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Spectroscopic properties and analytical applications of induction-coupled plasmas

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SPECTROSCOPIC PROPERTIES AND ANALYTICAL APPLICATIONS OF INDUCTION-COUPLED PLASMAS

by

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absorption spectroscopy, both qualitatively and quantitatively. The solution of specific analytical problems is now simplified by the distinctive features of the discharge which are reported here.

INTRODUCTION

A plasma is a gas in which a significant percentage of its atoms have been ionized. It is therefore a good conductor of electricity and is affected by magnetic fields.

An induction-coupled plasma is a gaseous discharge which is maintained by a high-frequency, axial magnetic field and is usually contained in a quartz tube. The magnetic field is induced from a circular coil carrying a radio-frequency, alternating current which surrounds the discharge and the quartz tube. A carefully controlled flow of gas holds the plasma in the center of the tube, and thus a very pure discharge is obtained.

Because no direct current flows through the discharge, and because it is physically isolated from any electrical conductor, the induction-coupled plasma is electrically neutral and also free of contamination from electrodes. This physical isolation allows a wide variety of gases to be used. Any gas or mixture can form a plasma, and gases which have been employed include argon, helium, nitrogen, oxygen, hydrogen, water vapor, and combinations of these. The environment of a foreign particle in the discharge can thus be varied from extremely oxidizing to inert to very reducing. These characteristics of induction-coupled plasmas suggest many applications and areas for exploration which will be reviewed briefly.

Prior Investigations

The induction-coupled plasma was first investigated in 1941 by Babat (1). He described the general appearance, the electric and magnetic properties, and the circuit requirements of static electrodeless discharges in air at frequencies of 10^6 to 10^8 cps, at pressures of one atmosphere and less, and at power levels up to 100 kw.

The induction-coupled plasma was developed into a torch-like discharge by Reed, (2, 3) in 1960. He utilized a standard induction-heating generator of 10 kw maximum power output operating at a frequency of 4 mc to form argon plasmas in a one-inch diameter quartz tube. The argon was introduced into the tube at a tangential angle so that it would spiral along the inner wall, thus centering the plasma in the tube. The temperature profile of the discharge was measured by the Fowler and Milne normalized intensity method and revealed a peak temperature of 16,400° K. The thermal equilibrium question was discussed to justify the use of this temperature measuring technique, and Reed concluded that the induction-coupled plasma was very close to local thermal equilibrium. An energy balance of input power to heat and radiation output was also performed on argon plasmas at various flow rates and power levels, and also on an argon-oxygen plasma.

Reed then used the induction-coupled plasma to grow crystals (4) by blowing powders of oxides or metals through the discharge and collecting the molten particles on a suitable seed rod. The Verneuil oxy-hydrogen flame process used to grow synthetic sapphires is similar, but the plasma

yields higher temperatures and a choice of atmospheres. These advantages allowed Reed to grow crystals of stabilized zirconia and metallic niobium which were formerly impossible. The plasma device was redesigned to include a second quartz tube which surrounded the inner tube and the crystal being grown. The discharge was formed just beyond the end of the inner tube and was stabilized by a vortex flow of argon in both tubes.

In a later paper, Reed (5) reported the heat-transfer intensity of induction-coupled plasmas and oxy-hydrogen flames to be similar, apparently because the higher thermal conductivity of the oxy-hydrogen flame compensates for its lower temperature. Reed (6) also classified a variety of discharges according to their power density, pressure, and whether or not electrodes are required. Several types of discharges of neon, helium, and argon at pressures from 0.3 to 760 Torr were studied as to the power required in the plate circuit of the RF generator and the visible light intensity.

Much of Dr. Reed's work was condensed and reported in 1963 (7) and in 1964 (8). He has suggested many other applications of induction-coupled plasmas in his papers, including chemical synthesis of highly endothermic compounds, studies on magnetohydrodynamics, use as a spectral source for general purposes and for determining spectral transition probabilities, and as a preheater of gases for hypersonic wind tunnels.

In 1962, Hedger and Hall (9) used an induction-coupled plasma to prepare spherical powders. Their plasma device was a single-tube, vortex-flow design which used 1 to 50 l/min of argon and the discharge absorbed

2 to 5 kw of power at a frequency of 2.5 mc. Particles of 100 to 150 μ diameter of chromium, molybdenum, tantalum, tungsten, alumina, magnesia, and several uranium compounds were passed through the discharge at a rate of 1 to 5 g/min. Near perfect spheres were produced at yields of 50 to 70%. Plasmas of argon-hydrogen, argon-nitrogen, and pure oxygen at atmospheric pressure and pure argon at two atmospheres were also maintained using a water-cooled silica tube.

Spherical powder production by induction-coupled plasmas has also been a useful technique for making ceramic nuclear fuels. Jones and others at Mound Laboratory (10, 11, 12) have prepared plutonium dioxide and zirconium dioxide-plutonium dioxide microspheres of 10 to 250 μ diameter by passing the appropriate powder through an argon-oxygen plasma in a system very similar to that of Hedger and Hall (9). The ceramic spheroids have a high density and exhibit remarkable freedom from airborne, surface, and solution contamination.

Researchers Galtier, Leprince-Ringuet, Reboux, Collongues, Chaudron, and Cezaire authored several papers (13-18) during 1962-1963 in which they described the construction, operation, properties, and applications of induction-coupled plasmas. A single-tube, vortex-flow design was utilized, sometimes with a water-cooled silica tube, to contain plasmas of argon, argon-oxygen, argon-nitrogen, air, or hydrogen. The discharge was maintained by a 10 or 12 kw generator operating at 5 to 15 mc. Electrodes were also added so that a DC current could be superimposed on the plasma in order to raise the power of the discharge. In addition, the cathode was tubular so that powders could be carried into the discharge, and the

anode could serve as a support for heating samples. Many applications of induction-coupled plasmas were suggested, although apparently few were actually attempted.

A calorimeter study of induction-coupled plasmas was undertaken by Cannon in 1962 (19). The distribution of energy to radiation, to the walls, and to the gas was measured as a function of gas flow rate, gas composition, plate voltage of the generator, and discharge tube diameter. The discharge was maintained at power levels up to 50 kw at 400 kc, was vortex-stabilized, and contained in a water-cooled Vycor tube of 70 or 42 mm nominal inside diameter. A temperature profile indicated that the peak temperature was off-axis (that is, a cool center existed), although the published data were very incomplete.

A good theoretical treatment of RF heating of plasmas has been presented by Mironer and Hushfar (20) who discussed the effects of frequency and discharge diameter on efficiency of coupling and gas enthalpy. Qualitative results of various coil configurations were presented in addition to a short discussion on methods of discharge initiation and stabilization. In a second paper, Mironer (21) described a specially designed copper discharge tube which allowed gas enthalpies of 100 kcal/g-mole at one atmosphere of argon. This is about double the maximum enthalpy which can be obtained in a water-cooled quartz tube. The above work was performed with a 5.3 kw generator operating at 1 to 35 mc and a single-tube, vortex-flow system.

In 1961, Bauer, Longo, and Malek (22) reported on developments in electronic Verneuil furnaces, primarily with the production of high purity, high heat-capacity gases. Capacitively coupled discharges of the single-electrode, the parallel-plate, and the parallel-ring configurations were investigated both theoretically and experimentally. Induction-coupled plasmas were also studied theoretically, although estimates of temperature and electron density were quite low and caused erroneous conclusions.

An induction-coupled plasma was operated by Hill and McPartland (23) for high temperature studies of surface activity. A long focal length microscope allowed visual or photographic observations of samples in the plasma. Their plasma device was a single-tube, vortex-flow design.

Kana'an, in his thesis (24) and later with Beguin and Margrave (25, 26, 27), utilized an induction-coupled plasma and a DC arc plasma to study chemical reactions at high temperatures. A typical, single-tube, vortex-flow system contained the discharge which was maintained by a 3 kw generator operating at 5 mc. The discharge extended into a reaction chamber where compounds including CF_4, CCl_4, CF_3Cl, Teflon, SiF_4, $SiCl_4$, and BF_3 were introduced. The reaction products were identified by emission spectroscopy to include SiF, SiO, BO, C_2, CN, Si, B, and C (26, 27). A literature review of successful syntheses with plasma devices plus future applications was also presented (25, 27).

A modified crystal-growing plasma device is currently being studied by Sauer (28). A water-cooled tube containing a feed tube and a seed rod is evacuated and partially back-filled with argon. An induction coil

surrounding the system is activated which establishes a glow discharge in the tube, and the argon pressure is increased to form a high power yet static discharge. Crystal growth then proceeds by the addition of powder and appropriate lowering of the seed rod. The advantages of Sauer's design are increased stability, very low argon consumption, and control over the gas temperature via pressure.

An electrical-thermal investigation of induction-coupled plasmas has been carried out by Scholz, Brodwin, and Anderson and reported in 1963 (29) and also in more complete form as a thesis (30). In this work, an argon plasma was operated at 1490 to 1900 watts at a frequency of 4.4 to 15 mc and a gas flow rate of 7 to 12 l/min in a single-tube, vortex-flow system. The discharge was studied to test an oscillator efficiency theory which related the oscillator frequency, the electrical parameters of the oscillator, and the torch-coil geometry to the ratio of power dissipated in the plasma to oscillator input power. However, the average gas temperature assumed in the theoretical work yielded an electrical conductivity which was rather low to represent the discharge core and erroneous conclusions may have resulted. A plasma initiation study was also presented as was a spectral line identification study.

The application of induction-coupled plasmas for heating a gas flow was reported by John, Debolt, Hermann, Hogan, and Kusko (31) in 1963. A circular, segmented, copper nozzle served to contain an argon discharge which was maintained by 1 to 10 kw of power at a frequency of 5 mc. The conversion efficiency of electrical energy to gas enthalpy was found to be

low and the authors concluded that use of the plasma could be justified only when exceptionally clean gases are required.

The radio-frequency generation of thermal plasmas was recently discussed by Marynowski and Monroe (32, 33). Experimental operating characteristics were described, principally with respect to equipment at the Stanford Research Institute which included a 10 kw and a 50 kw generator operating at 3 to 10 mc. A single-tube, vortex-flow plasma device was used to determine the operating parameters of argon, argon-oxygen, and pure oxygen plasmas. A plasma initiation study was included as well as a discussion on plasma stabilization and confinement. An interesting stabilization technique was the adaptation of a work coil with one reverse turn on the downstream end. This technique, also used in levitation melting, causes the flux from the reverse turn to exert a repulsive force on the plasma which is carrying current induced from the other turns. The levitation coil reportedly improved the constancy of the plasma position during injection of powders. This reverse turn, however, neutralizes some of the inductive field and thus a more powerful generator is required.

Marynowski and Monroe also compared arc and radio-frequency heating of gases, and several applications such as crystal growing, spheroidization, and chemical reactions were discussed. Two patents concerning chemical applications were mentioned although neither actually refers to induction-coupled plasmas. The British patent #915,771 issued to Imperial Chemical Industries Ltd. describes a parallel-ring, capacitively coupled discharge,

and the British patent #926,716 issued to DuPont does not describe any type of RF heating nor any type of discharge but only a process which requires pure, hot oxygen.

Dymshits and Koretskii (34) investigated induction-coupled argon plasmas in the frequency range of 0.29 to 3.3 mc, at pressures of 200 to 1500 Torr, and flow rates of 33 to 166 l/min with high-frequency generators of 10 and 40 kw. Their plasma device was a single-tube, vortex-flow design in which the diameter of the tube was varied from 33 to 62 mm. The temperature of the plasmas under various conditions was measured by comparing the intensity of the spectral continuum to the brightness of a standard ribbon lamp. A maximum temperature of 10,500 to 11,000° K about 5 mm off-axis and a core temperature of about 10,000° K were found. These temperatures and also the diameter of the discharge were shown to be unaffected by the diameter of the discharge tube, the pressure, or the flow rate. The diameter of the plasma was a function only of the skin depth of the electric field.

