (S/N) Ratio. The flow rate of the plasma gas plays an important role in the performance of the He-HEMIP with respect to S/N. Figure 39 demonstrates that as the plasma flow rate is decreased from 2.2 L/min to 0.8 L/min, the S/N ratio continually improves. Therefore, the lower flow rates seem desirable, but this lower plasma flow diminishes the cooling of the torch, which can lead to the melting of the plasma torch. Therefore, consideration is being given to the redesigning of the torch to accommodate the lower flows without detrimental effects to the lifetime of the torch.

Effect of Plasma Position on the Signal-to-Noise S/N Ratio. The axial profile of the He plasma in Figure 40 shows the effect of the plasma position on the S/N ratio of a S-containing analyte where each peak represents an independent injection. These data suggest that the optimum positioning of the plasma with respect to the monochromator entrance slit is approximately the center (0 mm) of the plasma discharge.

If significant skirting of the excited species about the plasma discharge was occurring, then the optimum signal should have been located off center. However, near the O position the signal appeared to be maximized, while the noise was unchanged. This suggests that a new torch design (with a smaller inner diameter) could reduce the plasma flow rate and increase the analyte residence time. This would reduce the probability of the analyte missing the plasma, thus increasing the analytical sensitivity. Effect of Applied Power on the Signal-to-Noise (S/N) Ratio. The effect of applied power on S/N ratios for a S-containing analyte (thiophene) is shown in Figure 41. A loss of S/N occured when the power exceeded 150 W. Below the 150 W level, the He HEMIP was lied power for all studies using the He-HEMIP.

Effects of Plasma Flow and Chromatographic Pressure on Minimum Detectable Quantities (MDQ). A 3-D plot of MDQ, chromatographic pressure, and plasma flow for a chlorine-containing analyte is presented in Figure 42. As can be determined from this figure, there were no statistically significant differences (factor of 3) in the MDQs with respect to pressure for the 2 L/min and the 3 L/min He plasma flow rates. These MDQ levels are in accordance with Hartmann's procedures for GC measurements [37]. However, this trend did not hold for the L/min He plasma flow, which exhibited a statistically significant change in the MDQ as a function of chromatographic pressure. This change is accounted for by the plasma size at 1 L/min (approximately 3 mm wide), which yielded a lesser discharge volume to promote analyte excitation. The plasma also was not as visibly intense when compared to the other two flow rates.

Effects of Plasma Flow and Chromatographic Pressure on Signal-to-Noise (S/N) Ratio. This measurement of S/N takes into consideration the noise of the entire experimental system, not just the noise of the detector (as with the MDQ data previously mentioned). The effect of plasma flow and chromatographic pressure on the S/N ratio of a chlorine sample is shown in Figure 43. This plot illustrates that there was no difference (factor of 3) in the S/N ratio as a function of pressure or plasma flow, except at 100 atm and 1 L/min. Under these conditions the S/N ratio was a maximum but decreased as the pressure increased. Since the mass flow of CO₂ increased with increasing pressure, the noise of the system grew while the signal remained relatively constant, thus giving a net loss in the S/N ratio with increasing pressure.

Reported MDQs. Table 21 gives the MDQ for S (thiophene), CI (methylene chlorine), and P (Paraoxon). These MDQs were calculated using the method set forth in reference 37. The experimental parameters employed for these measurements were as follows: 100 atm isobaric pressure, -800 V PMT, 50- μ m slits, current-to-voltage convertor at 10⁻⁶ A/V sensitivity, and 105°C. Under these experimental conditions the MDQs were 50 ng for CI, 30 ng for S, and 0.1 ng for P with monitoring lines of 479.5 nm, 581.9 nm, and 255.3 nm respectively. In addition, the MDQ for S was determined to be 50 ng and 30 ng at 180.7 nm (Ar purged) and 921.2 nm respectively.

