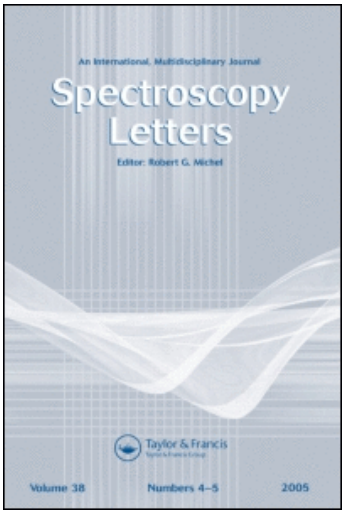

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An Active Nitrogen Plasma Atom Reservoir for Laser-Induced Ionization Spectrometry

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AN ACTIVE NITROGEN PLASMA ATOM RESERVOIR FOR LASER-INDUCED IONIZATION SPECTROMETRY

Key Words: Active Nitrogen, Laser-enhanced Ionization, Dual Laser Ionization

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ABSTRACT

A microwave-induced, atmospheric pressure active nitrogen plasma has been investigated as an atom reservoir for laser-induced ionization spectrometry. Discrete analyte samples were introduced into the active nitrogen plasma by a microarc atomizer. Both laser-enhanced ionization (LEI) and dual laser ionization (DLI) were carried out in the plasma plume that extended from the Beenakker cavity.

INTRODUCTION

Because of its interesting energetic properties, the active nitrogen plasma has been investigated as an alternative to the analytical flame as an atom reservoir for laser-induced ionization spectrometry. The laser-induced ionization techniques examined in

this study were laser-enhanced ionization (LEI) and dual laser ionization (DLI). Ionization from a laser-excited state proceeds by collisional processes in the former case and absorption of photons in the latter.

LEI spectrometry is among the most sensitive methods available for trace metal analysis. Detection limits reported for LEI[1-4] are comparable to those reported for laser-excited atomic fluorescence spectrometry [LEAFS].[5,6] LEI has several advantages over conventional spectroscopic methods, including nonoptical detection and an abundance of usable transitions within a relatively narrow spectral range which makes possible the excitation of several elements by using a single laser dye.[4]

LEI and DLI[7] may be viewed as complementary techniques and are similar in their implementation and methodology. LEI occurs whenever a laser is tuned to a resonance transition of an atom in a flame. Whether or not an additional photoionizing laser will supplement the LEI signal depends on how closely its wavelength matches the energy defect between the laser-excited level and the ionization potential of the analyte atom.[8] The atom reservoir is also an important consideration. Photoionization makes a greater contribution to the total ionization signal (i.e., current) in atom reservoirs where the rate of collisional ionization is relatively low, such as a hydrogen-oxygen-argon flame.[7,8] Photoionization of a laser-excited atom usually requires the addition of a second laser, but there are cases where a single laser may be adequate, or a third laser may be required.

Most of the laser-induced ionization studies, to date, have employed analytical flames as atom reservoirs. Flames are commonly used to desolvate and atomize samples for spectrometry. In addition, they provide effective collisional cells for LEI. However, spectroscopic techniques that employ flames can be limited by interferences associated with flame atomization and ioniza-

tion. This is most evident in laser-induced ionization techniques where group IA and IIA elements interfere with signal (i.e., ion) collection. These elements are easily ionized in the flame, resulting in the formation of a positive ion sheath which shields the cathode and, consequently, suppresses the analyte ionization signal. This problem has been effectively addressed for LEI in air/acetylene flames by the use of the immersed cathode which permits laser enhancement within the collecting field.[9] Use of the immersed cathode has allowed complete LEI signal recovery from samples containing high sodium concentrations.

The most significant LEI improvements have resulted from changes in electrode design,[9] access to UV wavelengths through the use of advanced laser technology,[10] and sample pretreatment for removal of interferents.[11] Only recently have alternative atom reservoirs for LEI received attention. Turk and Watters[12] reported the use of an argon inductively coupled plasma for LEI spectrometry. The authors attributed a lack of sensitivity to a low atom population in the plasma tail flame where the LEI measurements were carried out.