Huffman and Rolinski (35) have experimented with a single-tube plasma device which operated with 1.4 kw at 7.1 mc on argon. Background information on electron acceleration by electric and magnetic fields was given, and the acoustical noise emitted by the plasma was analyzed. In the acoustical spectral range from 40 to 20,000 cps, intensity peaks were found at 120, 180, 530, 1200, and 2000 cps. The temperature of the discharge was measured by comparing the intensities of two argon ion lines and found to be 24,000° K.

The use of the induction-coupled plasma as a spectroscopic source has been investigated independently and concurrently by two groups of researchers. Greenfield, Jones, and Berry (36) reported their work with a dual-tube, vortex-flow system in which an argon plasma was maintained by a generator producing 1.5 kw at 36 mc. The discharge had an apparent low-temperature region in the center, and aqueous aerosols were injected through this hole. The rate of aerosol addition was not measured but estimated to be about 1/4 ml/min. The emission from the tailflame of the plasma was observed spectrographically. Orders of the levels of detection for Al, Ca, Co, Cr, Cu, Mg, Mn, and Ni were reported in the range of 1 to 100 ppm. The interference from phosphate and aluminum on the emission intensity of calcium, which is quite severe in air-acetylene flames, was shown to be negligible in the induction-coupled plasma. The stability of calcium emission intensity was measured photographically and photometrically, and found to be high.

The analytical applications demonstrated by Greenfield, Jones, and Berry led Wendt and Fassel (37) to publish a communication on their preliminary work which is described more completely in this thesis.

In 1962-63, several induction-coupled plasma devices became commercially available, principally designed for growing crystals but adaptable to nearly any use. The firms mentioned all supply a standard Class C, high-frequency generator of virtually any power output and any desired frequency. Powder feeding equipment is available as well as seed rod controls, collection chambers, and other auxillary equipment. The

significant differences for analytical spectroscopy involve the design of the gas-flow system.

The TAFA plasma device (TAFA Division, Humphreys Corporation, Concord, N. H.) is a water-cooled tube in which the work coil is imbedded. The gas flow pattern is variable and operation can be achieved with pure argon, helium, nitrogen, oxygen, or air, or 50% hydrogen in argon (by volume). An uncooled device is also available which is adequate for operation with argon or argon mixtures. This uncooled device is a typical, dual-tube design in which the discharge is stabilized just beyond the end of the inner tube. For spectroscopic purposes, this latter design would probably be more useful.

Lepel (Lepel High Frequency Laboratories, Woodside, New York, N. Y.) markets two plasma devices for containing induction-coupled plasmas. A single-tube torch is available into which 12 to 38 l/min of gas can be introduced through two tangential ports into either a 28 mm or 35 mm ID quartz tube or a 27 mm ID, water-jacketed quartz tube. For higher stability and lower gas velocity in the core of the discharge, a dual-tube, vortex-flow device is available. A modified ball-joint in this system allows the outer tube to be accurately centered around the inner tube.

Forrest Electronics (Forrest Electronics Corporation, Las Vegas, Nev.) produces a dual-tube plasma device in which a laminar flow of gas stabilizes the discharge. The two quartz tubes are held in place by a single coupling ring, and the inner tube is held in the center of the outer tube by four small quartz feet fastened to the inner tube. Quartz tubes

of various diameters up to five inches are available and all fit the same base. By insertion of a special plate into the base, a vortex-flow pattern can be obtained and single-tube operation is then possible.

The equipment used by Reboux (15) and other French researchers is available through P. M. Grosz (International Research Consultants, Inc., Princeton, N. J.). The plasma device is a single-tube, vortex-flow design which is available with tube diameters ranging from 15 to 99 mm.

Radyne (Radyne International, Inc., Des Plaines, Ill.) is marketing the equipment designed and demonstrated by Greenfield, Jones, and Berry (36). This is the only device specifically designed for spectroscopy and includes flexible, high-frequency leads and an optical bench housing.

Summary

The induction-coupled plasma has developed rather rapidly since 1961 into several fields although, until late in 1964, no work had been reported on its use as a source for analytical spectroscopy. Perhaps few spectroscopists had access to induction-heating generators, especially units with a frequency in the low megacycle region. In addition, many researchers may have been misled by incorrect statements in the literature regarding the necessary flow pattern of the gas. Reed (2); Greenfield, Jones and Berry (36); and Beguin, Kana'an and Margrave (25) all stated that a portion of the plasma must be recirculated in order to heat the incoming gas and maintain the discharge. They accomplished this recirculation by introducing the gas at a tangential angle so that it would spiral along the inner wall of the quartz tube. In a single-tube

system, this tangential gas introduction and the resulting vortex gas flow is the only means of creating a flow pattern with the required high velocity at the walls and low velocity in the center. In a dual-tube system, however, the required flow pattern is easily obtained without resorting to a vortex flow. Yet the dual-tube devices of Reed (4); Greenfield, Jones, and Berry (36); Lepel; and Radyne introduce the gas at a tangential angle which has several disadvantages for both spectroscopy and crystal growing. As noted by Bauer, Longo, and Malek (22, p. 69) and by Reed (8, p. 5), a vortex flow tends to throw heavy particles against the inner wall of the quartz tube and to recirculate the lighter particles. This effect would occur with powders, aerosol droplets, and vapors. In addition, a vortex flow is drastically affected by minor distortions in the walls of the tubes, and loss of stability results.

In the work now being performed, a dual-tube plasma device has been designed with a laminar flow of gas in both tubes. This laminar flow is not affected by even major distortions in the quartz tubes, and the complete lack of recirculation does not decrease the stability or intensity of the discharge. The details on this design and the resulting discharge characteristics are discussed later in this thesis.

Discharge Properties

Two properties of induction-coupled plasmas--temperature and enthalpy--are of great importance for all applications of the discharge. From these two properties, several other physical properties can be calculated and the plasma can then be studied more accurately.

The temperature of the discharge operating on pure argon and on argon with 20% oxygen was measured by Reed (2) using the Fowler and Milne normalized intensity method. This method requires that the relative intensity of a single emission line be measured across the discharge. The intensity profile is converted by the Abel integral to a radial intensity profile which is then compared with the theoretical intensity peak for that particular line. The major advantage of this technique for measuring temperature is that it is not necessary to employ transition probabilities with their inherent uncertainty. Five other criteria must be assumed, however. One, the source must be radially symmetrical, which is valid, although some distortion occurs when light must pass through a curved quartz tube off-axis. Two, local thermal equilibrium and a Boltzmann distribution of energy must exist in the discharge--probably true since the collision rate is very high, the mean free path is very small, and the electric field strength is quite low. Three, the discharge must be optically thin, a criterion which was not verified. The argon emission line which was measured results from a transition in which the final state is a metastable state and thus self-absorption could have occurred. Four, the transition of interest must occur spontaneously from an excited energy state. However, the collision rate in a discharge at atmospheric pressure is so high that collision-stimulated transitions may occur in significant proportions. Five, the Saha equation for degree of ionization must hold. This requires (for a pure argon plasma) thermal ionization only, local thermal equilibrium, ideal gas behavior, and monatomic species

only. However, three of the four 4s states of argon are metastable states which may cause many collisions of the second kind, and the Ar_2^+ molecule forms in significant quantities to affect the recombination rates of electrons (38). Thus three of the five criteria are not strictly met, and the experimental difficulties in measuring intensities of emission lines which may be pressure broadened have not been considered.

Nevertheless, the peak temperature of 16,400° K measured by Reed for an argon plasma absorbing 1.6 kw of power with a flow rate of 9.4 to 14.2 l/min is probably accurate within a few thousand degrees. This temperature correlates well with the theoretical peak electron density which occurs at 16,700° K in argon at one atmosphere, according to Olsen (39), and it seems reasonable that maximum inductive coupling would occur at the peak electron density. That is, the discharge would probably expand in volume rather than exceed a temperature of 16,700° K.

Reed's application of this temperature measuring technique to an oxygen-argon plasma revealed a core temperature of 19,200° K, but the necessary theoretical assumptions for this mixture cannot be justified with any certainty.

The temperature of 24,000° K noted by Huffman and Rolinski (35) was measured by the two-line or intensity ratio method. This temperature is not considered too reliable, however, because only a 5% error in each of the intensity measurements and each of the transition probabilities could lower the calculated temperature to 17,500° K. In addition, the lines

chosen were in a region of strong spectral continuum, which would make true intensity measurements difficult.

Dymshits and Koretskii (34) determined a temperature of 10,500 to 11,000° K in their discharges by measuring the absolute intensity of the spectral continuum. The absence of a true blackbody continuum makes these temperatures highly questionable, though.

Greenfield, Jones, and Berry (36) determined an electron temperature of 8000° K in the plasma tailflame by measuring the relative intensity of a calcium atom and ion line. The degree of ionization of calcium was calculated and the temperature found via the Saha equation for ionization.

Clement, Consoli, Gormezano, Ricateau, and Weill (40) used three methods to measure the mean temperature of their argon plasma: relative intensity measurement of eight argon lines, Stark broadening of the H_β line, and absolute intensity measurement of argon lines. The temperatures ranged from 7550 to 9800° K and apparently represented a mean temperature of the discharge, not a peak core temperature.

Cannon (19), when he measured the temperature of his plasma, used the method described by Reed (2), but found a core temperature of less than 15,000° K and a peak temperature of near 15,000° K in a thin sheath near the edge of the plasma. The discharge in this work was about 6 cm in diameter, it was maintained by a 400 kc, 50 kw generator, and the temperature study was admittedly very incomplete.

Other authors have visually noticed a cool or dark core region in their plasmas, notably Greenfield, Jones, and Berry (36) who examined a

3/4" diameter plasma maintained at 36 mc; Marynowski and Monroe (32) who studied a similar size plasma at 37 mc; and Huffman and Rolinski (35) who showed photographs of a cool center in their 3/4" plasma operating at 7.1 mc. This cool center is apparently caused by the skin effect of induction heating discussed in a later section.

Many applications of induction-coupled plasmas involve the transfer of thermal energy from the plasma gas to another substance. For this reason, the theoretical enthalpy and heat capacity of several gases and the ability of the induction-coupled discharge to heat these gases has been studied by many researchers.

The thermodynamic properties of argon, oxygen, and nitrogen at pressures of 0.01 to 5.0 atmospheres and temperatures up to 35,000° K have been calculated by Drellishak (41) and presented in graphical form. The data for argon only was also published earlier by Drellishak, Knopp, and Cambel (42) and by Olsen (39).

The maximum enthalpy obtainable in a water-cooled torch with an argon discharge is about 50 kcal/mole (20, 32) although 100 kcal/mole has been obtained in a special copper-jacketed torch (21), 68 kcal/mole in a segmented copper chamber (31), and 110 kcal/mole in a ceramic torch (43). An enthalpy of 50 to 100 kcal/mole for argon corresponds to an average gas temperature of 9000 to 12,000° K which is reasonable for a high power plasma.

The diatomic gases have an appreciable heat content even at relatively low temperatures due to dissociation and thus can transfer more thermal energy than argon as was demonstrated by Reed (5). The TAFA plasma

reportedly produces enthalpies of 450 kcal/mole on diatomic gases which is four times the enthalpy obtainable with argon (43).

Table 1 lists approximate calculated properties of argon plasmas for purposes of comparison with other discharges and to predict or substantiate experimental findings. This table assumes thermal equilibrium and ideal gas behavior at one atmosphere initial pressure.

Table 1. Calculated values of argon plasmas

Temperature (°K)	8,000	10,000	13,000	16,000
Number density (cm^{-3})[a]				
Atoms	$9x10^{17}$	$7x10^{17}$	$3x10^{17}$	$6x10^{16}$
Ions or electrons	$1x10^{15}$	$2x10^{15}$	$1x10^{17}$	$2x10^{17}$
Energy (ev)[b]	1.0	1.3	1.7	2.1
Velocity (cm/sec)[c]				
Atoms or ions	$2x10^{5}$	$2x10^{5}$	$3x10^{5}$	$3x10^{5}$
Electrons	$6x10^{8}$	$7x10^{8}$	$8x10^{8}$	$9x10^{8}$
Enthalpy (kcal/mole)[a]	40	58	170	410
Conductivity, electrical (mho/cm)[d]	7	40	80	110
Skin depth (cm)	0.9	0.4	0.3	0.2

[a]Number densities from Olsen (39).