Summary

In this chapter, a He-HEMIP was evaluated as an element-selective detector for SFC. The excitation temperature and electron number den-

sity were shown not to be affected by the introduction of CO_2 as Ar plasmas are. Optimum applied power to the cavity was found to be 150 W. Although the plasma constricted in diameter with the addition of CO_2 , the maximum analyte emission was found to occur in the center of the plasma discharge. MDQ levels for nonmetals were determined and found to be in low to sub ng level. The use of pressure programming was shown not to affect the MDQ at higher plasma gas flow rates. At low flow rates, an increase in MDQ levels was noted with the increase in the SFC pressure ramp. In a similar fashion, S/N ratios were affected only at low plasma gas flow rates when pressure ramps for the CO_2 gas were used.

The helium high efficiency microwave induced plasma (He HEMIP) has been demonstrated in this work to be a sensitive and selective spectrometric detector for nonmetals and metals in aqueous and organic samples. The He HEMIP fulfills the set of ideal requirements for an elemental detector. It possesses a high excitation and thermal temperature, thus allowing efficient analyte desolvation, vaporization, atomization, and excitation of liquid and gaseous samples. Inter-element interferences are minimal using atomic emission spectrometry (AES) and nonexistent with atomic fluorescence spectrometry (AFS). Analyses may be performed rapidly. The precision and accuracy of the He HEMIP are well suited for trace and ultratrace analysis. It is applicable to the analysis of liquids and gaseous samples with minimal preliminary sample preparation or manipulation. It provides ppb detection limits for metals and large linear working ranges of up to five and one-half orders of concentrative magnitude.

Through the characterization studies, the He HEMIP was shown to function better as an atomization reservoir for AFS than for AES. In contrast to AES, AFS required only that the plasma vaporize and dissociate the analyte. The excitation process occurred through the use of the source radiation. The effect of solvent loading on the plasma could be reduced by utilizing heated tubes and condensers or cooled spray chambers. The limits of detection for metals were shown to be decreased by a factor of 100 by using a cooled spray chamber for an Ar HEMIP.

The He HEMIP also was shown to be capable of sensitive and selective detection of nonmetals in water samples. Detection values compared favorably with those for certified standards of NBS rain water samples. Limits of detection for the nonmetals studied (Br, I, CI, P, and S) were in the sub to low ppm (μ g/mL) level. Through the use of a desolvation system, a limit of detection for CI of 30 ppb (ng/mL) was obtained for aqueous samples.

Nonmetal detection also was examined in the use of the He HEMIP as an element-selective detector for packed column supercritical fluid chromatography (SFC). The HEMIP is able to detect both nonmetals and metals in simultaneous fashion. The minimum detectable quantities (MDQ) for S, P, CI, Fe, and Sr were in the sub ng to pg range.

Although sub ng detection levels are not yet obtainable for CI aqueous sample injection with this system, the He HEMIP possesses significant advantages over other detectors for the spectrometric determination of nonmetals and metals in water or organic samples. The He plasma described in this work possesses the most sensitive metal and nonmetal detection limits of any multi-element spectrometric detector that has been described in the literature. Compared to other plasma sources, the He HEMIP is much simpler to operate and maintain and more cost effective. The gas flows for the HEMIP are generally 1 L/min, compared to 20 L/min for Ar inductively coupled plasmas (ICP). The power source for a HEMIP is a commercial magnetron generator, while the power source for an ICP is a 2-5 kW RF generator. Plasma torch life for the HEMIP is currently several months.

Indeed, the HEMIP may be suited to replace the ICP as a plasma source for multi-element detection in aqueous samples. It is believed by our research group that with further research into the plasma torch design and plasma gas composition, the limits of detection for nonmetals and metals can be further improved. trease that we a stream of the set around a first the set of the s

FIGURES

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Figure 1 Schematic Diagram of Atom-Formation and Processes