More recently, Magnusson et al.,[2] and Axner and Rubensztein-Dunlop[3] have reported LEI detection of trace elements in a graphite furnace. Both one and two-step excitation schemes were reported. The two-step excitation scheme allowed background correction.[3] The authors suggested that a change in furnace purge gas from argon to nitrogen, or a mixture of argon and methane might create a better collisional environment in the furnace. This could lead to further enhancements in ionization and, thus, higher sensitivity.

Niemczyk and Na[13] have reviewed the fundamentals and applications of the microwave-induced active nitrogen plasma which has been demonstrated to be an efficient source for atomic emission spectrometry. Microwave-induced plasmas (MIPs) using a variety of

gases and gas mixtures, have been well characterized in the literature.[14,15] In an active nitrogen plasma, non-thermal energy transfer of up to several electron volts is possible through very efficient collisions of analyte atoms with plasma species.[13] This is in contrast to the air/acetylene flame in which the nitrogen molecule with a Boltzmann energy of around 0.2 eV is the major collisional partner in the LEI process.[12] Hood and Niemczyk[16] have recently reported excitation temperatures, measured in a low-pressure active nitrogen plasma, that are higher than in most flames. Active nitrogen is relatively easy to generate in a microwave discharge and has the potential for excitation and ionization of a large number of elements.[17] Thus, the active nitrogen plasma should present a comparable, if not superior, collisional environment for LEI.

Most of the published research involving the use of active nitrogen for atomic emission was carried out at pressures below atmospheric using low microwave power (<100 W). Low power microwave-induced plasmas are very efficient excitation sources, but lack the thermal energy required to vaporize samples. In the past, conventional sample introduction into MIPs presented many difficulties including the plasma's intolerance for sample solvent.[14] Successful liquid aerosol sample introduction into a low power MIP has recently been reported however.[18]

In the present study, a microarc atomizer was used to introduce discrete samples into a microwave-induced, atmospheric pressure active nitrogen plasma. Deutsch and Hieftje[19] used a microarc atomizer to introduce samples into a microwave-induced nitrogen plasma for atomic emission studies. The microarc atomizer separates sample desolvation and atomization steps. It employs both sputtering and thermal desorption to efficiently atomize small samples.[20] The microarc atomizer has more recently been explored as an atomic emission source[21] and as an atom reservoir for LEI and DLI.[22]

The preliminary results presented here demonstrate the feasibility of using an active nitrogen plasma atom reservoir for both LEI and DLI spectrometry. LEI has also been observed in an MIP by Lysakowski.[23] In the present work, a comparison of LEI and DLI signals for indium indicates that DLI photoionization enhancement[8] of the LEI signal is small. These results suggest that the rate of collisional ionization in the active nitrogen plasma may be comparable to typical analytical flames.

EXPERIMENTAL SECTION

A schematic diagram of the instrumentation used in this study is given in Figure 1. A linear flashlamp-pumped dye laser (CMX-4, Chromatix), with a 0.8 μs pulselength and frequency doubling capability, was used as the excitation source for all experiments. The laser was operated with rhodamine 590 at a repetition rate of 30 Hz. A UV-transmitting, visible absorbing filter was used to block the laser fundamental output during the LEI experiments. The laser wavelength was optimized prior to each experiment by observing the optogalvanic effect in a hollow cathode lamp. A standard LEI detection system was used, including a preamplifier[24] and a boxcar signal averager, for signal processing. A strip chart recorder provided the signal readout.

Active Nitrogen Plasma

An active nitrogen plasma was generated using a laboratory-constructed Beenakker type microwave cavity.[25] The microwave power oscillator (Micro-Now, Skokie, IL) was used to deliver powers between 50 and 150 W. The microwave cavity was carefully designed so that reflected power was always less than 10% of the forward power value, and in some cases, was too small to measure accurately. The active nitrogen plasma plume was generated at atmospheric pressure by exciting a mixture of argon (1.2 L/min)

