

Laser Resonance Ionization Mass Spectrometry

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Laser ionization mass spectrometry is a generic concept applicable to a large number of experiments that use laser radiation to produce ions in a mass spectrometer for conventional analysis (Fig. 1A). However, the properties of laser radiation—time and space coherence, high fluence, and high monochromaticity—provide the combined laser ionization–mass spectrometer system with capabilities that are far from conventional. A variety of ionic species can be easily distinguished (Fig. 1B), and the measurement system has already been applied to many of the chemical elements (Fig. 2).

LEI, provides a significant increase in selectivity by measuring elemental isotopic information. The combination of laser spectrometry for ionization with mass spectrometry introduces an entirely new procedure for chemical analysis.

Vaporization and Atomization Processes

Resonance ionization requires free atoms. Elements that exist as atomic gases at ambient temperatures pose no problem in this regard. However, most elements in natural or even matrix-free

Summary. The analysis of inorganic atomic species is greatly facilitated by the coupling of lasers with mass spectrometers. A tunable dye laser, alone or in combination with a pump laser, ionizes atoms by resonant excitation processes; the ions are then analyzed in the mass spectrometer. The laser–mass spectrometer system promises to overcome traditional limits of sensitivity and selectivity and to have diverse applications in analytical chemistry.

Potential and ongoing research applications for multiphoton resonance ionization mass spectrometry range from basic spectroscopic studies of atoms and molecules to the detection of solar neutrinos and quarks. This article describes the resonant photoionization of inorganic species, with particular emphasis on chemical analysis; there are, of course, many important applications in other fields (1).

Resonance ionization mass spectrometry (RIMS) is an outgrowth of the work of Hurst and colleagues (2, 3). In parallel with their efforts in resonance ionization spectroscopy (RIS), the discovery of the optogalvanic effect (4) led to the development of laser-enhanced ionization (LEI) in an analytical flame (5). As in RIS (6, 7), the signal in LEI is produced by the electrons emitted in ionization. The detection of the atomic ion by mass spectrometry, compared to RIS and

form exist as compounds or complex mixtures, and the formation of free atoms from such species is not a trivial problem. Although a variety of atomization approaches have been employed (some of which are discussed below), efforts in our laboratory have focused on the thermal vaporization and dissociation of condensed-phase compounds in the Langmuir vaporization setting employed for many years in conventional thermal ionization mass spectrometry (TIMS). For TIMS, a solution of the element is deposited on a metal ribbon and dried according to a protocol, and the resulting deposit is heated in the mass spectrometer source to produce atoms and ions. The thermal ionization process is usually described by the classic Saha–Langmuir expression, although the analytical conditions of thermal ionization diverge considerably from the ideal conditions that the theory describes. In TIMS, the vaporization of even simple binary alkali halides, such as potassium chloride, results in an equilibrium vapor-phase mixture of K^+ , Cl^+ ,

K^+ , Cl^+ , KCl , and K_2Cl_2 (8, 9). Chemical interactions with the host substrate [for example, $Ca(NO_3)_2$ with Re] can produce complex vapor-phase species such as $Ca_xRe_yO_z$ (9, 10). Evidence indicates that elemental metallic deposits vaporize as atoms and atom clusters, and a generic approach to atomization has been developed by means of external or in situ reduction techniques; these include heating the sample in hydrogen gas or drying the sample on a graphite substrate.

In thermal vaporization, the energy levels of the neutral species are populated according to a Boltzmann distribution (11). Therefore, the vapor phase is in thermodynamic equilibrium with the condensed phase. Long-lived, thermally populated states are still available for resonance ionization after tens of microseconds of travel time in vacuum.

Molecular dissociation is a viable alternative for elements not amenable to reduction techniques. Electronegative elements of the upper right-hand portion of the periodic table (for example, the halogens) can be vaporized as binary compounds and then dissociated thermally or by photodissociation to form the atom reservoir. For example, silver iodide has been shown to dissociate efficiently into silver and iodine atoms. Evidence indicates that even complex salts, such as $Sr_xRe_yO_z$, can be vaporized and thermally dissociated to form gaseous atoms of the primary metal and volatile refractory oxides of the secondary metal, such as $Re_2O_7(g)$ (12). However, dissociation can also lead to the production of background ions by way of nonresonant multiphoton ionization.