Figure 2 Block Diagram of the MIP-AES System



Figure 3 Block Diagram of the MIP-AFS System



Figure 4 Viewing Geometries Used for the He-HEMIP



Figure 5
Purge System for the He-HEMIP



Figure 6 Block Diagram of the Radial Mode Apparatus





Figure 7 Block Diagram of the Axial Mode Apparatus

Figure 8 Central Introduction of SFC Effluent into the HEMIP



Figure 9 Sidearm Introduction of SFC Effluent into the HEMIP



Figure 10 Schematic Diagram of the He-HEMIP













Figure 13 Diagram of the Desolvation System



Figure 14 Diagram of the Cooled Spray Chamber/Condenser System



Figure 15 Restrictor / Plasma Gas Right Angle Configuration




Figure 17 Spatial lodine Intensity Profile of Position vs. Intensity







Figure 19 Radial Emission Profile for a 50 ppm Calcium Solution









Figure 23 Effect of Phosphate on the Calcium Fluorescence Signal (Calcium Concentration =10 ppm)

Figure 24 Wavelength Calibration Device Used for MIP-AES of Nonmetals



Figure 25 Wavelength Scans for Carbon Emission in the He-HEMIP







Figure 28 Abbreviated Wavelength Scan for Chlorine Emission in the He-HEMIP



Figure 29 Plot of Uptake Rate vs. Spray Chamber/Condenser Temperature



UPTAKE RATE vs. SPRAY CHAMBER TEMPERATURE

Figure 30 Plot of Scatter Intensity vs. Spray Chamber/Condenser Temperature

SCATTER INTENSITY vs. SPRAY CHAMBER TEMPERATURE



Figure 31 Plot of Excitation Temperature vs. Spray Chamber/Condenser Temperature



Figure 32 Plot of Electron Number Density vs. Spray Chamber/Condenser Temperature



Figure 33 Plot of Mg Emission Profiles for Different Spray Chamber/Condenser Temperatures







Figure 35 Lateral Profile of the Axial Plasma



Distance (mm)

100% CO₂ Eluent: **Temperature:** 105°C 150 atm Pressure: Column: None 50 μm 479.5 nm Slits: Line: Chloroform Sample: Cavity Mode: Axial Plasma Gas: Helium

Figure 36 Effect of Pressure Programming on Background Emission on an Improperly Tuned Cavity





Eluent:100Temperature:90°Pressure:150Column:Del

100% CO₂ 90°C 150-350 atm in 5 min. DeltaBond Cyano 10 cm x 1 mm 5 μm particles

Slits: 50 Line: 21 Sample: N Cavity Mode: A Plasma Gas: H

50 µm 213.6 nm None Axial Helium

Figure 37 Effect of Pressure Programming on Background Emission on a Properly Tuned Cavity



Pressure (atm)

Eluent: Temperature: Pressure: Column:

•

100% CO₂ 90°C 150-350 atm in 5 min. DeltaBond Cyano 10 cm x 1 mm 5 μm particles

Slits: Line: Sample: Cavity Mode: Plasma Gas:

50 μm 213.6 nm None Axial Helium

Figure 38 Scan of CI Lines



Figure 39 Effect of Plasma Flow Rate on S/N Ratio for CI Emission



ciuent.		
Temperature:	105°C	
Pressure:	100 atm	
Column:	None	
Slits:	30 µm	
Line:	479.5 nm	
Sample:	Methylene Chlorid	e
Cavity Mode:	Axial	
Plasma Gas:	Helium	

Fluor



Figure 40 Effect of Plasma Viewing Position on Analyte Signal

Figure 41 Effect of Applied Power on S/N Ratio



X S/N







Table 1 Equipment Used in MIP-AES and MIP-AFS

Component	Model/Size	Manufacturer
Microwave Cavity	Highly Efficient	Laboratory built
Generator	HI-2450	Holaday Industries Edina, MN
Discharge Tube	Tangential flow	Laboratory built
Coaxial Cable	RG 214	Times Fiber Co. Wallingford, CT
Monochromater	01-512 0.25 m	PTI Princeton, NJ
PMT	R955	Hamamatsu Corp. Bridgewater, NJ
Nebulizer	Concentric TR-50-C2	J.C. Meinhard Santa Anna, CA
Spray Chamber	Scott	Laboratory built
Chopper	Model 125A	Eg & G Princeton, NJ
Lock-in	Model 5101	Eg & G Princeton, NJ
Lens	f/3, suprasil	Oriel Corp Stratford, CT
Computer	Apple IIe	Apple Computer Ir Cupertino, CA
Flow Controllers	MM3	Air Products Allentown, PA