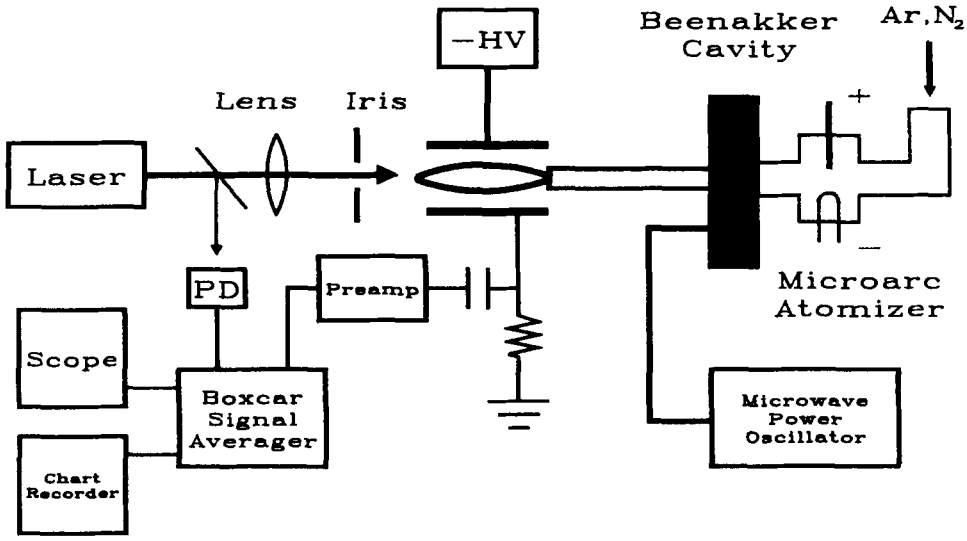

FIG. 1. Schematic diagram of instrumentation. Diode-array spectrometer is omitted.

and nitrogen (10-50 mL/min). The nitrogen was obtained from liquid nitrogen boil-off. The atmospheric pressure plasma was chosen over a low-pressure plasma (<10 Torr) to facilitate sample introduction and eliminate the need for a vacuum system. An 8-mm I.D. x 150-mm long quartz tube was used to direct the gas mixture through the microwave cavity. The tube extended about 100 mm beyond the cover plate of the microwave cavity. The active nitrogen plasma plume extended about 50 to 60 mm beyond the end of the quartz tube. The plasma plume exhibited the active nitrogen afterglow; the characteristic yellow emission was monitored using a diode-array spectrometer (Tracor-Northern, Middleton, WI). The most stable plasma conditions were obtained with applied microwave powers in the range of 60 to 70 W and nitrogen flow rates between 30 and 40 mL/min.

Signal Collection

The laser beam was directed along the longitudinal axis of the plasma plume. Ion collection electrodes (12 x 60 mm) were positioned on either side of the plasma plume and were separated by a distance of 10 to 12 mm. The electrodes were operated at a potential of -1500 V. At potentials higher than this, arcing through the plasma plume occurred. The plasma plume, ion collection electrodes, and preamplifier were shielded by a copper screen and plexiglass enclosure to minimize pickup of RF interference from the laser, eliminate drafts, and to facilitate the exhausting of ozone.

Microarc Atomizer

A laboratory-constructed microarc atomizer was positioned at the rear of the Beenakker cavity in direct line with the gas flow to the plasma. This arrangement was found to facilitate sample transport to the plasma. The gas flow through the microarc and Beenakker cavity was higher than the flow rate normally used in a microarc atomizer but close to the minimum flow rate required to sustain the microwave plasma. Therefore, the gas flow rate used was a compromise between a stable plasma and optimum operation of the microarc. A tungsten rod was used as an anode and a nichrome wire loop was used as the cathode. The sample was desolvated by resistive heating of the wire. When a 1-μL sample droplet was placed on the cathode, a visible change in the active nitrogen emission spectrum was observed. The presence of water in the plasma resulted in a momentary quenching of the nitrogen afterglow. The completion of sample desolvation was indicated by the reappearance of the yellow nitrogen afterglow in the plasma plume. The microarc power supply is described in Refs. 21 and 22.

LEI Measurements

Indium was chosen as a test element for the initial experiments because of the proximity of one of its resonance lines to a peak in the frequency-doubled tuning curve of rhodamine 590. Excitation at the indium resonance line at 303.9 nm resulted in promotion to a level that was within 1.70 eV of the 5.78 eV ionization potential of indium. Energetically, these are favorable conditions for a good LEI yield in a collisional environment. LEI measurements for 10-ng samples of indium were made while adjusting the plasma parameters of applied microwave power and nitrogen gas flow. These parameters directly affected the concentration of plasma species and, hence, the collisional efficacy of the plasma.

