

4.48 μm and σ^* to be 1.518. In the present case we can use the values presented and also neglect the problem of evaporation redistribution of the aerosol droplets reported in ref 9, because we are only interested in the trends and not in the absolute values of the efficiency and the aerosol concentration. For an ICP nebulizer system not only the trends but also the absolute values of the efficiency and aerosol concentration are obtainable because the flows commonly encountered in ICP system, less than or equal to 1 L/min, give rise to negligible redistribution problems due to evaporation. The value of d_c is in close accordance with Figure 4 in ref 2 and the experimentally obtained value in that paper (4.5 μm). It is further assumed that σ^* is not influenced by an exchange of the liquid being nebulized. The values presented in Table II.1 (having the same surface tension and viscosity values as Table I.1) show the influence of sample temperature on the efficiency and the aerosol concentration. The same trends were reported by Cresser and Browner (1). They made measurements of the efficiency showing that it was decreasing with increasing sample temperature. They could explain the behavior in a semitheoretical way but with the present model the behavior can actually be calculated. The decreased efficiency is counteracted by the increased uptake and therefore we obtain the increase in aerosol concentration. In the table we also see the values obtained if we allow for the temperature dependence (expansion/contraction) of the aerosol concentration. The aerosol is in this case assumed to have the same temperature as the liquid. This example as well as Table I show how unfortunate a choice of the efficiency, instead of the aerosol concentration, would be as a measure of nebulizer performance. The self-stabilizing property reported on earlier in ref 1 and 3 is also clearly seen here. The influence of an increased sodium chloride content (at constant temperature) on nebulizer performance is shown in Table II.2. The slowly increasing efficiency is counteracted by a decreasing uptake (due to the increase in viscosity). The small change in aerosol concentration, only $\approx 2\%$, when increasing the salt content from 0 to 3.5%, is not in accordance with actual measurements of nebulizer performance. The change in aerosol concentration is usually much larger. The difference can be attributed to

the clogging of the nebulizer. The values in Table II.2 show that if we could design a concentric nebulizer free from clogging, then sodium chloride would be an excellent ionization buffer due to its small influence on the aerosol concentration. Table II.3 is included to show the effect of the presence of an organic compound in the solution to be nebulized. Although the efficiency values are higher than in Table II.1,2 the aerosol concentration values are lower. This is because a natural uptake of 6 mL/min was assumed as a reference in the calculations whereas the uptake will be reduced by 40-50% by the aspiration of a mixture of water and alcohol due to its higher viscosity.

There are three major conclusions to be drawn:

- (1) The Nukiyama and Tanasawa equation is not valid for cross-flow nebulizers (with one exception (6)).
- (2) The Nukiyama and Tanasawa equation is strictly valid only for $15 < d_0 < 90 \mu\text{m}$.
- (3) The present model (3) is strictly valid only for gas flows encountered in ICP nebulizer systems.

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Glow Discharge Atomization Source for Resonance Ionization Mass Spectrometry

Sir: The tunable dye laser is finding increasing application as a selective excitation and ionization source in atomic spectrometry. Young et al. (1) have reviewed the multiphoton absorption process that yields stepwise ionization by means of several alternate schemes. Donohue et al. (2, 3) showed the analytical utility of resonance ionization mass spectrometry (RIMS) for problems of isobaric interferences. The atomization source in these studies was a hot filament, a means which permits volatilization of solution residues or of solids applied directly on the filament. Other means of atomization have also been demonstrated. Travis and co-workers have coupled a tunable dye laser to a hollow cathode discharge in studying optogalvanic spectroscopy (4, 5) and also to flame atomization sources to achieve laser-enhanced ionization (LEI) (6-8). Gonchakov and co-workers (9) have used a graphite furnace as an atomization source for multiphoton ionization.

Winograd (10) employed an ion gun to sputter-atomize directly a solid sample for subsequent laser ionization of the sputtered neutral atoms.