Table 2 Equipment Used in SFC-MIP-AES

Component	Model/Size	Manufacturer
Microwave Cavity	Highly Efficient 7M _{@10)}	Laboratory built
Generator	HI-2450	Holaday Industries Edina, MN
Discharge Tube	Tangential flow	Laboratory built
Coaxial Cable	50 ohm, RG-214	Time Fiber Wallington, CT
Monochromator	01-512 0.25 m	PTI Princeton, NJ
PMT Housing with I/V	PTI MOD 01-512	PTI Princeton, NJ
PMT	R955	Hamamatsu Corp. Bridgewater, NJ
Nebulizer	Concentric TR-50-C2	J.C. Meinhard Santa Anna, CA
Spray Chamber	Scott	Laboratory built
Lens	f/3, suprasil	Oriel Corp. Stratford, CT
Rotameters	MM3	Air Products
Column	Delta Bond 10 cm x 1 mm 5 um particles	Keystone Sci. Pittsburgh, PA
Pump	SFC/200A	Suprex Corp. Pittsburgh, PA
Oven	Single Wall Transite	Blue M Electric Co

Table 3 He-HEMIP Operational Parameters

	AES	AFS
Forward Power	150 W	150 W
Reflected Power	0 W	O W O
Observation Height [*]	2-3 mm	8 mm
	(+0.5 mm) ⁺	
Nebulizer Uptake	0.46 mL/min	0.46 mL/min
Aux. He Flow	0 mL/min	0 mL/min
Total He Flow	l L/min	l L/min
Probe Penetration	96 %	96 %
Time Constant	3 sec	3 sec
HCL Power	-	10-25 mA

* Radial height above the top of the cavity.

+ Axial distance from the center of the cavity.

Table 4 Operational Parameters for SFC-MIP-AES

Forward Power		150 W
Reflected Power		0 W
Observation Height Radial Axial		0.5 mm 0.0 mm
Plasma Support Gas Argon Helium		1.8 L/min 1.0 L/min
Auxiliary Flow Central (Ar only) Sidearm (Ar) Sidearm (He)		1.2 L/min 0 L/min 0 L/min
Probe Penetration		96 %

Wavelength	(nm)	E _p (cm ⁻¹)	a ^b	Apq
				yara se na pag
370.5		27395	7	0.0328
372.2		27560	5	0.0505
373.5		33695	11	0.886
374.8		27560	5	0.0904
375.8		34329	7	0.611
382.0		33096	7	0.638
385.6		45295	11	0.87
389.6		49461	11	0.14
390.0		51771	7	0.086

Table 5Wavelengths and Constants Used for IronTemperature Determinations

Table 6Wavelengths and Constants Used for HeliumTemperature Determinations

Wavelength (nm)	E _p (cm ⁻¹)	a ^b	Apq
		anda ya ku	,
388.87	185565	9	0.09478
447.15	191445	15	0.246
471.31	190298	3	0.0955
501.57	186210	3	0.1338

 Table 7

 Data for Saha-Eggart Electron Number Density Determinations

Spe	ecies	Wavelength (nm)	E _q (cm ⁻¹)	aď
Ca	I	422.7	23652	3
Ca	II	396.8	23192	2
Cd	I	228.8	43692	3
Cd	II	226.5	44136	2
Thermometric Species		 Temper	ature (K)	
----------------------	--------------------	------------	-----------	
He		6100		
He	+ H ₂ O	5800		
Fe	(aqueous)	5600	(axial)	
		5800	(radial)	
Fe	(Ferrocene)	5100		

Table 8 Exicitation Temperatures by Slope Method

Table 9 Excitation Temperatures for Several Helium MIPs

Operating Power (W)	Texc	Reference
		,
130	4500	74
75	3400	75
75	6000	76

Element	λ (nm)	MIP-AES He	MIP-AES ^a Ar	
Ag	328.1	7	120	in Specification (Party
Al	396.2	130	1400	
Ba	553.5	-	180	
Li	570.8	-	43	
Ca(I)	422.7	5	40	
Co	240.7	50	1800	
Cr	357.9	70	8000	
Fe	248.3	30	650	
к	766.5	-	24	
Mg	285.2	6	630	
Mn	279.5	11	6900	
Na	589.0	1	2	
Sr	460.7	11	25	
Zn	213.9	8	420	