An experiment was carried out to determine whether the resonant transition at 303.9 nm was optically saturated. The laser beam was attenuated with calibrated neutral density filters and the corresponding LEI signals for replicate 10 ng samples of indium were recorded. A plot of LEI signal vs. laser power revealed a non-linear dependence of LEI signal at the higher laser powers. Optical saturation of this transition helped minimize the effect of pulse-to-pulse amplitude differences in laser output on the outcome of the indium LEI experiments.

DLI Measurements

DLI studies usually require the addition of a second laser to photoionize laser-excited analyte atoms. In this case, a DLI excitation scheme for indium was conveniently arranged using a single dye laser with both frequency-doubled and fundamental output beams.[22] The fundamental laser wavelength of 607.8 nm was frequency doubled to produce the second harmonic at 303.9 nm. The 303.9 nm beam was used, as in the LEI experiments, for the excitation step. The 607.8 nm fundamental output was used for the

photoionization step. The addition of the 2.04 eV ionizing photon resulted in a 0.34 eV energy overshoot beyond the ionization potential of indium. This overshoot was relatively small and, therefore, near optimal for observing a DLI enhancement over LEI.[8]

In DLI studies, the degree of overlap of the excitation and ionization laser beams in the atom reservoir is critical.[8] The tunable dye laser used in the present study produced a second harmonic beam that was displaced vertically above the fundamental output beam. The cross-sectional overlap between these beams was about 30%, creating a non-optimum condition for DLI enhancement. To circumvent this problem, the laser output beam was expanded and a 2-mm iris was positioned in the region where the fundamental and second harmonic overlapped. This approach allowed the plasma plume to be irradiated by a composite beam with nearly 100% overlap between the fundamental and second harmonic. The resonance transition of indium was still optically saturated despite losses in laser intensity due to expansion and spatial filtering of the beam. Comparative DLI/LEI experiments were run under the same conditions of illumination. An applied microwave power of 60 W and a nitrogen flow rate of 30 mL/min were used for the DLI measurements. These conditions provided less than optimum LEI yields (see Figs. 2, 3) but promoted the most stable plasma.

RESULTS AND DISCUSSION

Laser-enhanced ionization signals were detected for indium excited under optical saturation conditions. With the excitation step saturated, the amplitude of the ionization signal was influenced primarily by the efficacy of collisions of the excited-state analyte atoms with plasma species. The concentration of active nitrogen in the plasma was controlled by varying the nitrogen flow rate or the microwave power. The active nitrogen concentration in the plasma plume could be increased by

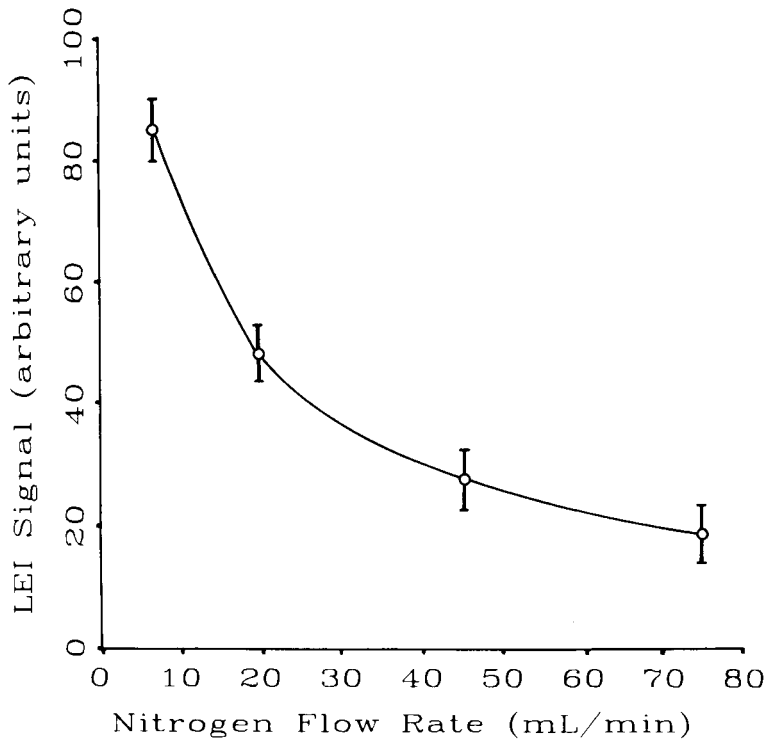

FIG. 2. Effect of nitrogen flow rate on LEI signal for 10 ng indium samples. Error bars represent 95% confidence interval.