[b]Calculated as $E = \frac{3kT}{2}$.

[c]Calculated as $v = \frac{\sqrt{3kT}}{M}$.

[d]Conductivity from Olsen (45).

STATEMENT OF PROBLEM

The induction-coupled plasma has the properties of high temperature, inertness, and purity which indicate usefulness as a spectroscopic source. The additional properties of high stability and continuous operation plus the ease of introducing foreign substances indicates applications in analytical spectroscopy. The project undertaken here was to study the induction-coupled discharge with respect to its spectroscopic properties and especially its analytical applications. This study required the design and construction of a plasma device and sample introduction system plus a demonstration of the properties and usefulness of the plasma.

The design of the device required, above all, high stability. In addition, the design should permit good visibility of the entire discharge, easy initiation, and modification during development. The design should also be adaptable to a variety of sample introduction systems by which samples can be added to the discharge in a continuous, reproducible, and variable manner.

The spectroscopic properties of a discharge can be demonstrated by comparing sensitivities or limits of detection of various elements with data for other discharges. Analytical applications are best shown by demonstrating stability, by performing quantitative analyses, and by evaluating atomic absorption possibilities. The results of this project are presented in the following sections.

EXPERIMENTAL

The initial design of the apparatus used in this study was based principally upon the suggestions of Reed (2, 3, 4). He recommended a frequency of about 4 mc for a discharge in a one-inch diameter tube, and this suggestion was adopted. A power of five kilowatts was initially considered adequate as it will easily ignite and sustain an argon plasma. The addition of water or other gases tends to quench the discharge, however, and the power of the generator was later found to limit the amount of aerosol which can be added to the plasma.

Radio-Frequency Generator

High-frequency generators are invariably a Class C design for which a simplified circuit diagram is shown in Figure 1. The line voltage is

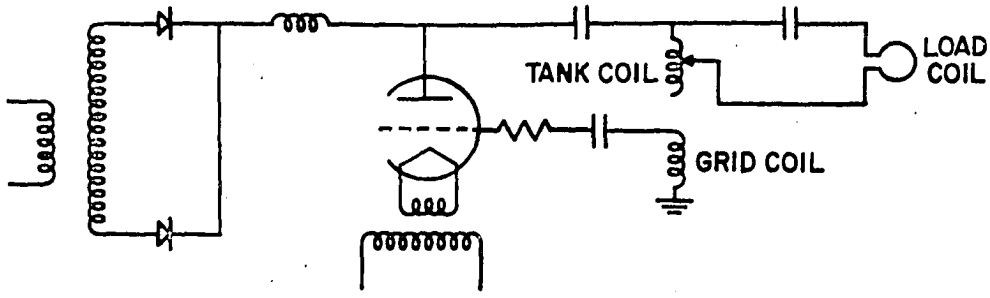

Figure 1. Simplified circuit diagram of Class C generator

stepped up and rectified to produce a high voltage, DC supply for the plate circuit. The flow of current in the tank coil causes a magnetic flux which is then picked up by the grid coil. The current in the grid coil changes the grid potential and thus stops the current flow in the oscillator tube. The current stored in the tank capacitor then

surges back through the tank coil, the grid potential is restored, and the cycle begins again. The frequency at which the tank circuit oscillates is determined by its LC characteristics.

The power output of a high-frequency generator can be controlled in several ways, of which a saturable reactor is probably best. This control varies the input voltage and is completely independent of fluctuations in the output power or changes in the load impedance.

The proper choice of frequency of the induction power supply and the optimum diameter of the plasma have been considered by many authors (3, 29, 30, 32) and always involves the "skin depth." The skin depth is that thickness of the object within which the fraction 1/e or 37% of the inductive energy is dissipated, and is defined as

$$S\ (\text{cm}) = (\pi\ \mu\ \sigma\ f)^{-1/2}$$

where μ = permeability

$= 4\pi \times 10^{-9}\ \mu_r$,

μ_r = relative permeability,

σ = conductivity (mho/cm), and

f = frequency of generator (cps).

A plasma is assumed to have a relative permeability equal to unity since it is an excellent electrical conductor.

Several problems are involved in evaluating these factors. First, a discharge is a poor approximation to a solid, cylindrical conductor because its conductivity changes rapidly across the profile. In addition, the

conductivity is very hard to measure, and any estimate is usually based on temperature which is equally hard to measure. Approximate values of the skin depth at 4 mc are tabulated in Table 1 and a median value of 0.3 to 0.4 mho/cm would be appropriate for most calculations.

Second, the estimated or effective skin depth must be correlated with the diameter of the discharge. Brown, Hoyler, and Bierwirth (44, p. 31) have calculated theoretically that a discharge diameter greater than 4 1/2 times the skin depth must be maintained or coupling efficiency will be poor. The discharge diameter is not necessarily related to the quartz tube diameter, however. Dymshits and Koretskii (34) observed that the discharge will only partially fill an oversize tube and may then wander around in the tube.

Third, the actual diameter of the discharge cannot be exactly specified. In this situation, a reasonable definition might be that diameter beyond which the electrical conductivity of the plasma is less than 5% of the conductivity in the core. Assuming a core temperature of 16,000° K, the temperature at which the conductivity equals 5% of maximum is about 7000° K (45). A temperature of 7000° K would probably correspond to the visible boundary as sketched by Reed (2). The minimum diameter can thus be approximated and equals about 16 mm at 4 mc or 5 mm at 40 mc.

The optimum frequency for induction-coupled plasmas can only be found by experimentation. The work of Greenfield, Jones and Berry (36), who were able to add about 1/4 ml/min of aqueous aerosol to only a 1.5 kw plasma at 36 mc, indicates that the optimum frequency may be about ten times the

minimum frequency and that a ring or donut-shaped discharge may be most desirable. For a given high-frequency generator, however, maximum output power can be obtained at only one frequency and this factor will invariably determine the operating frequency. The generator used in this work was operated at 3.4 mc for this reason.

A plasma is an unusual object to be heated by induction because its size is a function of the power of the generator. Any fluctuation in the plasma will cause a change in the impedance of the tank circuit which will affect the coupling efficiency and thus cause an "echo" in the discharge. Any ripple in the plate circuit voltage will be absorbed by the plasma and cause a hum. Therefore, a three-phase, full-wave rectifier circuit (which has only 4% ripple) is preferred, and, for this work, a choke-input ripple filter was added. The ripple was thus reduced to about 1/2%, and the audible noise is very low.

Because high visibility of the discharge is important for spectroscopy, the load coil chosen for this work was a five-turn pancake design with a concentrator ring. The core of the plasma is centered at the top of the concentrator ring and is quite stable in the vertical direction. Coupling efficiency seems as good or better than three-, five-, or seven-turn solonoid coils which have been tried.

Plasma Discharge Chamber

Initial experiments were conducted with a system similar in design to that of Reed (2). Argon was admitted at a tangential angle through four small orifices into a one-inch diameter tube. The resulting vortex

flow caused a high gas velocity at the walls and a low velocity in the center of the tube. The recirculation of the hot gas was considered by Reed to be essential for operation. This design was extremely hard to initiate, however, and the discharge could only be sustained at low gas flow rates. The quartz tube overheated easily, especially if minor distortions were present in the tubing. Part of this trouble was apparently due to the small gas orifices which caused excessive turbulence. In addition, the distance of the load coil from the gas entrance is quite important and this position can only be determined by trial-and-error.

These problems led to the design of a new plasma device which utilized two tubes as by Reed (4) but incorporated a strictly laminar flow of gas. This flow pattern has several advantages over a vortex-flow configuration. First, a vortex flow has more turbulence than a laminar flow and this turbulence may decrease the stability of the discharge. This loss of stability is greatly enhanced by minor distortions in the walls of the tubes, whereas the laminar flow torch has sustained a plasma even with the coolant tube purposely bent and kinked. Second, the addition of aerosols of solutions or powders to a vortex flow of gas tends to cause them or their vapors to be thrown against the inner wall of the coolant tube, thus decreasing the transmittance of the tube and devitrifying the quartz. For spectroscopic purposes, the laminar-flow design is thus distinctly better and has also been found to ignite easily.

The final design of the base assembly is shown in Figure 2. The double o-ring seals will firmly hold tubes even with a variation in

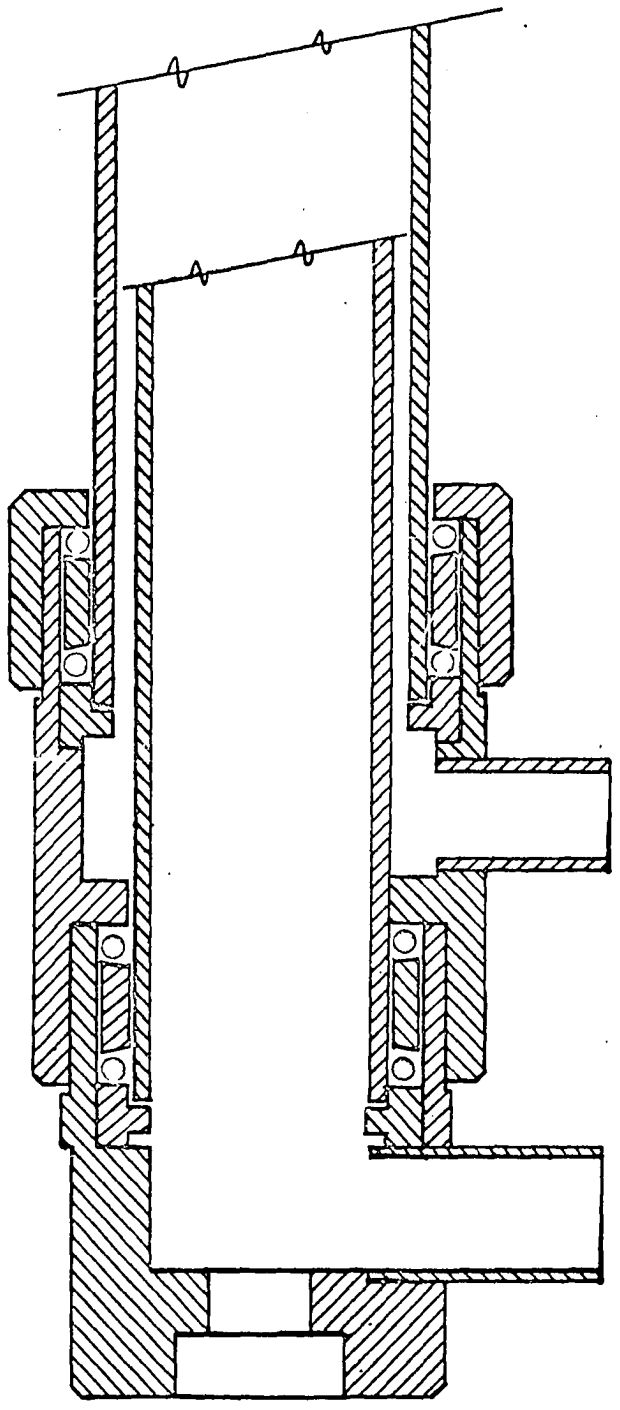

Figure 2. Base assembly

diameters and will allow operation at reduced pressure even if the quartz tubing has chips or cracks near the lower end. Figure 3 shows the complete plasma discharge chamber and the relative positions of the load coil and discharge.

Aerosol Generator

Several sample introduction systems have been examined by which samples could be added to the discharge in a continuous, reproducible, and variable manner. Solutions were chosen rather than powders since the former can be diluted, mixed, and generally handled much easier than powders. Powders could be an advantageous form in some situations, however.