Resonant laser ionization of the neutral species produced by the impact of energetic primary beams (neutrals, ions, and photons) with solid materials is being investigated in a number of laboratories (13–15). Measurement of the ejected charged species produced by the impact of primary particle beams is well established in analytical chemistry by routine applications of secondary ion mass spectrometry and laser microprobe mass spectrometry. Winograd and co-workers (13) have described the systematics for ion bombardment of solids and multiphoton resonant ionization of the sputtered neutrals. The technique combining ion bombardment and resonance ionization of the sputtered neutral species has been patented and named sputter-initiated resonance ionization spectrometry (SIRIS) (16).

Laser ablation was used in an early demonstration of resonance ionization for trace analysis of solids in which sodi-

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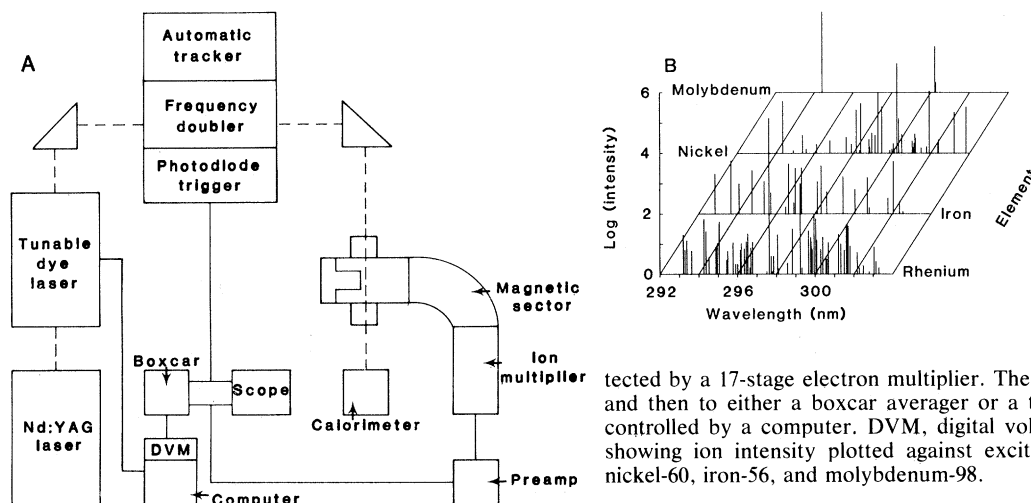


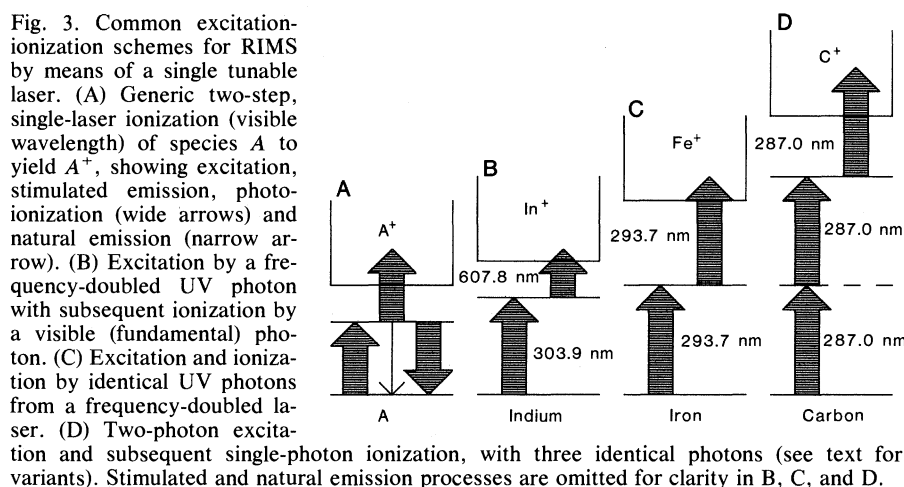
Fig. 1. (A) The experimental system. A pulsed laser produces 4-nsec pulses at 10 Hz, with the doubled dye laser output directed into the source of the mass spectrometer parallel to the sample filament and focused by a lens with a 30-cm focal length. The source chamber is modified for laser-beam entry and exit with quartz windows. The thin-lens ion source accommodates the geometries of the laser beam and sample filament, and the ions are de-