increasing either of these two variables. The nitrogen flow rate was the predominant influence as indicated by the emission intensity of the nitrogen afterglow which was monitored with the diode-array spectrometer. Figure 2 illustrates the effect of the nitrogen flow rate on the LEI signal. The nitrogen flow rate was varied between 7 mL/min and 75 mL/min and LEI measurements were made for 10 ng aqueous samples of indium. The applied microwave power was fixed at 60 W. The nitrogen flow rate was small in comparison with the argon flow rate, which was maintained at 1.2 L/min in order to keep the rate of sample transport through the system constant. The LEI signals were maximum at a flow rate

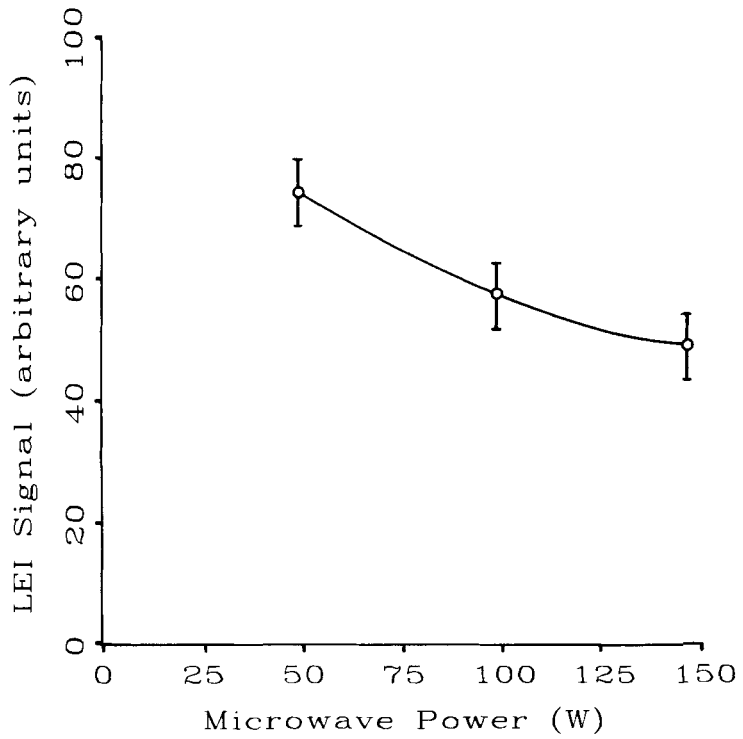

FIG. 3. Effect of microwave power on LEI signal for 10 ng indium samples. Error bars represent 95% confidence interval.

of 7 mL/min and decreased by a factor of four as the flow rate was increased to 75 mL/min. At nitrogen flow rates lower than 7 mL/min, the plasma became unstable and began to pulsate. When the nitrogen flow was reduced to zero, the remaining argon plasma retreated back into the Beenakker cavity and LEI signals were too small to detect at the same gain setting of the boxcar. The observed decrease in LEI signal size with increasing active nitrogen concentration may have been the result of depletion in the population of ground state analyte atoms due to effective excitation and ionization of the analyte by the plasma itself.[17] The reduced sensitivity for atomic fluorescence as compared to atomic

emission measurements made in active nitrogen plasmas,[26] provides further evidence for the depletion of ground state analyte atom populations.

Figure 3 illustrates the effect of applied microwave power on the LEI signal. The microwave power was varied between 50 and 150 W and LEI measurements were made for 10-ng samples of indium. The argon and nitrogen flow rates were fixed at 1.2 L/min and 12 mL/min, respectively. Measurements were not attempted below 50 W applied power because the plasma became unstable below this power level. The LEI signal was maximum at 50 W and decreased gradually with increasing microwave power and the subsequent increase in active nitrogen concentration.

DLI Enhancement of the LEI Signal

A comparative study of DLI and LEI was carried out in the active nitrogen plasma. In both cases, indium was excited at 303.9 nm. Measurements for replicate 10 ng samples of indium were made with and without the addition of a photoionizing beam. The addition of the photoionizing laser beam resulted in DLI signal enhancements of up to a factor of two relative to LEI measurements made under the same conditions. Since saturation of the excitation step at 303.9 nm was maintained throughout all experiments, it was assumed that laser intensity losses due to reflection off the UV transmitting-visible absorbing filter, did not contribute significantly to the difference between the LEI and DLI signal amplitudes.

