

# A Low-Power, Reduced-Pressure Inductively Coupled Helium Plasma Source for Atomic Emission and Absorption

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## INTRODUCTION

Although atomic emission, fluorescence, and absorption have been utilized in inductively coupled plasma (ICP) spectroscopy for plasma diagnostics and elemental determination, emission spectroscopy from argon ICPs has been the dominate technique in elemental analyses involving ICPs.<sup>1-3</sup> This is probably due to the numerous emission lines accessible in conventional ICP and the complexity of the instrumentation required for absorption and fluorescence measurements compared to the relatively simple instrumentation required for emission measurements.

This work utilizes a low power, reduced pressure helium ICP in a commercial flame unit as both an emission source and a reservoir of ground-state atoms for absorption. Helium was chosen as a plasma gas due to its high ionization potential and its concurrent ability to electronically excite most other atoms, especially the halogens. A low power, reduced pressure system was employed for several reasons. Since helium is so efficient at electronic excitation, low power was selected to help ensure that there were sufficient ground-state atoms for absorption to be practicable. A reduced pressure system excludes atmospheric interferences, reduces the number of collisions in the plasma, and, in the current configuration, provides a long optical path for absorption measurements.

Since the system operates at reduced pressure, sample introduction is accomplished using gaseous analytes in a flow injection system. The analytes chosen for this study were argon, arsine, Freon-116, and dichlorosilane.

## EXPERIMENTAL

A Perkin-Elmer 1100 flame atomic absorption system (Perkin-Elmer, Norwalk, CT) was interfaced with a low power, reduced pressure ICP system as shown in Fig. 1. The burner head was removed and a U-shaped plastic support was inserted into the burner to support the plasma torch. The plasma torch consisted of an approximately 6-in.  $\times$  1/2-in. Pyrex tube with quartz windows affixed to each end. Two 1/4-in. Pyrex arms were blown onto the main tube to serve as a gas inlet and vacuum outlet. The plasma torch was encompassed by a 20 turn load coil, which was connected to the plasma generator. The generator was based on a design by May and May,<sup>4</sup> and it has been described previously.<sup>5</sup> The generator was constructed in house for approximately \$100 and was operated at a constant forward power of approximately 15 watts, as measured at the generator, in this study. The actual power delivered to the plasma is certainly less than 15 watts, and it can not be easily estimated since neither the phase angle between the current and voltage nor the reflected power have been measured for this generator. The helium (commercial grade, Airgas, Inc.) carrier gas flowed into a six-port injection valve (Valco Instruments Co, Houston, TX) and then into the left-hand inlet of the plasma torch. The flow of the carrier gas was monitored by a Model 8112 mass flow meter (Matheson Gas Products). A small piece of vacuum tubing connected the plasma torch to the laboratory vacuum manifold on the right-hand side of the torch. The laboratory manifold consists of approximately 24 feet of 1/2-inch tubing, which is connected to a Trivac, Model D8A vacuum pump (Leybold Vacuum Products, Export, PA). The plasma was ellipsoidal, centered on the load coil, and occupied approximately one half of the torch length.

Samples were introduced through the six-port injection valve equipped with calibrated sample loops ranging from 10 to 1000  $\mu$ L. Argon was commercial grade (Airgas, Inc.). Arsine and dichlorosilane were purchased as certified mixtures in helium at 6.5% and 1.00% from Matheson Tri-Gas, and the Freon-116 at 1.08% in helium was purchased from Air Products. Sample flow was set at approximately 0.002 L min<sup>-1</sup> and was measured by a soap bubble meter.

The data were collected from the printer output of the Perkin-Elmer 1100 by a Visual Basic program written in-house. Initial optical alignment was accomplished with the instrument in a continuous mode using the 800.6 nm line of the argon fill gas from a hollow cathode lamp.

## RESULTS AND DISCUSSION

Initial studies were performed using argon as the sample gas. The 800.6 nm line was selected since it was present as a fill gas line in the hollow cathode lamp. This line was used for both emission and absorption studies. The absorption signal was optimized with respect to the carrier gas flow, lamp current, and sample loop size. Carrier flow was varied from 0.002 to 0.016 L min<sup>-1</sup> by increments of 0.002 L min<sup>-1</sup>, the lamp