um was detected in high-purity silicon (17). In contrast to this experiment, in which no mass selection was done, Beekman and co-workers coupled a time-of-flight mass spectrometer with a laser microprobe and made thermodynamic measurements of the laser-ablated atoms (18). By separating the sampling and excitation steps in the analytical process, resonance ionization of sputtered and ablated neutrals from solid materials may overcome the large differences in ionization efficiencies among elements for a given material and the large difference in ionization efficiency for a given element among materials (matrix effects); such differences have previously limited quantitative analysis by these techniques.

cross section into the ionization continuum is virtually independent of wavelength. However, for optical saturation, only that portion of the laser's spectral width that overlaps the absorption profile is effective. The originators at Oak Ridge National Laboratory of RIS chose flash lamp-pumped dye lasers (2, 3, 7). Such lasers are capable of furnishing hundreds of millijoules in pulses of about a microsecond for peak powers of hundreds of kilowatts. These lasers tend to be somewhat broadband (~ 0.1 nm), but they still provide kilowatts of effective power for ionization features 100 times narrower than the laser bandwidth.

Ionization Processes

The operational principles of RIS (3, 19, 20) may be understood from the simple, generic illustration in Fig. 3A. For this case, the RIS process consists of the photoexcitation of atom A from its ground state to the excited state, with subsequent photoionization of the excited state (in competition with stimulated emission and natural emission), to yield the ground state of the ionic species A^+ . As shown, the excitation and ionization photons are of identical wavelength and are derived from the same light source. A typical excited-state photoionization cross section of 10^{-17} cm² requires a photon fluence much greater than 10^{17} cm⁻² to approach total ionization of the excited-state population. At the same time, "optical saturation" of the resonance transition and maintenance of a significant fraction ($\sim 1/2$) of the neutral atoms in the excited state for ionization requires that absorption and stimulated



saturation intensities when moderately focused, but thermal atoms transit the active volume with velocities of about 10^5 cm sec^{-1} , giving short residence times relative to the optimal times (of the order of milliseconds) derived above (11, 21). Short-pulse ($\sim 5 \text{ nsec}$) dye lasers pumped by nitrogen, excimer, or Nd:YAG (yttrium-aluminum garnet) lasers provide energies from hundreds of microjoules to tens of millijoules and can thus yield ionization fluences with appropriate focusing. When this is done, however, the resulting power densities exceed optical saturation by orders of magnitude, resulting in an increase in line width called power broadening (22, 23).

The ionization scheme of Fig. 3A is applicable only to elements for which the discrete energy level used is more than halfway to the ionization limit and for which the limit is less than twice the energy of available photons. To achieve widespread applicability of resonance ionization, Hurst and co-workers defined four additional schemes and identified transitions by which all but two elements (helium and neon) could be ionized (3). Complexities added to the simplest scheme include (i) the generation of wavelengths down to 217 nm by nonlinear optical interactions in crystals, (ii) the use of two separate tunable lasers, and (iii) the use of multiphoton excitation for high-lying excited states.

The practical application of RIS to mass spectrometry has involved deviations from the original premises and recommendations. RIMS has been demonstrated with dye lasers pumped with Nd:YAG lasers (11, 22, 24–29), nitrogen lasers (30, 31), excimer lasers (32), and even cw ion lasers (33) as well as with the recommended flash lamp-pumped laser (34, 35). Ionization schemes have also departed from those recommended, usually to allow single-laser ionization of

elements for which two lasers were originally proposed. Such compromises are often made for practical reasons and are often of less consequence in the mass spectrometric application than in many of the stand-alone atom-counting applications of RIS (3). Loss of spectral resolution due to power broadening is largely offset by the addition of mass selectivity. Total ionization is rarely necessary, and even cw resonance ionization is competitive in certain cases with conventional thermal ionization and has the added advantage of elemental selectivity (33).