A Beckman aspirator (Beckman Instruments, Inc., Fullerton, Calif.) was tried first, but the high volume of gas required (about 2 to 3 1/min) and the very high exit velocity of the gas disrupted the discharge. Next, the aspirator used by Lauterbach, Hayes, and Coelho (46) was tested and produced a very fine mist at low gas flow rates but had too low a solution flow rate to be useful.

The aspirating system selected was an ultrasonic design very similar to that of West and Hume (47). The ultrasonic system produces an aerosol of solution completely independent of gas flow and thus is ideally suited for a plasma. Because ultrasonic atomization is seldom employed in analytical chemistry, a brief review of the background theory will be presented.

When sonic waves are transmitted through a liquid and meet a surface, ripples form on the interface in a crisscrossing pattern. If the sonic

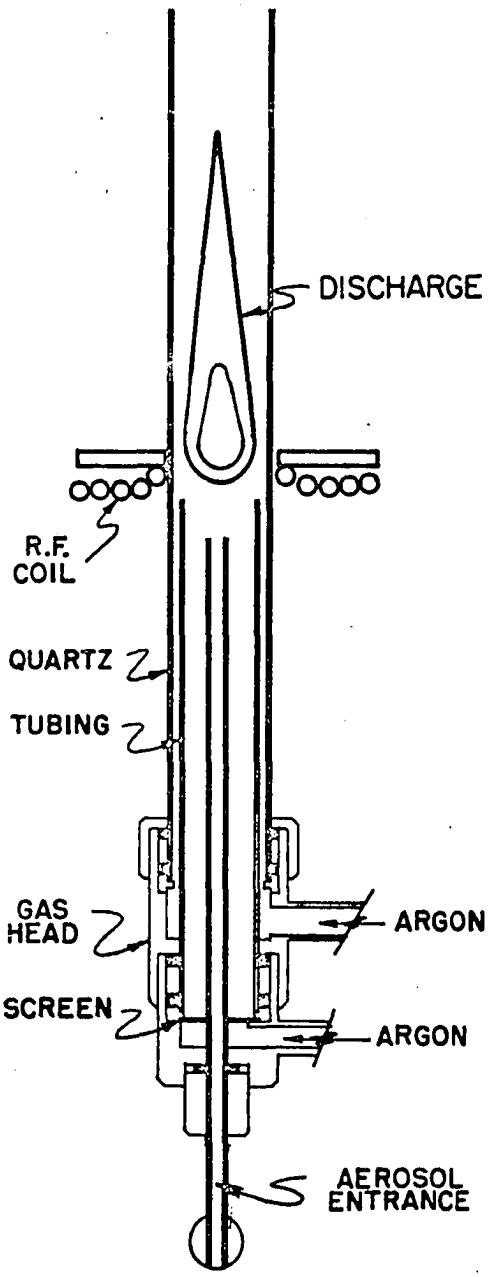

Figure 3. Plasma discharge chamber

intensity is sufficiently high, these intersecting ripples will break away from the surface and form small droplets. The size of the droplets is related to the wave-length of the ripples, which in turn is related to the frequency of the sonic waves. Under ideal conditions, the median droplet diameter has been experimentally determined by Lang (48) to be

$$D = 0.34 \left(\frac{8\pi\sigma}{\rho F^2}\right)^{1/3}$$

where σ = surface tension,

ρ = density of liquid, and

F = frequency of exciting sound.

The frequency of 870,000 cps employed in this work yielded a calculated median droplet diameter of 5 μ with aqueous solutions. This particle size is easily carried by a slow flow of gas and will not wet the surfaces of connecting ductwork.

Focusing systems are commonly used with ultrasonic devices in order to achieve the necessary power density without excessive power requirements or unnecessary heating problems. The most efficient focusing system is a curved or mosaic transducer, but the expense is seldom warranted. Reflectors are also quite efficient and can handle high power densities, but the required parabolic or compound surfaces are difficult to make. Lenses are the simplest focusing system since a plano-concave shape is easy to machine and easy to attach to a flat transducer. Lenses, however, may suffer from reflection losses at interfaces and may over-heat and damage themselves or the transducer.

Nevertheless, a lens focusing system was chosen for this study because of the low operating power, and it contributed to the simplicity of the design. When a material is chosen for the lens, the efficiency of sonic transmission into and out of the lens must be carefully considered.

The transmission of sound at normal incidence through a plate (49, p. 260) is

$$T_E = \frac{1}{1 + \left(\frac{M^2-1}{2M}\right)^2 \sin^2\left(\frac{2\pi d}{\lambda_p}\right)}$$

where T_E = energy-transmission coefficient,

M = impedance ratio of plate to medium

$= \frac{\rho_p C_p}{\rho_o C_o}$ where ρ = density

C = sound velocity,

d = plate thickness,

λ_p = wavelength of sound in plate

$= \frac{C_p}{F}$ where F = transducer frequency.

Thus, perfect transmission is achieved whenever $M = 1$ or $d = \frac{n\lambda_p}{2}$ where n is an integer. When a lens system is designed, it is impossible to keep $d = n\lambda_p/2$, so M must be kept small. Yet, the lens material must be sufficiently different in sonic velocity than the surrounding medium so that focusing can be achieved with a reasonable curvature. Plexiglass lenses in conjunction with water have the desired properties of a low impedance ratio ($M = 2.1$) and a moderate refractive index ($n = 1.8$). Data on other

materials and combinations can be found in the literature (50, 51). A general discussion on ultrasonic lenses and transmission plates has been written by Ernst (52), and focusing systems are discussed by Hueter and Bolt (49, p. 263).

The Plexiglass lens used in this study had a diameter equal to the diameter of the transducer housing and a radius of curvature of 3.6 cm. The focal length of an ultrasonic lens (49, p. 265) is $f = \frac{Rn}{n-1}$ where R = radius of curvature and n = refractive index, and this lens has a focal length of 8.1 cm. The transducer-lens assembly is cemented together and held in the bottom of the focusing chamber, as shown in Figure 4. The sonic energy passes through the Mylar bottom of the sample container and is focused at the surface of the sample solution.

The aerosol produced in the sample container is carried upward by a flow of argon and any minor fluctuations in aerosol production are smoothed by the baffles. A polyethylene ring floats on the surface of the sample solution to prevent major surface disturbances. The production rate of aerosol is about 0.3 ml/min, and 0.03 to 0.24 ml/min can be carried smoothly out of the aerosol generator by 0.3 to 0.9 l/min of argon. The aerosol is added to the discharge via a small central tube which is connected to the outer ball joint in Figure 4.

The ultrasonic aerosol generator has proven to be a reliable device and possesses several important advantages. Because no small orifices exist in the system, high concentration solutions can be employed without fear of clogging. In fact, even emulsions can be utilized as long as the

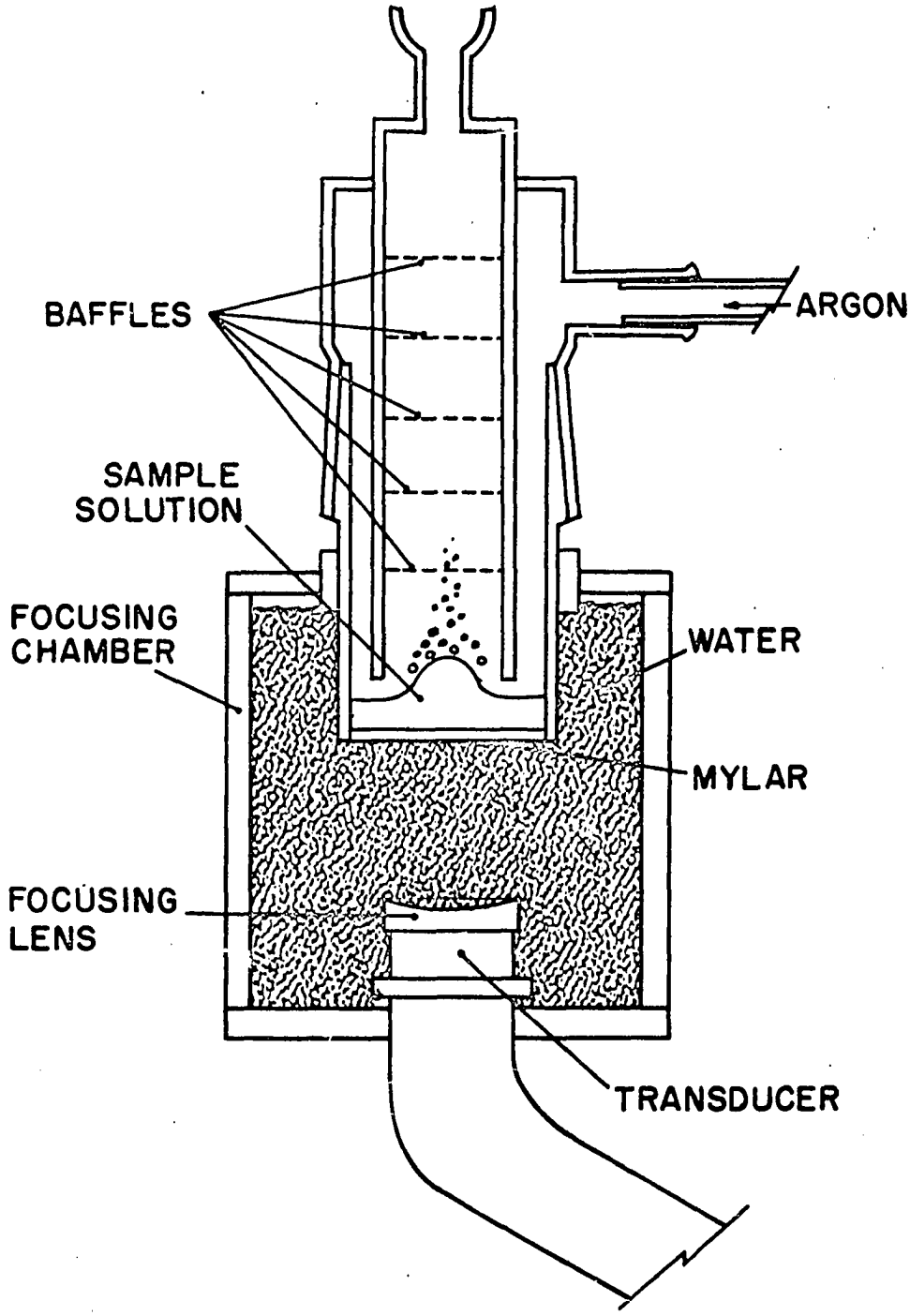

Figure 4. Ultrasonic atomizer

viscosity does not become too high. Thus, solids could be analyzed by preparing a fine powder of the sample and emulsifying the powder with water and an appropriate surface-active agent. The construction materials of the aerosol generator allow acids, bases, or other solvents to be used without corrosion problems. Thus, the ultrasonic system is a very versatile device and is an ideal companion for the plasma.

An example of the versatility of the ultrasonic aerosol generator--plasma combination is the possibility of direct atomization and analysis of molten steel. Ultrasonic energy could be focused at the surface of the molten steel as the steel leaves the blast furnace. The resulting aerosol of steel droplets could then be carried into the discharge by a flow of gas. The induction-coupled plasma would vaporize the steel, excite the atomic species, and allow the spectral analysis of the various components. Many technical problems obviously exist because of the high temperatures involved, but the attractiveness of the very high-speed analysis makes this approach worth investigation.

Spectroscopic Apparatus

Two types of spectroscopic equipment have been used to observe the plasma. The first reported studies (37) employed a Wadsworth spectrograph. The films obtained with this instrument revealed the manner in which the emission intensity of various species changed with height in the discharge, and also yielded many detection limits. The atomic absorption work, the quantitative emission studies, and further determinations of detection limits were performed with an Ebert scanning spectrometer equipped with a photomultiplier detector which was coupled to a strip-chart recorder.