Table 10 MIP-AES Metal Detection Limits in ppb (k=2)

Element	λ (nm)	HCL-MIP-AFS	HCL-MIP-AFS ^a	HCL-ICP-AFS ^b
		He	Ar	
			Sector Sector	
Ag	328.1	10	40	2
Al	396.2	80	700	20
Ba	553.5	8	20	50
Li	570.8	1.2	20	0.4
Ca(I)	422.7	1.7	20	0.4
Co	240.7	19	100	3
Cr	357.9	40	2000	8
Fe	248.3	30	600	10
К	766.5	1	20	0.8
Mg	285.2	1.3	20	0.5
Mn	279.5		500	3
Na	589.0	0.1	10	0.3
Sr	460.7	5	20	2
Zn	213.9	1.2	40	0.4

Table 11 MIP-AFS Metal Detection Limits in ppb (k=2)

^a ref. 51 ^b ref. 55

 Table 12

 Organic Solvents Used for Nonmetal Emission Measurements

Element	Solvent
and and a second s	
с	Decane
F	Fluorobenzene
P	Triethyl Phosphate
Br	Bromobenzene
Cl	Carbon Tetrachloride
I	Diiodomethane
s	Carbon Disulfide

Wavelength	Transition ^a	Energy $(cm^{-1})^b$
247.48	$2p^2S_o - 3s^1p^o$	21,648 - 61,982
193.09	$2p^2 D_2 - 3s^1p^0$	10,194 - 61,982

Table 13 Carbon Lines Observed in the He-HEMIP

^a ref. 64-66

^b ref. 63

λ(nm)	Transition ^a	Energy (cm ⁻¹) ^b	1
623.964	3s ⁴ P _{5/2} -3p ⁴ S ⁰ _{3/2}	102,407-118,429	
634.85	^{3s⁴P_{3/2}-^{3p⁴S⁰_{3/2}}}	102,681-118,429	
641.37	$3s^{4}P_{1/2} - 3p^{4}s^{0}_{3/2}$	102,841-118,429	
677.40	$3s^{4}P_{5/2}-3p^{4}D^{0}_{3/2}$	102,407-117,165	
683.43	$3s^{4}P_{3/2}-3p^{4}D^{0}_{3/2}$	102,681-117,309	
685.60	3s ⁴ P _{5/2} -3p ⁴ D ⁰ 7/2	102,407-116,988	
687.00	$3s^{4}P_{1/2} - 3p^{4}D^{0}_{1/2}$	102,841-117,393	
690.25	$3s^{4}P_{3/2}-3p^{4}D^{0}5/2$	102,681-117,165	
690.98	$3s^{4}P_{1/2}-3p^{4}D^{0}_{3/2}$	102,841-117,309	
703.75	3s ² P _{3/2} -3p ² P ⁰ _{3/2}	104,732-118,938	
712.80	$3s^{2}P_{1/2}-3p^{2}P^{0}_{3/2}$	105,057-119,083	
720.24	$3s^{2}P_{1/2}-3p^{2}P^{0}_{3/2}$	105,057-118,938	
731.10	^{3s²P_{3/2}-3p²S⁰1/2}	104,732-118,406	
733.20	$3s^{4}P_{5/2}-3p^{4}P^{0}_{3/2}$	102,407-116,042	
739.87	3s ⁴ P _{5/2} -3p ⁴ P ⁰ 5/2	102,407-115,919	
742.57	$3s^{4}P_{3/2}-3p^{4}P^{0}_{1/2}$	102,681-116,144	
748.27	3s ⁴ P _{3/2} -3p ⁴ P ⁰ 3/2	102,681-116,042	
755.22	$3s^{4}P_{5/2}-3p^{4}P^{0}_{5/2}$	102,681-115,919	
757.34	3s ⁴ P _{3/2} -3p ⁴ P ⁰ _{3/2}	102,841-116,042	
775.47	^{3s²P_{3/2}-3p²D⁰_{5/2}}	104,732-117,624	
	-, -		