Figure 3 illustrates four excitation-ionization schemes widely used for RIMS. The first scheme (Fig. 3A) is commonly used for a number of rare earth elements (31, 35). The other three schemes require ultraviolet (UV) light or multiphoton excitation to access the lowest excited states beyond the energy range of a single visible photon. Ultraviolet photons down to 217 nm are generally produced by second-harmonic generation (frequency doubling) or sum-frequency mixing, with a relatively small fraction of the visible laser light being consumed in the process. Figure 3B illustrates a scheme for indium, which uses frequency-doubled 303.9-nm light for resonant excitation and the more intense fundamental wavelength at 607.8 nm for photoionization of the excited state. Besides offering the advantage of higher intensity, the fundamental wavelength reaches the continuum closer to the ionization potential, with a consequent increase in the photoionization cross section.

A simple UV extension of the basic one-color scheme, illustrated in Fig. 3C for iron (25, 26), has been applied to a number of transition metals and is broadly applicable (24, 27). The ionization scheme illustrated for carbon in Fig. 3D uses two-photon excitation with subsequent single-photon ionization (36). This scheme again uses UV light generated by

a single tunable dye laser, but it accesses higher lying excited states and higher ionization potentials. A variation involving three visible photons with one intermediate resonance has recently been used at Oak Ridge to reduce interferences among actinides (34) and at Los Alamos National Laboratory to improve the spectral definition of tantalum, which is often used as a sample substrate (32). Some of the resonances observed in the latter application correspond to single-photon excitation and subsequent two-photon ionization (1 + 2) instead of the 2 + 1 sequence shown in Fig. 3D.

It may be predicted that most elements can be ionized by one of these schemes with the fundamental and UV light generated from a single tunable dye laser; there would be some disadvantages relative to the original five schemes (3), which employed two lasers for many of the elements with higher ionization potential. A second laser would usually operate at visible wavelengths, exciting atoms stepwise from a UV-populated first excited state to a second excited state and then photoionizing the doubly excited atom. Spectral resolution would be maintained with a UV intensity only slightly greater than that required for optical saturation, while total ionization would be ensured by use of the high-flux visible light without regard to possible saturation broadening in the second excitation step. When the scheme of Fig. 3C is used instead, the UV flux represents a compromise between resolution and ionization efficiency and may provide unwanted background ionization of matrix species or organic vacuum contaminants (or both). Such background ions may often be identified by their mass, but many peaks due to organic fragment ions overlap critical elemental isotopic masses.

Although the performance degradation caused by using short-pulse dye lasers is often inconsequential in RIMS, it is not possible to achieve the ultimate sensitivity of RIMS without recovering the 100 percent ionization ideal of RIS. Three methods have been recommended for improving the ionization yield for short-pulse lasers (19): (i) collisional ionization has been demonstrated for RIS in room-temperature proportional counters (37) and constitutes the optogalvanic effect (4, 5) if the buffer gas is a high-temperature plasma; (ii) excess pump-laser light may be added to the photoionization step (19), especially for doubled or tripled Nd:YAG-pumped lasers, since tens to hundreds of millijoules of light at 1064 nm are available to ionize excited states within about 1 eV of the limit; and (iii)

field ionization of Rydberg states has been accomplished for ytterbium after three-stage excitation (38), with the required electric field being strongly related to the proximity of the highest excited level to the ionization limit (19). All three methods require that the high-lying excited state be relatively close to the ionization threshold, which in turn generally requires at least two, and sometimes three, stepwise excitations.

The last two of these methods are of particular interest for RIMS. Method (ii) is appealing because the implementation is straightforward and the choice of excited level is less restricted than for the other two. Method (iii) is well adapted for use with a mass spectrometer because the ion extraction field can be used for ionization as well, and it may be especially useful for pump lasers other than Nd:YAG lasers (which are required to achieve repetition rates greater than the 30-Hz Nd:YAG limit).

A somewhat less general method for increasing ionization yield uses autoionizing states (19), representing the simultaneous excitation of two electrons whose pooled excitation energy exceeds the ionization energy of the atom. Because of their relatively short lifetimes, autoionizing resonances in the continuum are broad; nevertheless, the cross section at the peak may be a significant improvement over the surrounding continuum. Although many autoionizing resonances have been found and identified by conventional spectroscopic means, a far greater number await experimental verification by the combined laser-mass spectrometer system. The National Bureau of Standards' second-generation RIMS spectrometer is being used for just such studies (39). In one of the first demonstrations of inorganic laser ionization mass spectrometry, researchers at Los Alamos used accidental coincidences between excimer laser wavelengths and broad autoionizing resonances in rare earth elements (40). Because of the breadth of autoionizing levels, elemental selectivity of the single-photon method is less than it would be if a bound energy level were involved. Thus, the use of RIMS with autoionizing levels would require at least two tunable lasers and associated UV generation.