The optical system for emission studies employed a simple lens system which focused the desired portion of the plasma on the slit of the monochromater. Atomic absorption required a more complex optical system as shown in Figure 5. The light emitted from the hollow cathode lamp was rendered parallel by the first lens and passed through the discharge. The multipass system reflected the beam and caused it to pass through the discharge two additional times, whereupon the second lens focused the beam on the slit. A mechanical chopper intersected the beam before the light passed through the discharge so the photomultiplier received an alternating signal from the primary source and a constant signal from the discharge. Only the AC signal was amplified and displayed on the strip-chart recorder. The recorder scale could be expanded about three-fold by appropriate adjustment of the zero and gain controls to allow more accurate background measurement.

The details of all the experimental facilities described here are summarized in Table 2.

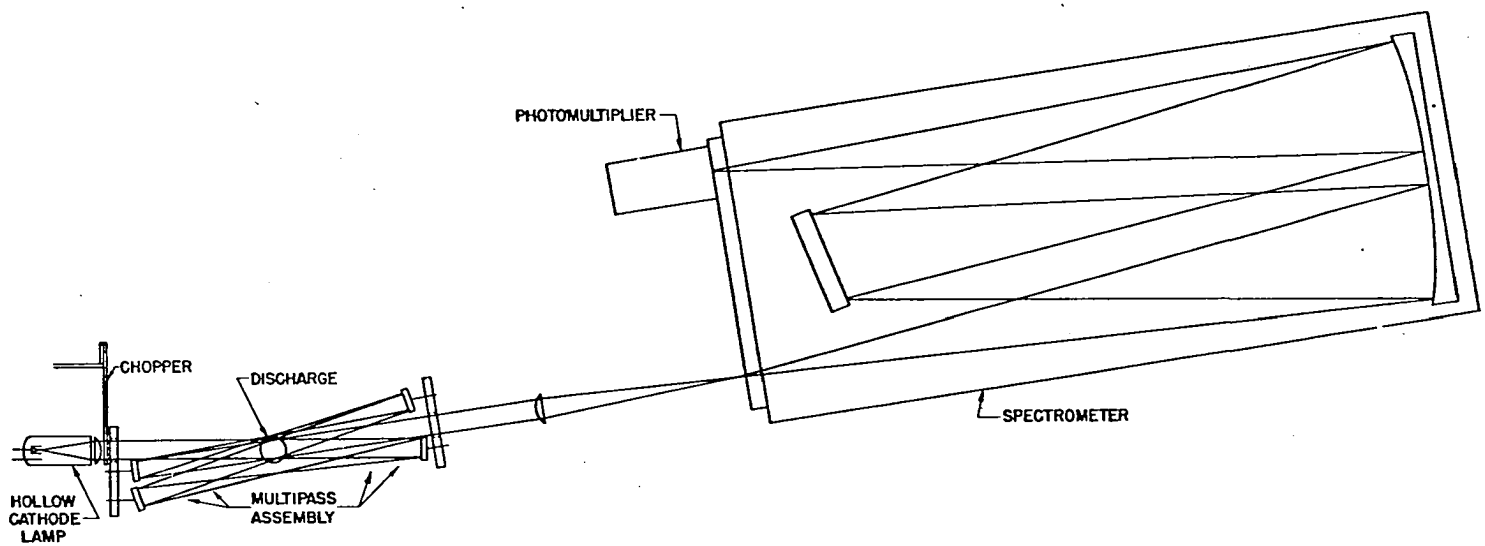

Figure 5. Optical system for atomic absorption studies

Table 2. Summary of experimental facilities

Plasma	
Power supply	Lepel High Frequency Laboratories (Woodside, N. Y.) Model T-5-3-MC-J-S generator; 3.4 mc frequency; 5 kw nominal output; choke-input ripple filter added using 1.0 henry choke and 2 microfarad capacitor.
Coil	Lepel pancake-concentrator type, 5-turn.
Coolant tube	Clear fused quartz; 22 mm id, 24 mm od; 22 cm total length, extending 11 cm beyond coil for emission studies; 19 cm total length, extending 8.2 cm beyond coil for absorption studies.
Plasma tube	Clear fused quartz; 16 mm id, 18 mm od; 12.5 cm total length, terminating 17 mm below top of concentrator ring; centered within coolant tube by four "feet" located 3 cm from open end.
Aerosol tube	Quartz; 5 mm id, 7 mm od, terminating 4 mm below end of plasma tube.
Base	Brass, double O-ring seals on each quartz tube; optional screen to insure laminar flow.
Flow rates to discharge	Coolant: 22 l/min of Ar Plasma: 0.4 l/min of Ar Aerosol: 0.5 l/min of Ar which carried 0.12 ml solution/min for qualitative work; 0.3 l/min of Ar which carried 0.05 ml solution/min for quantitative work.
Ignition	Graphite rod, not grounded; lowered into high field region until plasma is formed, then withdrawn.
Aerosol generator	
Power supply	Siemens (Siemed Inc., Hinsdale, Ill.) Sonostat 631; 12 watt output from transducer; 870 kc frequency.
Lens	Acrylic plastic (Plexiglass), planoconcave; 8 cm focal length; attached to transducer with Eastman 910 cement.

Table 2 (Continued)

Aerosol generator	
Sample container	Inner glass joint, Ⓣ 50/50, with 0.003" Mylar bottom; 10-25 ml capacity.
Aerosol chamber	Borosilicate glass (Pyrex) tube, 28 mm od, 18 cm long, with five polyethylene baffles, sealed into Ⓣ 50/50 outer glass joint.
Spectroscopic apparatus	
Monochromaters	Jarrell-Ash (Boston, Mass.) 1.5 meter Wadsworth Model 78 spectrograph with 590 rulings/mm grating and 11 Å/mm reciprocal linear dispersion; also: Jarrell-Ash 0.5 meter Ebert Model 82000 scanning spectrometer with 1180 rulings/mm grating blazed for 5000 Å and 16 Å/mm reciprocal linear dispersion; first order employed throughout.
Emission studies	Both monochromaters used: Wadsworth for survey work and first detection limits; Ebert for later detection limits and quantitative studies.
External optics	Six mm portion of discharge observed with center measured from top of concentrator ring; field lens and slit lens focused image on collimator of Wadsworth; single field lens focused image on slit of Ebert.
Slit	Fifty microns wide and 16 mm high on Wadsworth; 25 μ wide and 6 mm high on Ebert.
Detector	Kodak SA-3 or 1-N film, 35 mm, on Wadsworth; EMI 6255B photomultiplier (Electra Megadyne Inc., North Hollywood, Calif.), operated at 1100 volts on Ebert. Photomultiplier signal amplified with Keithley Model 410 Micro-microammeter and recorded on Leeds and Northrup Speedomax G 10 mv recorder with 1 sec response.
Absorption studies	Ebert spectrometer used by resting on wavelength of peak intensity.

Table 2 (Continued)

Spectroscopic apparatus	
Primary source	Commercial hollow cathode lamps from Westinghouse Electronic Tube Division (Elmira, N. Y.) and Ransley Atomic Spectral Lamps (Melbourne, Australia); operated by custombuilt DC power supply.
External optics	Primary radiation mechanically chopped at 13 cps and passed three times through discharge as parallel beam using four, back-surface, quartz mirrors of 14 cm focal length aligned as shown in Figure 5; portion of discharge traversed by primary radiation extended from 84 to 105 mm above core, 10 mm wide; image focused on slit by field lens.
Slit	Fifty microns wide and 6 or 10 mm high, depending on size of hollow cathode.
Detector	EMI 6255B photomultiplier operated at 1600 volts. Signal coupled to 13 cps amplifier of Perkin-Elmer Model 13 infrared spectrophotometer and recorded on its Leeds and Northrup Speedomax 10 mv recorder with 2 sec response.

OBSERVATIONS AND RESULTS

The induction-coupled plasma has the general appearance of a very bright flame with three regions or zones. The core or first region, as outlined in Figure 3, is centered at the top of the concentrator ring, and is about 8 mm in diameter, 25 mm long, non-transparent, and very brilliant. The core fades into the second region which is about 16 mm in diameter and about 75 mm long (depending to a great degree on the length of the coolant tube and whether or not aerosol is being added). The second region is also bright but slightly transparent. The third region or tailflame is distinctly separated from and extends about 150 mm above the tip of the second region. When the plasma is supported by pure argon, the tailflame is barely visible because the strong argon emission lines are outside the range of sensitivity of the eye. The tailflame assumes typical flame colors when solutions are added to the plasma.

The radiation from the core includes an intense continuum extending from about 3000 to 5000 Å which apparently arises from recombination and perhaps cyclotron radiation. The intensity of the continuum is sharply reduced in the second region and is negligible in the tailflame. A fairly well-developed spectrum of neutral argon is emitted from the core and second region but only two Ar II lines (4806 and 7589 Å) have been observed and these were weak even from the center of the core. The stronger Ar I lines are weak but still detectable in the tailflame more than 70 mm above the tip of the second region. Because these lines have excitation

potentials of 13.0 to 14.5 ev, a significant concentration of argon atoms in the metastable state probably exists in the tailflame.

When an aqueous aerosol is introduced into the discharge, the overall intensity of the plasma is reduced somewhat and the expected hydrogen Balmer-series lines and the 3064 Å OH band system appear in the spectrum. The hydrogen lines are strong and quite broad in the core, but become sharper and weaker in the second region, and disappear entirely high in the tailflame. The OH band head at 3063 Å is of moderate and relatively constant intensity throughout all three regions. The other OH band heads are weak or not visible in a normal exposure of the emission spectrum.

The portion of the tailflame which extends beyond the coolant tube emits band systems of O_2, N_2, NH, and N_2^+ in addition to OH. When the coolant tube is short (e.g., Greenfield, Jones, and Berry (36)), the second region also extends into the atmosphere and these band systems, especially N_2^+, becomes considerably more intense.

The emission spectra of these regions are illustrated in Figures 6, 7, 8, and 9 for plasmas of pure argon and of argon plus water. Figures 6, 7, and 8 represent the core, the second region, and the tailflame at 4, 45 and 90 mm above the concentrator ring, respectively. Figures 8 and 9 both illustrate the emission of the tailflame at 90 mm above the core, but Figure 8 spectra were recorded with a coolant tube which extended 110 mm beyond the core while the Figure 9 spectra were obtained with an 82 or 53 mm coolant tube as noted. Shortening the coolant tube is seen to quench the spectrum of argon and enhance the molecular band systems of OH, NH, and N_2^+, although this effect is not significant with the 82 mm tube.