Table 14 Most Intense F Emission Lines Observed in the He-HEMIP

	λ(nm)	Transition ^a	Energy (cm ⁻¹) ^b	
	-	Chlo	orine	
479	45	4s ⁵ S ⁰ 2-4p ⁵ P3	107,879-128,703	
481.	.01	4s ⁵ s ^o 2-4p ⁵ P2	107,879-128,663	
481.	95	4s ⁵ s ^o 2-4p ⁵ P1	107,879-128,662	
		Phos	phorus	
213.	55	$_{3p}^{3} _{D}^{o}_{3/2}^{-4s^{2}P_{3/2}}$	11,362-58,174	
214	.91	$3p^{3} 2_{D}^{O}_{3/2} - 4s^{2}P_{1/2}$	11,362-57,877	
		Ioc	dine	
206	.24	5p ^{5 2} p ⁰ 1/2 ^{-6s²P} 3/2	7,603-56,093	
	* 	Bron	mine	
470.	.49	5s ⁵ s ⁰ 2-5p ⁵ P3	93,927-115,176	
478.	.55	5s ⁵ s ⁰ 2-5p ⁵ P2	93,927-114.818	
481.	67	5s ⁵ s ⁰ 2-5p ⁵ P1	93,927-114,683	
			1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 - 1000 -	- 1

Table 15 Most Intense C1, P, I, and Br Lines Observed in the He-HEMIP

^a ref. 64-66

^b ref. 63

Table 16 Sulfur Emission Lines Observed in the He-HEMIP

-		
		Wavelength (nm)
s	(I)	180.73
s	(I)	182.04
S	(I)	182.63
s	(I)	190.03
s	(I)	191.47
s	(I)	216.89
s	(II)	481.55
S	(II)	492.41
S	(II)	545.39
S	(II)	560.61
S	(II)	563.99

Element	(nm)	LOD	LOD ^a
		and a sub-	
Br	478.5	2	60
I	206.2	1	7
Р	213.6	0.4	
S	217.1	1.2	
Cl	479.5	0.8	2

 Table 17

 He-HEMIP Nonmetal Detection Limits in ppm (k=)

^a ref. 48

 Table 18

 Determination (Values in Parentheses Represent Deviations)

 of Nonmetals in NBS 2694 Simulated Rain Water

Element	Accepted Value 2694-I	Measured Value 2694-I	Accepted Value 2694-II	Measured Value 2694-II
Ê4	0.054(0.002) ^a	0.061(0.001)	0.098(0.007) ^a	0.127(0.003)
C1	0.24 ^b	0.19(0.02)	1.0 ^b	0.84(0.05)
S	2.75(0.05) ^C	2.78(0.08)	10.9(0.2) ^C	10.7(0.1)
a Ion Chro	omatography, Cond	uctimetry		
b Ion Chro	omatography, Cond	uctimetry		

^C Ion Chromatography, Isotope Dilution Thermal Ionization Mass Spectrometry

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Table 19Effect of CO2 on Excitation Temperature

Helium Flow Rate (1 L/min)	<u>T(exc), (K)</u>
He + Carbon Dioxide (0 mL/min)	6300
He + Carbon Dioxide (70 mL/min)	6100
He + Carbon Dioxide (120 mL/min)	6100

Table 20 Effect of CO2 on Electron Number Density

Helium Flow Rate (1 L/min)						<u>(e-/cc)</u>
He	+	Carbon	Dioxide	(0 mL/min)	5.3	E+14
He	+	Carbon	Dioxide	(70 mL/min)	5.3	E+14
He	+	Carbon	Dioxide	(120 mL/min)		

Table 21 MDQ for C1, S, and P with the He-HEMIP

Element	<u>Wavelength (nm)</u>	MDQ (ng)	
CI	479.5	50	
Р	255.3	0.1	
S	180.7 581.9	50 30	
0	921.2	30	

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