So far in this discussion we have assumed that resonance ionization displays elemental selectivity and that mass (or isotopic) selectivity is afforded by the mass spectrometer. For the high-accuracy protocol of isotope-dilution mass spectrometry (41) to be used successfully, it is critical that all isotopes of a given element be ionized with equal efficiency.

For most elements, optical isotope shifts are small with respect to both the Doppler-broadened linewidth of thermally vaporized atoms and the spectral bandwidth of the tunable laser, and ionization bias is not a problem. However, for light elements (such as lithium) and heavy elements (such as uranium) and for those in the lanthanide series, appreciable optical isotope shifts typically yield an ionization bias unless the laser wavelength is adjusted as the mass spectrometer is scanned (a perfectly feasible operation).

For some applications, it is preferable to have isotopic ionization selectivity. Lucatorto and colleagues (42) have proposed the use of narrow bandwidth lasers and Doppler-free ionization schemes to extend isotopic selectivity to a variety of elements of particular interest. Two-photon excitations (Fig. 3D) are used for Doppler-free ionization. Theoretical calculations indicate that isotope ionization efficiency ratios range between three and six orders of magnitude for a number of applications of interest (42, 43).

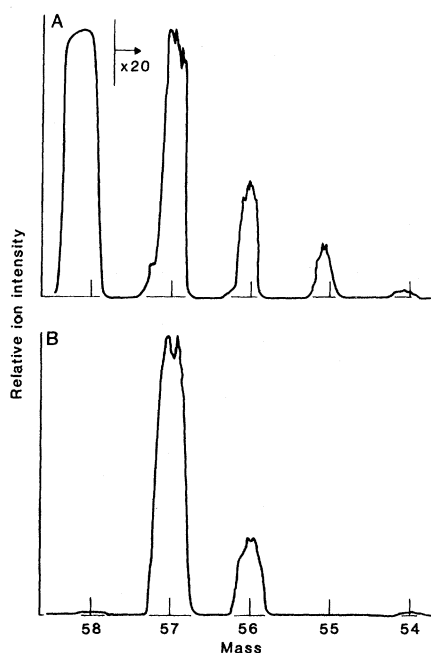


Fig. 4. Resonance ionization mass spectrum of thermally vaporized iron. The sample was spiked with 100 ng of ^{57}Fe (laser wavelength, 283.6 nm; magnetic field scanning, 1 second per point and 500 seconds total scan time). (A) Signal measured with an electrometer and without time discrimination of the ion signal. (B) Same signal measured by means of a boxcar average with a detector window of 500 nsec centered on $^{56}\text{Fe}^+$. This figure shows how a pulsed ion signal is differentiated from thermally produced hydrocarbon species that would otherwise dominate the mass spectrum of iron. The signal-to-noise ratio is improved through time discrimination by a factor equivalent to the reciprocal of the product of the laser repetition rate and the detector window.

Ion Manipulation and Detection

The resonance ionization process as described above has an inherently high elemental selectivity. Mass spectrometric detection provides an increased selectivity that is a practical necessity for analytical problems in which nonspecific background ionization, which may be caused in the atomization or ionization process, must be characterized and differentiated. Resonance ionization is ideally suited to mass spectrometry: ionization is well defined in both time and space, and only a small excess of translational kinetic energy is added to the atom by the process. The use of high-transmission ion optics coupled with the ability to detect single-ion events with extremely low noise means that the mass spectrometer will not degrade either the selectivity or the sensitivity of the resonance ionization process.

The degree of sophistication of the mass spectrometer will be dictated largely by the measurement needs of any particular problem. Mass spectrometry that uses magnetic sectors (14, 22, 30, 35) and quadrupole filters (44, 45) has been done with resonance ionization. For pulsed lasers that produce a temporally defined ion pulse, time-of-flight mass spectrometry is a practical and simple method for mass filtering (18, 46). Combining the momentum filtering of a magnetic sector with the velocity filtering of time-of-flight (47) may be particularly valuable for measuring large elemental and isotopic ratios.