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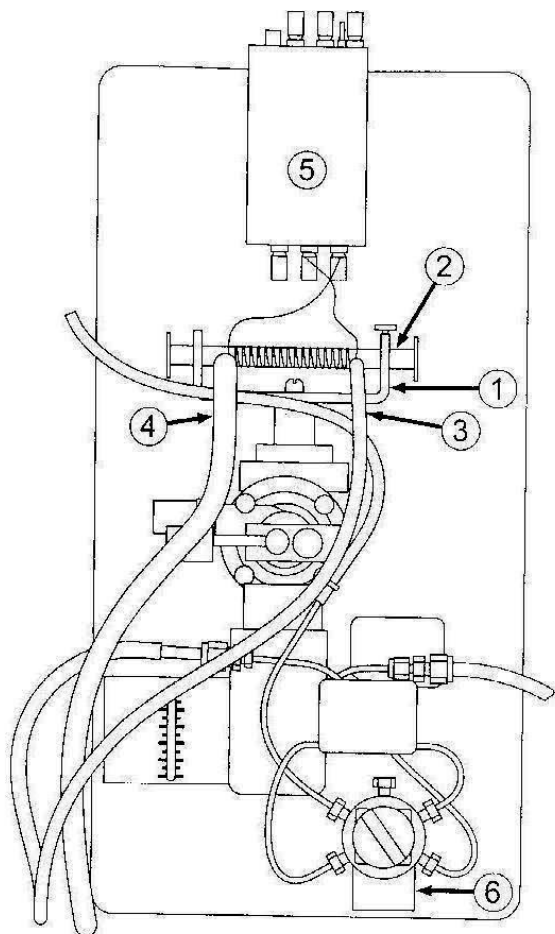


Fig. 1. Interface of the low power, reduced pressure ICP shown in its final configuration. (1) Plastic support, (2) plasma containment tube, (3) gas inlet, (4) vacuum outlet, (5) plasma power supply, and (6) injection valve. Note: Numbers 3 and 4 were switched in the initial configuration; the HCL is located to the left of the torch.

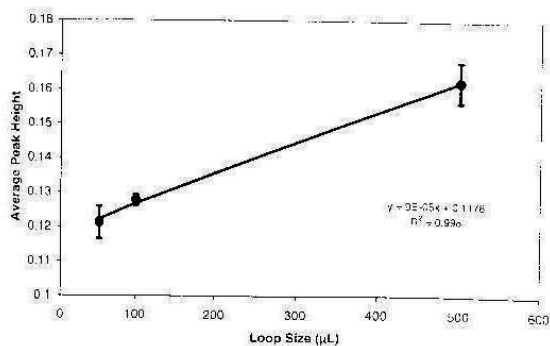


Fig. 2. Average absorption peak height versus sample loop size. Note: The non-zero intercept is present since no background correction was employed.

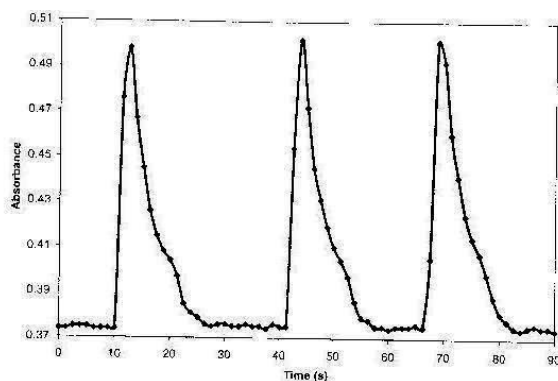


Fig. 3. Absorption signal obtained for three sequential injections of argon.  $\lambda = 800.6$  nm, lamp current = 7 mA, loop size = 100  $\mu$ L.

current was varied from 6 to 10 mA by 1 mA increments, and the loop sizes utilized were 10, 50, 100, 500, and 1000  $\mu$ L.

In these studies, the absorption signal dropped steadily with increasing flow rate. The initial rate of  $\sim 0.002$  L  $\text{min}^{-1}$  was optimal. The absorption signal increased linearly with loop size as shown in Fig. 2; however, no signal could be obtained at 10 or 1000  $\mu$ L. For the smallest loop the plasma could not be sustained, and at the largest size the plasma was quenched by the analytic injection. Each point represents three replicate injections. It is important to note that in order to obtain the data in Fig. 2 the plasma would have to be turned off and opened to atmosphere before the loop could be changed. The 100  $\mu$ L loop was chosen as optimal since it exhibited the smallest relative standard deviation for replicate injections, 1.2%. Lastly, lamp current was varied from 6 to 10 mA, and the absorption signal varied in a parabolic fashion with lamp current with a maximum at 7 mA. Figure 3 shows a typical absorption response from three replicate injections of argon, while Fig. 4 shows the emission response under similar conditions.

Detection limits were calculated from average peak heights and determination (10–15 points depending on the integration time) of the background signal prior to the peak. A  $3\sigma$  level was employed in the calculation.<sup>6</sup> The mass of gaseous atoms was calculated, assuming ideal gas behavior, from the loop

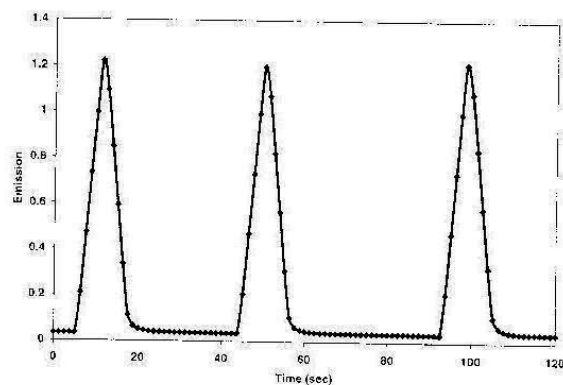


Fig. 4. Emission data obtained for three sequential injections of argon.  $\lambda = 800.6$  nm, lamp current = off, loop = 500  $\mu$ L.