A DLI detection limit based on a signal-to-noise ratio of three was estimated for indium. For quantitation purposes, the chart-recorded peak heights of the transient ionization signals were measured. The noise was taken as one-fifth the peak-to-peak noise on the baseline. A detection limit of 20 pg was estimated by extrapolation from signal-to-noise ratios of measurements made

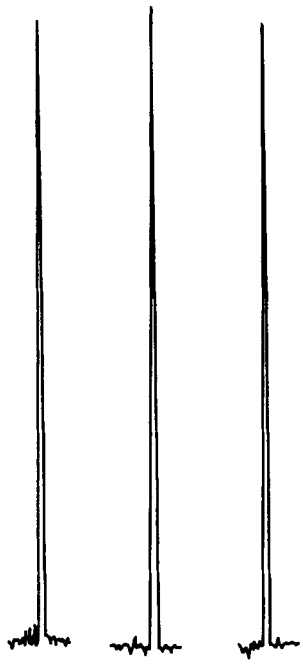

FIG. 4. Chart recorder tracings of consecutive DLI signals for 1 ng indium samples.

with 1-ng samples of indium. The reproducibility at this level was approximately 15% relative standard deviation. Figure 4 shows signals recorded for consecutive 1 ng indium samples. The best DLI detection limits for indium were comparable to the best obtained for LEI (using full illumination). The DLI enhancement factor offset the loss of LEI signal that was a result of reduced beam volume due to spatial filtering in the DLI/LEI comparison experiment.

Background Ionization and Limiting Noise

Measurements made in the active nitrogen plasma with the microarc atomizer turned off and no analyte present indicated the

presence of low level laser-induced background ionization. Signals were observed with laser excitation both on and off the 303.9-nm line. The signals disappeared when the laser beam was blocked, leaving a baseline signal that resulted primarily from pickup of RF interference from the laser. The combination of laser-induced plasma ionization and pickup of RF interference may present a fundamental limit on the sensitivity of this technique. An optimization of the plasma, in addition to improvements in electrical shielding and grounding, may help reduce the magnitude of these background signals and, hence, their contribution to the total noise.

CONCLUSION

The preceding results demonstrate the feasibility of using an active nitrogen plasma atom reservoir for laser-induced ionization spectrometry. Picogram level sensitivity for discrete samples of indium was obtained by both LEI and DLI techniques.

DLI enhancements of up to 1000 have been obtained for some elements by using excitation schemes with relatively small energy overshoots.[8] The DLI enhancement observed for indium in the present study was approximately the same as reported for indium in Ref. 8, but the energy overshoot was less than half as large. Thus, a larger DLI enhancement would have been expected in the present case, providing the atom reservoirs had similar collisional properties. Although several experimental differences prevent a direct comparison between the previous results and the present work, the absence of a larger DLI enhancement for indium in the present work suggests that a higher rate of collisional ionization exists in the active nitrogen plasma relative to the hydrogen-oxygen-argon flame used in Ref. 8. The collisional properties of the active nitrogen plasma may more closely approach the air/acetylene flame.

Low ground state analyte atom populations in the active nitrogen plasma, relative to analytical flames, implies that analyte atom excited states are more highly populated in the plasma. This is exemplified by the high sensitivity obtained for atomic emission in the active nitrogen plasma.[13] This being the case, non-resonant LEI excitation of analyte atoms in the active nitrogen plasma should demonstrate improved sensitivity over similar excitation schemes in flames.

The microarc atomizer is currently being optimized to improve the reproducibility of atomization and, hence, the precision. Synchronization of the laser firing to the transit of the analyte "plug" through the region of the plasma sampled by the LEI electrodes would improve both precision and sensitivity.

Experiments are being planned to investigate LEI and DLI for a series of other elements to further characterize the role of the active nitrogen plasma. Initial investigations of the effect of easily-ionized elements on the analyte ionization signal indicate that the electrical interferences may be similar to those in flames.[1] High voltage interferent removal schemes[27] may be more effective in active nitrogen plasmas than flames. The former should more efficiently ionize IA and IIA elements, leading to a more quantitative removal.

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