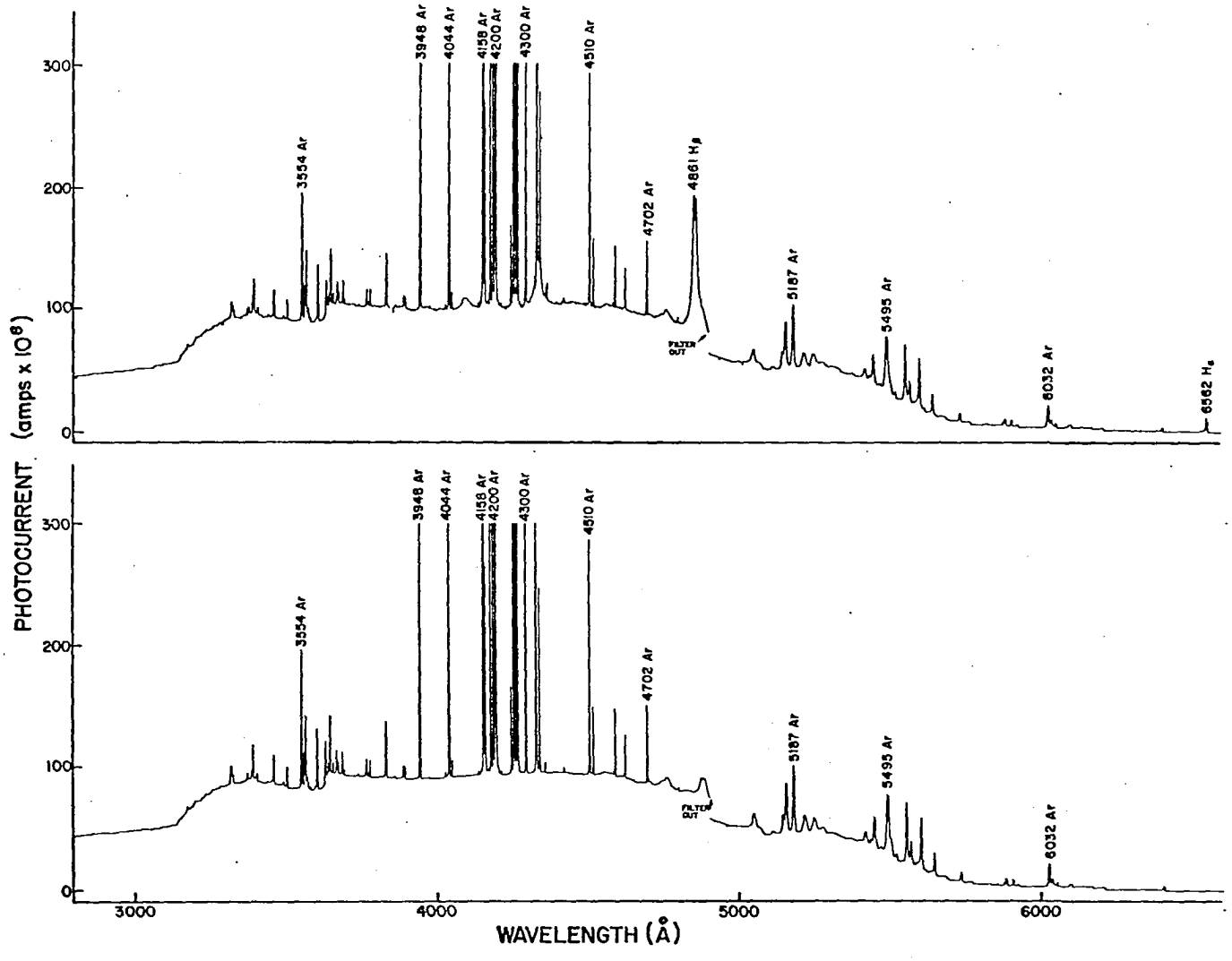

Figure 6. Emission spectra from core region of argon (lower) and argon-water (upper) plasmas

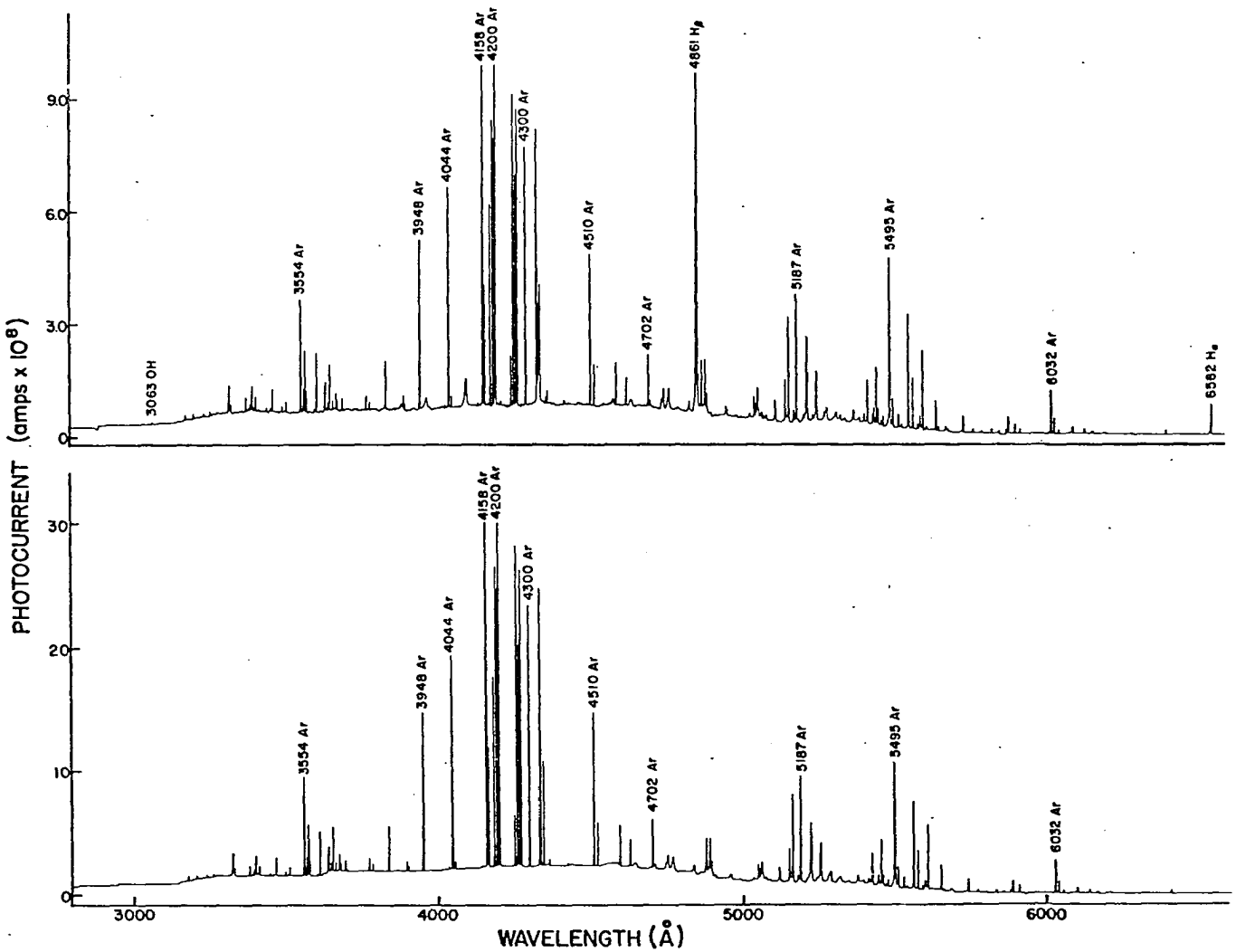

Figure 7. Emission spectra from second region of argon (lower) and argon-water (upper) plasmas

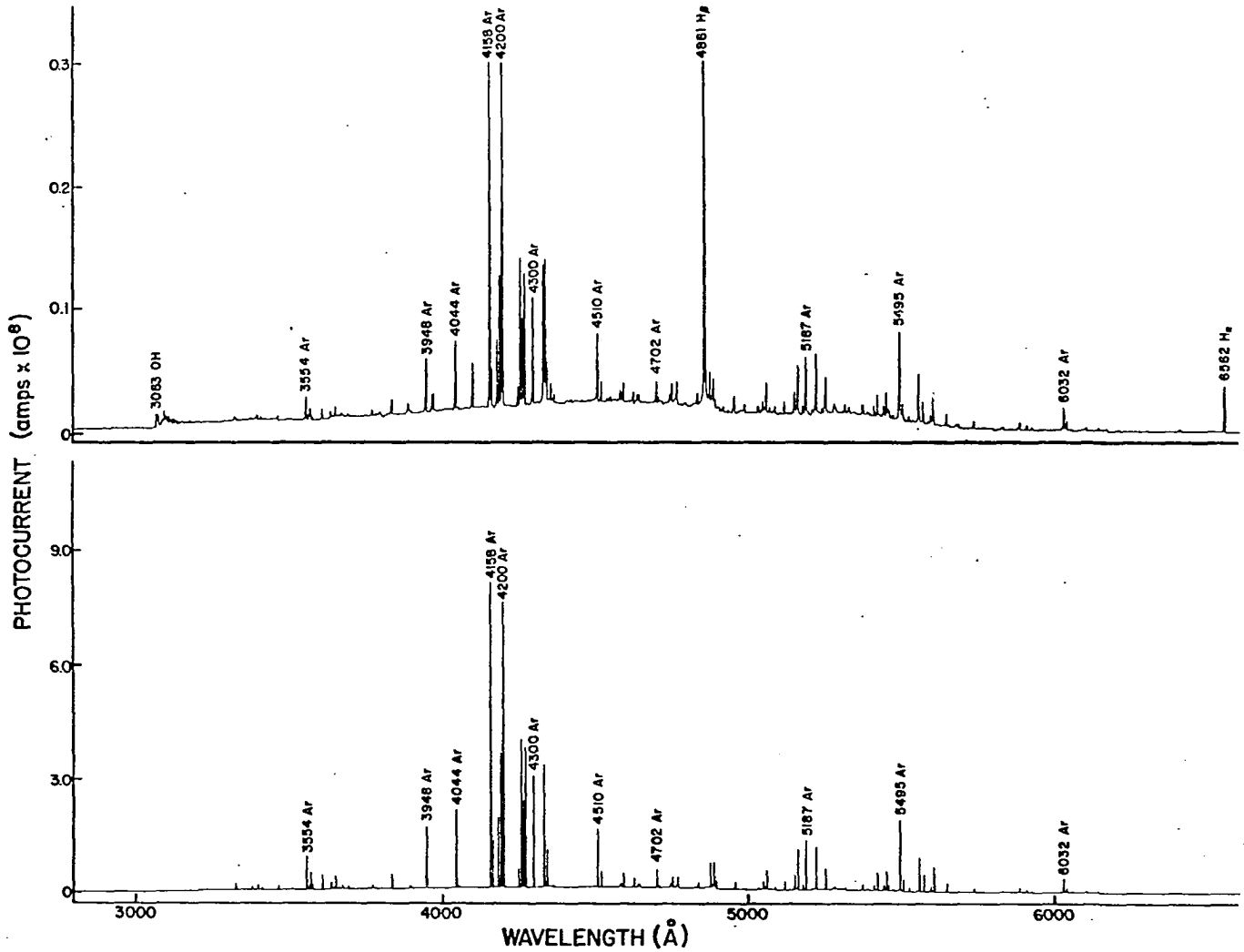

Figure 8. Emission spectra from tailflame of argon (lower) and argon-water (upper) plasmas

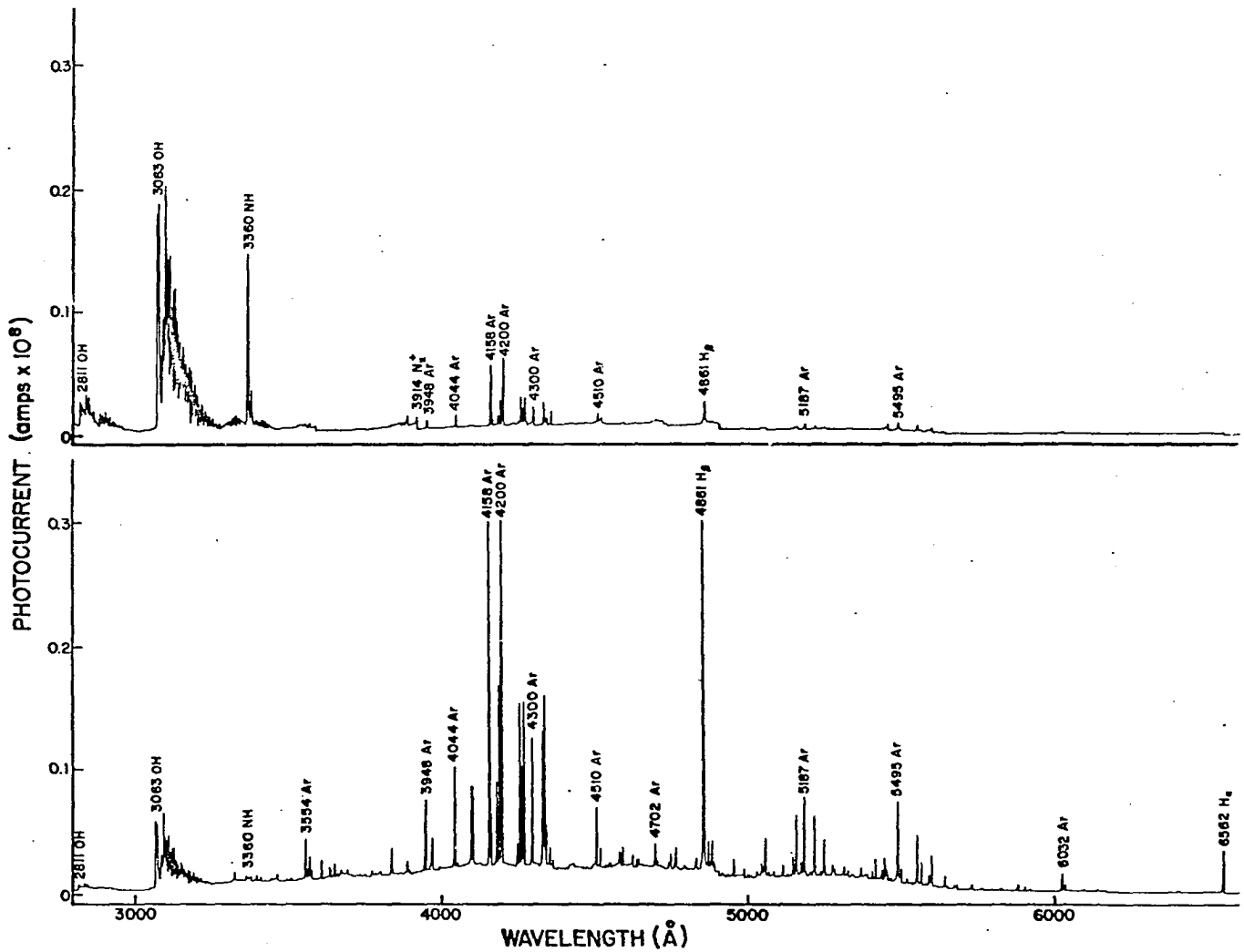

Figure 9. Emission spectra from tailflame of argon-water plasmas with 82 mm coolant tube (lower) and 53 mm coolant tube (upper)