We have used the glow discharge as an atomization/ionization source for a variety of applications over many years (11-17). Most of our studies have involved the glow discharge as an ionization source, even though the degree of ionization is suggested as $< 1\%$ (18). To take advantage of the excellent atomization properties of the glow discharge, we have used a dual-discharge approach (16) wherein an initial glow discharge served primarily to atomize the sample while a tandem secondary discharge just before the ion exit caused enhanced ionization of the neutral atoms.

This same principle of postsputter ionization has led us to couple a tunable dye laser to the glow discharge atomization chamber to produce a sensitive, selective ionization source for

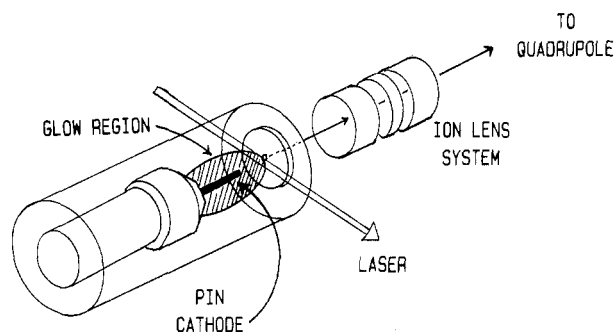


Figure 1. Representation of laser interaction with the glow discharge.

elemental analysis. The laser contributes enhanced sensitivity by ionizing up to 100% of a given microvolume and also adds the aspect of selectivity by tuning to a frequency which will ionize only a single element. We present here initial results which demonstrate the suitability of the glow discharge/laser combination.

EXPERIMENTAL SECTION

Apparatus. The quadrupole mass spectrometer with glow discharge source has been described previously (17). Figure 1 shows the position of the laser beam within the glow discharge region adjacent to the ion exit. Photons of specific frequency are absorbed by atoms sputtered from the pin cathode. Extraction by an einzel-type lens directs the ions to the quadrupole for analysis. Copper and iron pins serve as the analytical cathodes in an argon discharge operating at 0.3–1.2 torr, 800–3000 V, and 1–5 mA.

A Lumonics TE-860-4 excimer laser pumps a Lumonics EPD-330 dye laser which in turn is directed to an Inrad 5-12 frequency doubler. The copper frequencies were obtained with a KDP-C crystal and Rhodamine 640 dye, yielding a wavelength range of 310 to 330 nm. For iron measurements, a KDP-B crystal and Coumarin 540 dye permit a scan over the range of 265–280 nm.

The quadrupole mass spectrometer is fitted with both analog and ion counting electronics. A DEC MINC-11 microcomputer controls mass scans, data accumulation, and data presentation.

The excimer pump laser, operating at 50 Hz, triggers a Princeton Applied Research Model 1112 ion counter/processor operating in its subtracting mode. Following a 60- μ s delay, an 80- μ s data gate accumulates ion counts of the species formed as a result of the laser irradiation as well as those produced by the glow discharge. The glow discharge originating ions exist as a steady state and are subtracted by a second data gate of the same duration prior to the next pulse. Each data point is an accumulation of 50 laser pulses, with 40 data points per amu.

RESULTS AND DISCUSSION

The advantages of using a glow discharge as an atomization source for laser ionization include the following: (a) the glow discharge is a simple and stable source, (b) it can create a high atomic density, easily controlled by discharge current and pressures, and (c) the sputter yields for most elements fall within a factor of 3–5, producing generally similar sensitivities. The glow discharge is well known as a sputter deposition source for thin-layer production and has also been used as an atomization source for solids in atomic absorption spectrometry (19). These same characteristics make the glow discharge valuable in the direct atomization of solid samples for resonance ionization mass spectrometry.