The pulsed ion beam produced by a pulsed laser creates special problems in quantitative measurement. The range of signal levels produced by thermal vaporization with resonance ionization can be large. Ion detectors that combine ion-to-electron conversion with amplification do not have a large linear dynamic range. Two sources of nonlinearity in multipliers have been described (48): (i) a limit on the number of electrons that the multiplier can supply and (ii) space-charge defocusing of the electron beam in the last stages of the multiplier, which disrupts the interdynode field and the multiplication process. For measurement of large isotopic ratios, this limited dynamic range can be avoided by changing the calibrated gain of the electron multiplier between isotopic measurements. For simultaneous multichannel time-of-flight measurements, the saturation effects of the ion detector will limit the dynamic range of the measurement.

The methods used to quantify the pulsed electron output of the multiplier are best differentiated by the extent that

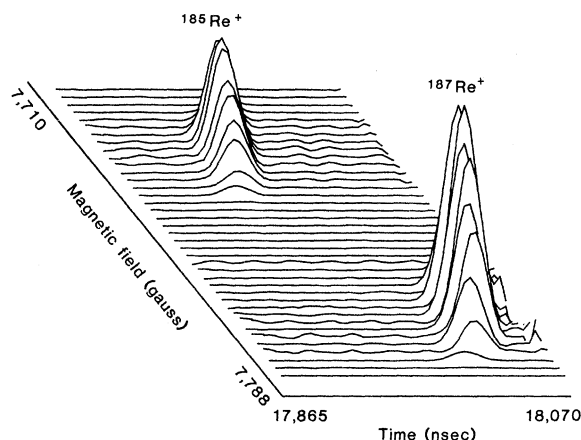


Fig. 5. Plot of Re^+ ion intensities as a function of magnetic field and time for time-resolved magnetic dispersion measurements of rhenium. The Re^+ ion pulses (typical width, 25 nsec per laser pulse) were detected by a transient digitizer that operated with 2048 5-nsec channels, was triggered from the laser pulse, and was delayed 10.24 μsec . The signal was averaged for 20 or 100 laser pulses as the magnetic field was stepped in 2-G increments from 7788 to 7710 G.

time-of-flight mass filtering is used. If the pulsed ion beam is focused through a magnetic sector mass spectrometer, the output of the electron multiplier can be directed into an electrometer without time discrimination. Ions of a given mass not produced by the laser are not excluded by this technique. These ions can be excluded by time-gated integration (boxcar averaging) of the output of the electron multiplier. If the time gate is made large enough to encompass the times of flight of all the isotopes of an element, isotope ratio measurements are readily made by switching the magnetic field among the isotopes. However, to accommodate the differences in times of flight of the different isotopes, the response of the boxcar must be verified to be constant across the time window. The effective use of this time discrimination technique is illustrated in Fig. 4.

For time-of-flight mass filtering, where the complete mass spectrum is produced for each laser pulse, the timing and amplitude of the pulses leaving the multiplier are best measured by transient waveform digitizers. These devices are analog-to-digital converters with digitization rates as high as 200 MHz at nominal 8-bit resolution with more than 2048 memory channels. The characteristics of the transient digitizer for isotope ratio measurement have been defined (49), and improvements in recently introduced models should greatly facilitate their use in time-of-flight mass spectrometry.

An increase in the dynamic range of isotopic ratio measurement can be made by combining time-of-flight mass filtering with magnetic sector mass filtering. One of the limitations in making large isotopic ratio measurements is the scatter of ions of a large abundance mass peak into the nearby mass channel of a low abundance peak. By using the time-of-flight information made available by the laser-induced ionization process, both elastically and inelastically scat-

tered ions can be time-resolved and identified. A convoluted time-of-flight/magnetic field spectrum is illustrated in Fig. 5. In addition, measurement of large isotopic ratios by RIMS will be limited by space-charge and charge-transfer processes in the source of the mass spectrometer. Space charge results in the defocusing of the ion beam, with loss of both ion-extraction efficiency and resolution, thereby limiting throughput (50). The abundance sensitivity and space-charge limitation can be effectively reduced by the use of isotopically selective RIMS (42, 43).