The application of induction-coupled plasmas as spectrometric sources is fairly obvious in view of the continuous and stable manner of operation of the discharge. The development and adaptation of an ultrasonic aerosol generator to the plasma has permitted the discharge to be utilized in much the same manner as a flame. In fact, several distinctive features of the plasma suggest that it may be superior to combustion flames in both emission and atomic absorption spectroscopy. First, the much higher temperature and longer residence time of particles in the plasma should lead to a greater degree of conversion of the aerosol to free atoms. Second, greater control can be exercised over the chemical environment in plasmas than in flames. Thus, the lifetime of free atoms in the plasma may potentially be extended by providing an optimal chemical environment. Third, the very high temperature core region, through which the sample must pass, should minimize the depressant effects of "chemical" interferences (i.e., formation of stable refractory compounds by the element being studied), which are common in flames. Greenfield, Jones, and Berry (36) have already demonstrated that the depressant effect on calcium emission by phosphate or aluminum ions is virtually eliminated in the tailflame of their plasma. Fourth, the background radiation emitted by the tailflame of an argon plasma fed by an aqueous aerosol is markedly less than that of combustion flames, especially those which burn hydrocarbons. Thus, the photomultiplier noise arising from the irradiation of the detector with uninterrupted background radiation (which is proportional to the square root of the light intensity) should be markedly less for a plasma than for hydrocarbon flames. Fifth, the much greater energy available in a plasma

gives it the potential capability of handling solid samples directly. Although we have not yet confirmed all of these expectations, the observations presented here demonstrate that induction-coupled plasmas are versatile and useful sources for both emission and atomic absorption spectroscopy.

Emission Spectroscopy

Initial observations of the discharge revealed that emission lines of foreign elements exhibit their best line to background ratio in the second region or tailflame of the plasma. The best ratio for neutral atom lines typically occurred in the tailflame approximately 90 mm above the core while most ion lines and high-energy neutral atom lines produced better ratios in the second region about 45 mm above the core. For most elements, however, the ratio did not change significantly between these two regions.

The ability of a spectral source to emit emission lines of elements at trace concentrations is an important indication of its analytical usefulness. The detection limits for a representative list of elements in aqueous solutions are presented in Table 3. Some of the data were obtained photographically and some photometrically but in both cases the detection limits represent that minimum concentration in solution which emits a detectable spectral line observable over the background.

Several conclusions can be drawn from the data in Table 3. Although only 0.12 ml of aerosol per minute passed through the discharge, the observed detection limits of many elements are comparable to the best reported

Table 3. Emission detection limits of elements

Element	Line (Å)	Detection limit (µg/ml) 45 mm	90 mm
Al	3961	3	3
As	2780	25	
B	2497	0.15	
Bi	2230	80	
	3067	50	
Ca	3933[a]	0.5	0.8
	4226	0.5	0.2
Cd	3261		20
Ce	4012[a]		100
	4186[a]		70
Cr	3578		0.3
	3593		0.4
	3605		0.5
	4254		0.6
	4274		0.7
Cu	3247	1.2	0.2
Fe	3440		4
	3581		6
	3719		3
	3734		6
	3737		3
	3745		6
Hf	2638[a]		20
	2641[a]		7
	2820[a]		7
	3505[a]		10
	3561[a]		5
	3682[a]		10
La	4086[a]	50	50

[a]Ion line.

Table 3 (Continued)

Element	Line (Å)	Detection limit (µg/ml) 45 mm	90 mm
Mg	2852	2	2
Mn	4030	2	1
Ni	3524		1
P	2535	3	
Pd	2476	7	
	3404	5	5
Pt	2659	20	10
	3064	30	30
Re	3460		3
Si	2516	3	
Sn	3034	50	50
Sr	4077[a]	0.15	0.15
	4607	0.09	0.09
Ta	2685	15	
Th	4019[a]	40	40
U	3584		50
	3670[a]		25
	3859[a]		50
W	4008	3	3
Zn	4810	30	
Zr	3391[a]	20	20
	3438[a]	15	15
	3496[a]	20	20

flame emission values (53, 54, 55). The easily excited elements (e.g., Ca, Sr) can be detected more easily in a flame, presumably due to excessive ionization in the plasma. The plasma, however, generally yields much better detection limits for elements with high excitation potentials (e.g., As, B, P, Zn), for elements which emit strong ion lines (e.g., Hf), and for elements whose strong lines coincide with one of the band systems prevalent in flames (e.g., Bi, Pt). The plasma can be expected to have useful sensitivities for virtually all elements and thus is an extremely versatile spectral source for quantitative analysis.

The ability of a spectral source to perform quantitative analysis requires both stability and reproducibility. The stability of the plasma is a function of the combined stabilities of the RF generator, the gas flow system, and the aerosol generator. Under typical operating conditions, emission lines of chromium, manganese, and aluminum were repeatedly scanned and their intensities measured photometrically. The relative standard deviations of the intensities were 1.9%, 1.7%, and 1.1% respectively.

The ability to reproduce intensities when the same solution is repeatedly analyzed requires careful duplication of the operating conditions which include the plate current and grid current on the RF generator, the power output of the ultrasonic generator, and the flow rates of argon in the three flowmeters. The low concentration, water-base, nickel-chromium solution used in the subsequent experiment was analyzed independently four

times and a relative standard deviation of 5% and 6% for the nickel and chromium intensities, respectively, was found.

The reproducibility of the system between different solutions is thus adequate to demonstrate the usefulness of the discharge for quantitative analyses. The inert atmosphere in which excitation of foreign species occurs and the very high temperature of the core region through which the samples must pass suggest that the induction-coupled plasma should minimize matrix effects and chemical interferences. Figure 10 illustrates analytical curves for the determination of nickel and chromium in aqueous solutions in various base materials. The straight lines were drawn through the points obtained for pure solutions of only nickel and chromium. The iron and copper base solutions were NBS standards 101E and 157, respectively, appropriately diluted or fortified, while the aluminum, cobalt, and magnesium base solutions were artificial samples. The concentration of the base material was 1/2% or 1% by weight in all solutions.

Some scatter is noted among the points in Figure 10, but the overall conclusion must be that the plasma definitely is capable of performing quantitative analyses. The data also suggests that magnesium and perhaps aluminum slightly enhance the intensities of nickel and chromium, and that iron may slightly suppress their intensities, but no major matrix effects are indicated. This means that a single analytical curve obtained with pure solutions can suffice for a wide variety of samples--a most desirable goal for any spectral source.

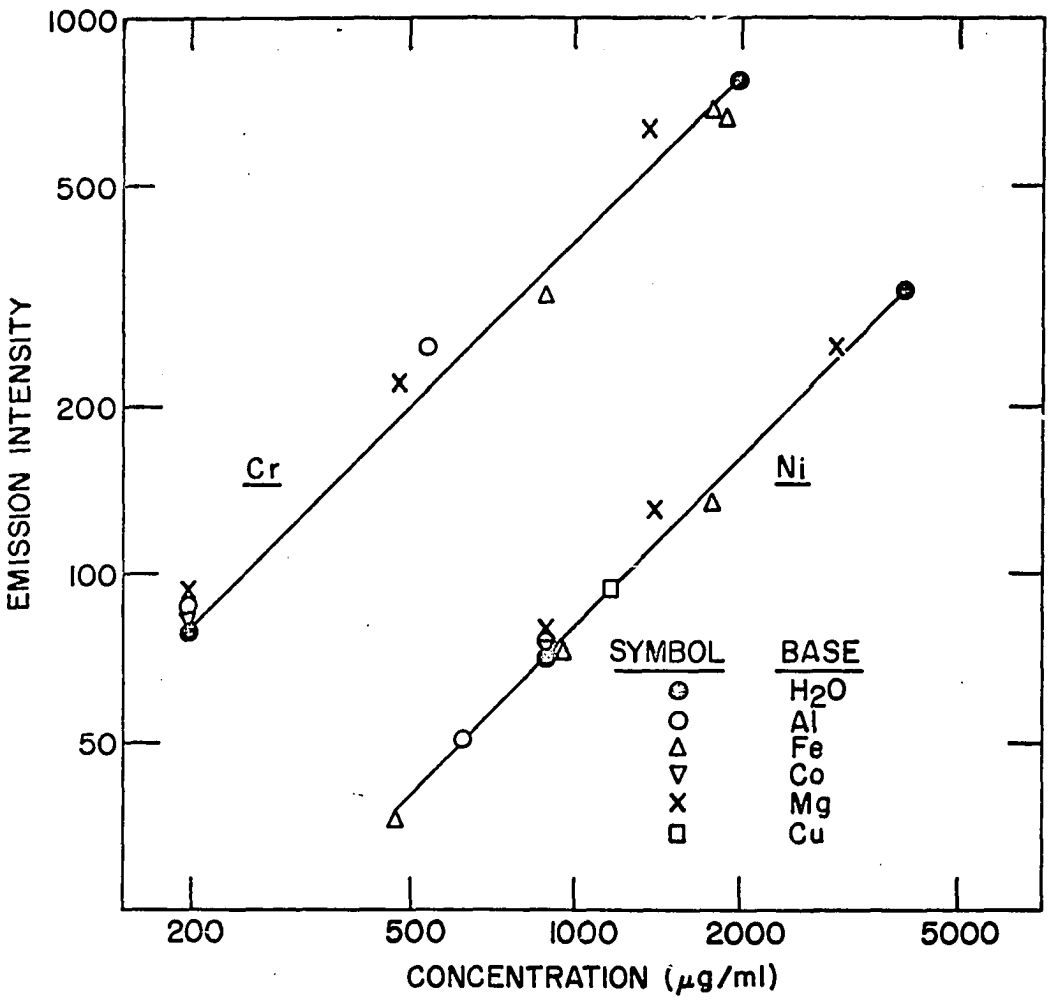

Figure 10. Analytical curves of nickel and chromium in various matrixes

Atomic Absorption Spectroscopy

Absorption spectroscopy of all types requires a primary source of radiation, an absorption cell which contains the sample to be analyzed, and monochromator-detector assembly to measure the wavelength and degree of absorption. The absorption cell in atomic absorption work is commonly a combustion flame which is fed solutions containing the elements to be analyzed. Flames are rather inefficient converters of samples to atomic vapor, however, and necessarily consist of a reactive atmosphere which may cause the formation of refractory oxides (56). Thus, the burner-atomizer system is the "weak link" in atomic absorption spectroscopy.