Iron and copper were selected as initial elements to evaluate the methodology. Both elements have been studied in our laboratory by glow discharge mass spectrometry, both elements sputter-atomize quite readily, and both have spectral transitions within the range of our instrumentation and dyes. A wavelength ionization spectrum was first run for iron. Of particular interest was the region 270–275 nm which includes a transition known to be useful in atomic absorption. Figure 2 shows that in scanning the dye laser over this wavelength

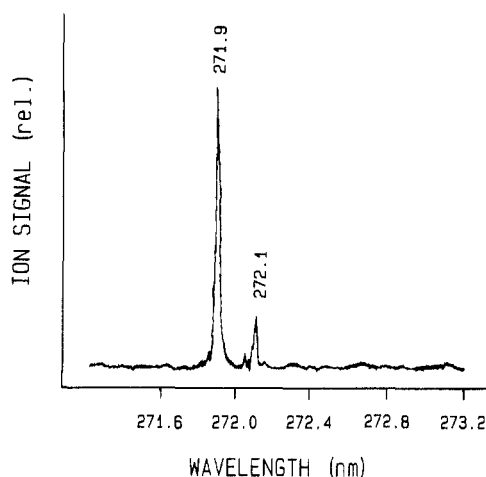


Figure 2. Wavelength ionization spectrum for $^{56}\text{Fe}^+$ in an argon glow discharge.

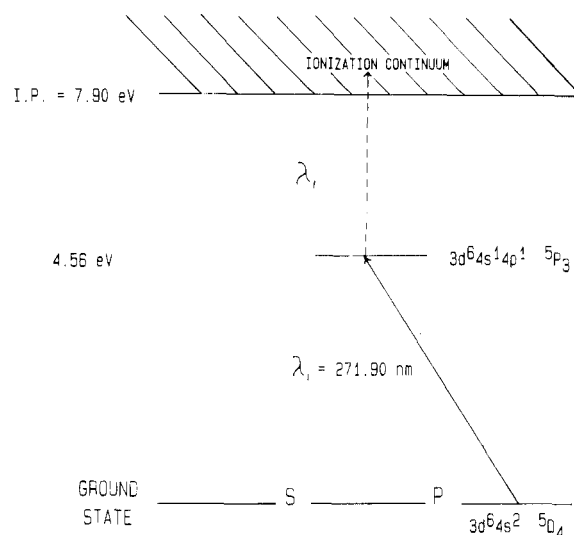


Figure 3. Term diagram showing the absorption of two photons (271.9 nm) to produce resonance ionization of iron.

range, monitoring the $^{56}\text{Fe}^+$ isotope, selective ionization of iron atoms is observed. As illustrated in Figure 3, this may correspond to the absorption of two photons which take the electron into the ionization continuum. The 271.9-nm line arises from a ground-state level (0–36767 K) and is recommended (20) as an atomic absorption analysis line based on a favorable transition probability. The glow discharge tends to thermalize sputtered atoms because of the high collision rates, thus greatly populating the ground states. There are nevertheless other atomic states populated, the extent of which depends on discharge conditions. The 272.1-nm line in Figure 2, for example, involves a transition beginning above ground level (416–37158 K). We plan a more systematic study of the energy levels populated in the glow discharge.

By selecting an efficient line for multiphoton ionization of a given element, it is possible to enhance greatly the selected ion while the intensities of the other ion species remain at their background level. Using the 271.9-nm line for iron, we obtained a mass spectrum from the glow discharge. Figure 4 shows the only peaks which result, the iron isotopes and a small argon signal. The various spectral contributions from water, residual nitrogen and oxygen, and the trace elements seen in the glow discharge ionization mode do not appear, due to the subtraction method of data accumulation. The efficiency of the laser compared to the glow discharge is reflected in the 50:1 ratio of $^{56}\text{Fe}^+$ ions formed during the laser pulse