TABLE 1. Detection limits obtained for various gases.

Analyte	$\lambda$ (nm)	Detection limits (ng)	
		Absorption	Emission
Argon	Ar, 800.6	29.5	3.78
Arsine	As, 193.7	9.61	176
	H, 656.3	N/A	0.30
Freon	F (bh), 519.3	N/A	1.72
	C (bh), 483.2	N/A	9.78
Dichlorosilane	Si, 251.9	3.00	0.70
	Cl, 754.7	N/A	1.60
	H, 656.3	N/A	0.13

volume, gas composition, and the prevailing laboratory temperature and pressure.

After the initial studies with argon were completed, similar studies were performed using the conditions for argon analysis with arsine, dichlorosilane, and Freon-116 mixtures in helium. In the case of the arsine mixture, absorption signals were obtained with an As hollow cathode lamp at 193.7 nm. Emission signals for As were obtained at the same wavelength without the hollow cathode lamp being energized. Detection limits were calculated as outlined earlier, and they are presented in Table 1. In the case of hydrogen emission from the arsine sample, only a large negative peak was observed at the hydrogen alpha (656.3 nm) and beta (486.1 nm) lines until the inlet and outlet lines were switched on the plasma tube. With the sample being introduced on the right-hand side of the plasma, closest to the detector, emission signals were obtained from the plasma for both hydrogen lines. The alpha line was used to calculate the detection limit in Table 1. At the conclusion of the arsine injection study, small shiny metallic deposits, probably arsenic, were observed on the inside of the plasma tube adjacent to where the load coil encompassed the tube. These deposits were easily removed by rinsing the tube with a dilute nitric acid solution.

In the case of dichlorosilane, absorption and emission signals were obtained for Si at the 251.9 nm line in a similar fashion. Once again, positive emission signals for hydrogen and chlorine (754.7 nm) were only obtained with the inlet and outlet lines switched as described previously. Signals were obtained and the detection limits were determined for the analyte wavelengths as shown in Table 1.

For Freon-116, hexafluoroethane, there are no elements present that are amenable to measurement by absorption. Carbon emission was monitored at 483.2 nm (bh) for these studies. In the case of fluorine emission, there were numerous possible emission lines and bands. In order to determine the prominent lines in the plasma, a spectrum was taken at a right angle using an Ocean Optics S2000 spectrometer (Ocean Optics, Inc., Dunedin, FL) with and without Freon-116 in the plasma. The two spectra were subtracted and the resulting spectrum is shown in Fig. 5. Two prominent peaks were noted at 519.3 and 501.5 nm; these were attributed to fluorine band heads and were investigated further. The 519.3 nm line produced the lowest detection limit.

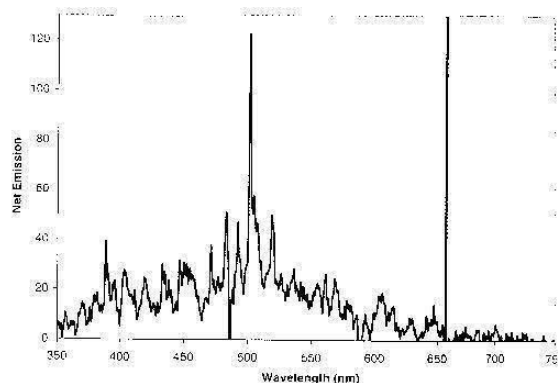


FIG. 5. Net emission spectrum obtained for a 100  $\mu$ L injection of 1% Freon R116. The background He plasma spectrum was subtracted.

## CONCLUSION

This work examined the feasibility of utilizing a low power, reduced pressure helium ICP as an inexpensive spectroscopic source for emission and absorption in a conventional atomic absorption instrument. The system was shown to be capable of obtaining absorption measurements for Ar, As, and Si and emission signals from Ar, As, H, Si, Cl, C, and F when analytes containing these elements were injected into the plasma. Detection limits under optimized conditions for argon were in the sub-microgram to sub-nanogram range based on peak height measurements. No attempt was made to obtain peak areas or correct for any background signals in the absorption measurements since the instrument was not equipped with background correction capability.

Although the system is rather crude in its current form, and numerous refinements could be made, it does show some promise as an inexpensive retro-fit to conventional atomic absorption systems for specialized analysis of certain gaseous samples. Based on this preliminary work, future studies of this system are probably warranted.

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