The distinctive features of the induction-coupled plasma which were discussed earlier suggest its application as an absorption cell. Of special importance for this purpose are the high temperature and the inert atmosphere of the discharge which produce and maintain the required atomic vapor.

The experimental arrangement for the absorption studies is shown in Figure 5. The tailflame of the discharge which extended beyond the end of the coolant tube was observed by the spectrometer. The occurrence of additional band systems in the background spectrum or chemical reactions due to air mixing with the discharge was found to be negligible, as shown by comparing Figure 8 Ar-H_2O with Figure 9 Ar-H_2O (82 mm tube). When the discharge is observed just beyond the coolant tube, no reflection or scattering losses of the primary radiation occurred and a significantly better signal-to-noise ratio was obtained. The addition of the three-pass

mirror system caused a slight loss due to reflections but the three-fold gain in sensitivity more than compensated for this.

Typical detection limits and sensitivities observed for elements in aqueous solution are given in Table 4. The detection limit is defined as the concentration in solution required to produce an absorption signal equal to twice the standard deviation in the background fluctuation. The sensitivity is that concentration required to produce 1% absorption.

Several significant conclusions can be drawn from the data presented in Table 4. Although only 0.12 ml of aerosol per minute passed through the plasma, the observed detection limits and sensitivities for the strong monoxide-forming elements (Al, Nb, Ti, W, Y) are comparable to the best reported flame absorption values (57, 58). Since aerosol flow rates for flames are commonly an order of magnitude greater, the comparable sensitivities observed indicate that either the degree of free-atom formation in the plasma is considerably greater or monoxide formation is greatly reduced.

The data in Table 4 also show that good sensitivities are observed for absorption lines in the 4600 to 5200 Å spectral region. This wavelength interval is usually avoided when flames are used as absorption cells because the strong C_2 band emission increases the DC noise component of the photomultiplier detector. The ability of the discharge to use aqueous solutions rather than organic solvents thus makes a greater portion of the optical spectrum available for analyses.

Table 4. Detection limits and sensitivities of elements

Element	Line (Å)	Detection limit (µg/ml)	Sensitivity (µg/ml for 1% absorption)
Al	3092	1	1
	3944	1	0.9
	3961	0.6	1
Ca	3933[a]	0.7	1
	4226	0.2	0.6
Mg	2852	0.06	0.1
Nb	3535	100	50
	4058	40	60
	4079	40	70
	4100	30	60
Re	3460	30	130
Ti	3635	15	20
	3642	7	20
	3653	9	20
	4667	5	15
	4681	9	15
	5171	5	20
W	4008	3	10
	4659	3	9
V	3184	2	3
Y	3327[a]	20	40
	3620	10	40
	3710[a]	20	30
	4077	20	40
	4102	10	40
	4643	10	40

The zone of the plasma examined in this study has virtually no band or continuum emission even when an aqueous aerosol is added. Figure 9 (82 mm tube) reveals that only the 3064 OH system shows significant intensity. It is worth noting that the hollow cathode emission lines employed in this investigation produced photocurrents from 8 to 200 times greater than the band head at 3063 Å.

Our expectations that chemical interferences would be markedly reduced in the plasma were confirmed, as shown in Figures 11 and 12, by the behavior of calcium in the presence of phosphate or aluminum ions. In contrast to the sharp depressive effect of these ions observed in flame absorption, the calcium absorption in the plasma shows a slight but surprising increase. Although this apparent enhancement invites speculation, it seems advisable to defer discussion until more definitive information on the various processes occurring in the plasma is available.

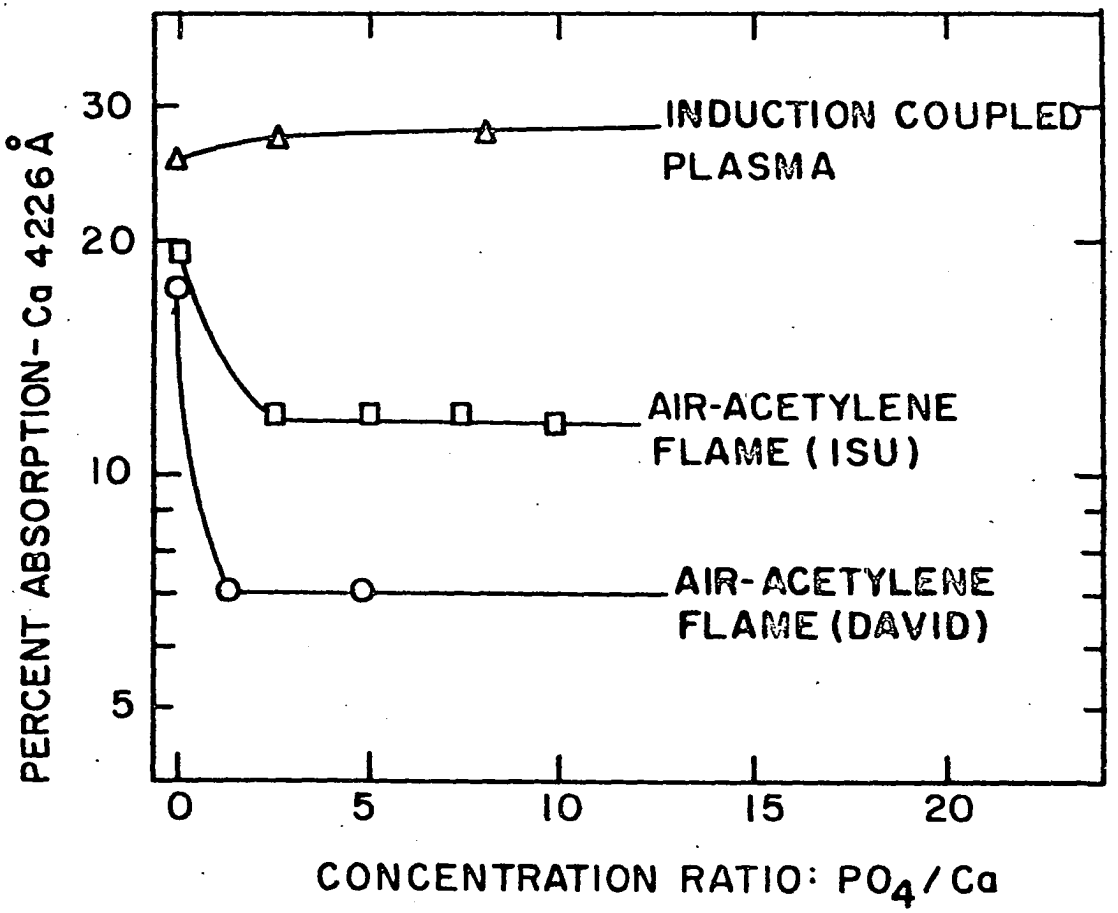

Figure 11. Interference effect of phosphate on calcium absorption

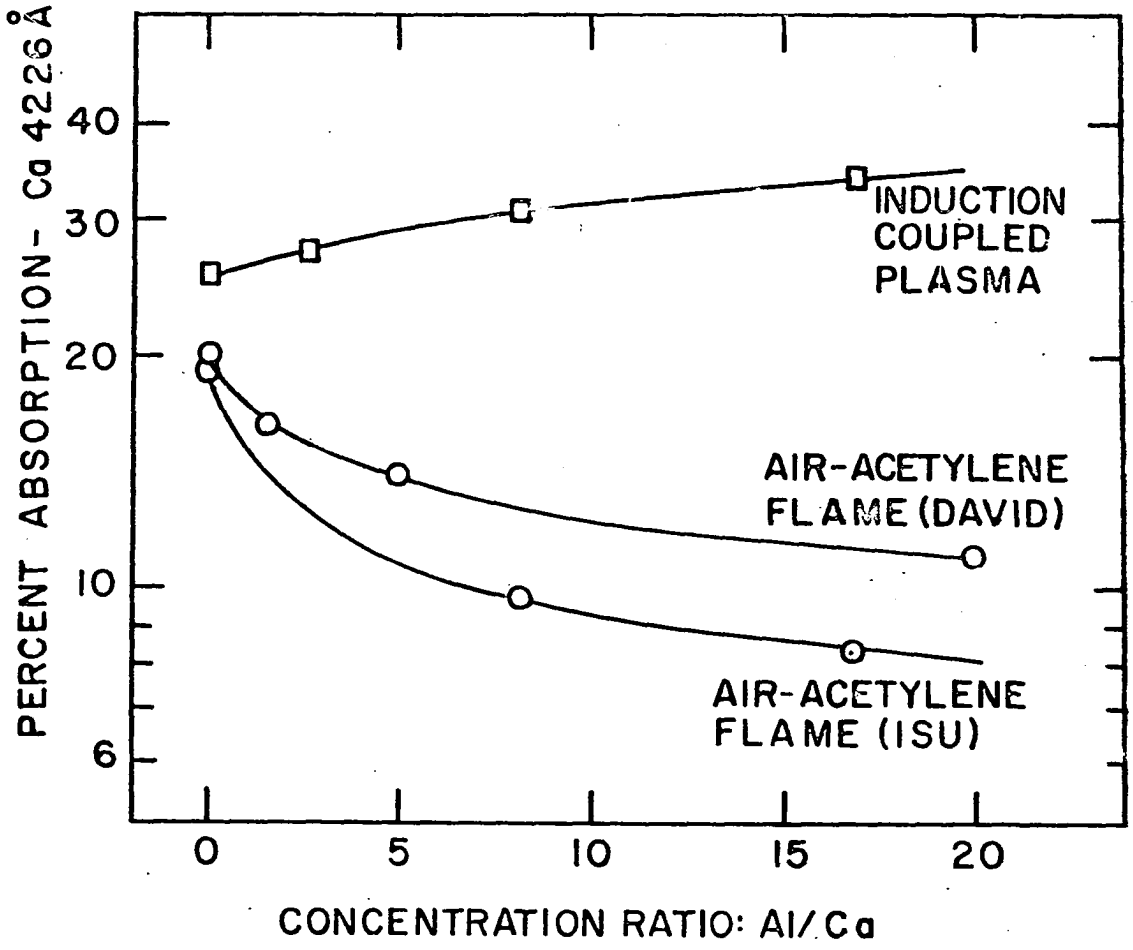

Figure 12. Interference effect of aluminum on calcium absorption

DISCUSSION

The induction-coupled plasma is obviously a very useful and versatile spectral source. It has the advantage of being a continuous, time-stable source, as is a flame, but it is not as seriously limited in temperature or excitation energy. In addition, the inert environment provided in the plasma for foreign elements prevents their destruction by chemical reaction. Thus, the discharge is very efficient in the production, maintenance, and excitation of atomic species. The detection sensitivities and the reduction of interelement effects reported here plainly demonstrate the value of this spectral source in emission and absorption spectroscopy, both qualitative and quantitative.

The ultrasonic aerosol generator, which is combined with the plasma, is equally versatile. Its ability to handle solutions of virtually any solute concentration, any degree of acidity or basicity, and even emulsions greatly increases the usefulness of the combined system.

The plasma does have some disadvantages, however. First, it is not as sensitive as a combustion flame for the easily excited elements (alkali metals and alkaline earths) although the sensitivity is adequate for many purposes. Second, the cost of the high-frequency generator and the inconvenience of the required electrical and water connections are a drawback. These difficulties are the same ones encountered with arc and spark discharges but not with flames. Three, the aerosol generator is also expensive and is rather bulky, although continuing development of this apparatus should decrease the size considerably. The current necessity of

disassembling and cleaning the aerosol sample container each time a solution is changed can probably be eliminated, too.

The appearance of five commercial devices in the last two years, including one specifically designed for spectroscopy, should stimulate research with the induction-coupled plasma and cause these disadvantages to be minimized or eliminated. Thus, future applications and further development of the discharge should lead to greater acceptance of this promising spectral source.

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