Implications and Conclusions

The combination of the laser and the mass spectrometer has generated several new capabilities for chemical analysis. The laser's monochromaticity results in removal of isobaric interferences in the mass spectrometry. The high photon fluence gives high ionization efficiency, which is somewhat tempered by the low duty cycle afforded by today's pulsed lasers. However, work at Los Alamos has demonstrated the use of cw lasers with thermal atomization sources (33). The lower ionization rate for cw RIS is compensated by the match of the duty cycle, which can be defined as the ratio of atoms irradiated by the laser to the atoms emitted from the atomization source. The ions randomly formed in time are mass-separated by a magnetic sector and are counted by conventional counting techniques. Therefore, measurement of isotope ratios is straightforward.

On the other hand, pulsed laser resonance ionization, although ideally suited for time-of-flight mass filtering, loses efficiency because of a duty cycle mismatch between the atomization and ionization processes. This duty cycle limits sensitivity of the measurement process.

The duty cycle is dependent on the geometries of the laser and atomization beams, the velocity and time distribution of the atom beam, and the repetition rate of the laser. Thermal atom velocities of 10^4 to 10^5 cm sec^{-1} define a limitation on the duty cycle of the measurement system. Each pulse of the Nd:YAG-pumped dye laser produces an ion packet whose shape is defined by the interaction volume of the laser and the atom plume. Such an ion "hole" produced in the atom plume requires 1 to 10 μsec to be replenished. For a laser repetition rate of 10 Hz, the duty cycle is in the range of 10^{-4} to 10^{-5} . To match more closely this duty cycle, a pulsed thermal desorption source has been developed that produces an atom burst with a full width at half-maximum approaching 1 msec, thus improving the duty cycle by a factor of 30 (28).

Pulsed atomization sources, such as laser ablation or particle sputtering, appear to offer a higher duty cycle. However, the wide spread in velocities of sputtered or ablated material makes it impossible to overlap the laser temporally and spatially with all the atoms emitted into the gas phase. Calculations and experiments with sputtering indicate a sampling duty cycle of 3×10^{-4} , at best, with a 30-Hz laser (13). Considerable modeling has been done to estimate the efficiency of resonance ionization with thermal or sputtered atom sources and with pulsed or cw lasers (13, 21, 29). Advances in laser technology will be required to remove the compromise that must now be made between duty cycle and ionization efficiency. Even so, resonance ionization of neutral species in ion-sputtered neutral atom plumes has permitted direct compositional analysis of gallium in silicon at 500 parts per billion (ppb) (51) and the sensitive measurement by Parks and co-workers of boron in silicon at 50 ppb (52). Detection limits of 2 ppb are projected for this system based on a 5-minute measurement with 10 percent statistical uncertainty.

A different analytical approach based on RIS has been developed by Bekov and Letokhov (53). It combines an atomization furnace, selective multiphoton excitation of the atomic beam produced by the furnace, and field ionization of the excited atomic species by a pulsed electric field. These investigators have quantitatively determined the concentration of aluminum in blood, calibrating the process by measuring the aluminum atomic beam produced from known amounts of aluminum placed in the furnace.

Through the extension of wavelength selectivity to isotopic analysis, a new generation of tools for geochemical and geophysical measurements may be expected to evolve. With narrow-bandwidth laser systems, isotopic resonance ionization selectivities in excess of 10^6 have been predicted for such important isotope pairs as carbon-12 and carbon-14 (43) and strontium-88 and strontium-90 (42). By combining the selectivities resulting from narrow-bandwidth laser systems with isotopic selectivities available from time-resolved magnetic sector mass spectrometry, isotope abundance sensitivities in excess of 10^{12} may eventually be achieved.

The potential for multi-element isotope dilution analysis at low concentration levels has been discussed (24), and isotope dilution analysis for iron has already been demonstrated (25). The elimination of isobaric interferences may permit simplified chemical separations to be made for such determinations. The use of pulsed lasers will allow improved mass resolution by means of time-of-flight techniques, with the possibility of reducing background by means of time-gated detection. With improvement of throughput efficiency to as much as 10^{-3} , elemental analysis by isotope dilution may be feasible at the subpicogram-per-gram level for most elements.

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