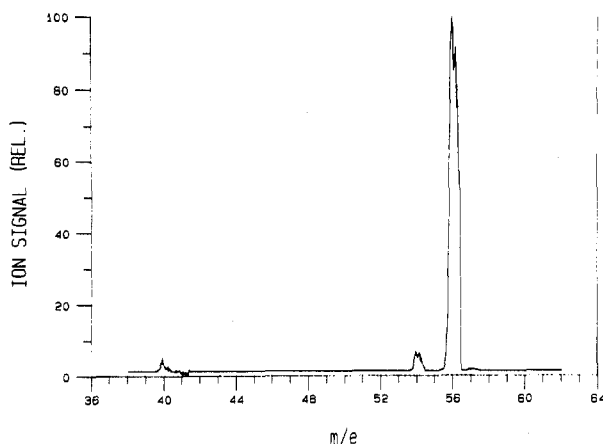


Figure 4. Mass spectrum of an iron cathode in an argon glow discharge showing the iron isotopes at masses 54, 56, and 57. Peak at mass 40 may result from imperfect background subtraction of $^{40}\text{Ar}^+$.

compared to the same interval from the glow discharge.

Copper ionization is an interesting example of an evidently non-RIMS process. The two major ground-state originating lines for copper are at 324.7 and 327.4 nm. A wavelength ionization spectrum taken over this region shows strong copper ion formation at each of these two lines plus several other weaker transitions. A mass spectrum at 324.7 nm reveals only the copper isotopes at masses 63 and 65. However, the absorption of two photons of this energy will not promote the electron into the ionization continuum. A two-photon absorption would bring the electron only very close to ionization, requiring supplemental energy from the plasma to then cause ionization. Alternatively, the mechanism may be similar to that proposed for laser-enhanced ionization in flames (8) wherein a single photon is absorbed, followed by collisional energy transfer to effect ionization. We are presently seeking additional information in other similar experiments.

Whether by direct resonant ionization or laser enhanced ionization, the result is a selective mass spectrum which features only isotopes of the selected element. The glow discharge offers possibilities for both RIMS and LEI with its various internal excitation possibilities. The combination of a tunable dye laser with the glow discharge can yield an ad-

vantageous method for the direct analysis of solids by mass spectrometry.

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Registry No. $^{56}\text{Fe}^+$, 51377-81-2; ^{54}Fe , 13982-24-6; ^{56}Fe , 14093-02-8; ^{57}Fe , 14762-69-7; Ar, 7440-37-1.

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Zeroth and Second Derivative Fluorescence and Phosphorescence Analysis of Mixtures of Hydroxyl Aromatics Adsorbed on Filter Paper

Sir: Recent research activity in the area of luminescence from compounds adsorbed on solid supports has centered around the development of room-temperature phosphorescence (RTP) as an analytical technique. Much of this work is summarized in recent reviews (1-5). Filter paper has been the most widely used adsorbent for inducing RTP from aromatic molecules. In addition, considerable work has been reported on room-temperature fluorescence (RTF) analysis of organic compounds adsorbed on solid surfaces (1). However, there has been only one report of the combined use of solid-surface RTF and RTP for qualitative analysis (6).

One limitation in the use of solid surface RTP and RTF for qualitative analysis arises from the fact that the spectra usually have broad bands. For this reason, the identification of individual compounds by examination of the luminescence

spectra from a mixture can sometimes be difficult. This is especially true for compounds whose spectra overlap extensively. In this study, the combined information of RTP excitation and emission and RTF emission spectra was used for qualitative analysis. Both zeroth and second derivative RTP and RTF spectrometry were used in the work.

EXPERIMENTAL SECTION

Apparatus. Luminescence excitation and emission spectra were obtained with a Farrand MK-2 spectrofluorimeter, fitted with a phosphorescence rotary chopper. Source radiation was provided by a 150-W Xe lamp and the detector was a R928 photomultiplier tube (Hamamatsu Corp., Middlesex, NJ). For RTP measurements, metal slits giving a bandwidth of 10 nm were used at the entrance and exit positions of both the excitation and emission monochromators. For fluorescence measurements, 10-nm