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Secondary Neutral Mass Spectrometry Using Three-Colour Resonance Ionization: Osmium Detection at the p.p.b. Level and Iron Detection in Silicon at the < 200 p.p.t. Level

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Secondary neutral mass spectrometry using three-colour resonance ionization: osmium detection at the p.p.b. level and iron detection in silicon at the < 200 p.p.t. level

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Among the many uses of resonantly enhanced multiphoton ionization (REMPI) spectroscopy, secondary neutral mass spectrometry (SNMS) is both one of the most demanding and one of the most important. Recently, we have demonstrated that the selectivity of REMPI, and thus the sensitivity of SNMS, can be greatly enhanced by using resonant excitation schemes involving multiple resonant processes. Of particular interest is the use of autoionizing resonances, resonances with energies in excess of the ionization potential of the atom, in the REMPI process. The use of autoionizing resonances can reduce the laser intensity required to saturate the ionization process by more than an order of magnitude. This reduction can strongly reduce non-resonant ionization of background constituents, enhancing the signal to noise of the SNMS measurement. Although this approach to laser ionization SNMS is generally applicable, the three-colour ionization method has been demonstrated using two widely disparate yet important systems.

Iron impurity atoms form deep level traps in Si, changing bulk electrical properties even at concentrations approaching 1 p.p.t. In this case, normal mass spectrometry of impurity atoms is complicated by the isobaric interference of ^{56}Fe and ^{28}Si$_2$ molecule. The required mass resolution of greater than 10^4 exceeds the capabilities of most mass spectrometers. Even for instruments with sufficient mass resolution, the concomitant reduction in useful yield limits detection sensitivity in the near-surface region to 1 p.p.m. REMPI has now been successfully used to separately ionize the impurity atoms of interest. Three-colour REMPI dramatically reduces the residual non-resonant ionization of the isobarically interfering ion, allowing SNMS measurements at levels below 100 p.p.t. This result is accomplished without significant reduction in the fraction of contaminant atoms ionized and, therefore, in useful yield.

Mass spectrometric analysis for Os and Re has long been recognized as an important analytical goal in geochemistry. The concentrations and isotopic compositions of these elements must be determined in order to utilize the radioactive decay of ^{187}Re to ^{187}Os ($t_{\frac{1}{2}} = 4.23 \times 10^{10}$ years) as a tracer of geochemical processes. Three problems have limited the analysis of Os and Re. First, the concentrations of Os and Re in naturally occurring samples are extremely low, ranging from 1 p.p.b. to 60 p.p.m. Second, the high-ionization potentials (IP) of Os (8.7 eV) and Re (7.9 eV) have precluded the use of thermal ionization and limited the sensitivity of secondary ion mass spectrometry (SIMS) measurement to parts per

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million. Finally, the ^{187}Re/^{187}Os mass difference is less than 1 p.p.m., making conventional mass analysis (without complex chemical separation) impossible. We have demonstrated the ability of three-colour resonant SNMS to detect and separate Os and Re in Ni samples at the 4 p.p.b. level. *In situ* analysis of Os in iron meteorites demonstrates an elemental selectivity of Os over Re of greater than 10^3 without prior chemical separation. Measurements on a suite of samples with Os concentration varying from 10‰ down to 100 p.p.b. show a linear correlation between concentration and signal with a precision of better than $\pm 13\%$ and a useful yield in excess of 1%. These results demonstrate the potential for three-colour resonant ionization to detect and selectively ionize most high IP elements, including all of the Pt group elements, with good sensitivity, accuracy, and precision.

1. Introduction

Solutions to many important materials problems hinge on an ability to identify and track low levels of unknown and often unwanted atomic or molecular species. This is particularly true for surfaces, since the chemical and physical nature of an interface may be strongly effected by minority constituents. For the analyst, trace surface analysis represents a particularly difficult problem. The difficulty arises from the need to combine excellent discrimination, to identify the trace impurity of interest, with efficient sample utilization. An additional complication often present is the need to limit the information depth of the analysis to single, surface layers. With surface sensitivity and careful stepwise removal of atomic layers, a depth profile of the trace constituents concentration may be measured (Grasserbauer 1985).

Historically, secondary ion mass spectrometry (SIMS) has been the technique of choice for trace analysis of atomic scale samples, particularly, for problems associated with surface analysis. SIMS can provide greater than 1 part per billion by mass (p.p.b.) analysis sensitivity for favourable impurity–matrix combinations (Grasserbauer *et al.* 1985; Werner 1975; Benninghoven 1975; Clegg *et al.* 1981; Wittmaack 1982; Reuter 1983; Wittmaack 1980; Wittmaack 1979; Hinton *et al.* 1988) even for non-conducting matrices such as silicates and oxides (Benninghoven 1975; Clegg *et al.* 1981; Wittmaack *et al.* 1982; Hinton *et al.* 1988). For trace analysis of atomic scale samples, however, SIMS analysis remains difficult. The useful yield (defined as atoms detected/atoms removed) of the SIMS technique is often low (Werner 1975; Wittmaack 1980; Benninghoven & Muller 1972; Krauss & Wright 1980) because the secondary ion fraction of the sputtering process is small and the mass spectrometers used on most commercial SIMS instruments have been optimized for high mass resolution, not high transmission (Gerlach 1982). The high mass resolution is often necessary to discriminate between the desired signal and secondary ions arising from other atomic and or molecular ions. This discrimination is complicated by the large (often several orders of magnitude) variations which occur in the fraction of sputtered secondary ions as a function of species, surface chemical state and bombarding primary ion.

Recently, laser ionization of sputtered atoms has been used with significant success as an alternative to SIMS (Pellin, 1990; Parks *et al.* 1983, 1988; Blum *et al.* 1990*a–c*; Pellin *et al.* 1987; Harrison *et al.* 1986; Young *et al.* 1986, 1987, 1988; Gruen 1986; Becker & Gillen 1984*a,b*, 1985*a,b*, 1986; Pappas *et al.* 1989; Winograd *et al.* 1982; Kimock *et al.* 1984; Donahue *et al.* 1985; Becker & Gillen 1985; Gruen *et al.* 1988;

Pellin *et al.* 1988; De Bisschop & Vandervorst 1988; Pallix *et al.* 1988; Becker 1987; Christie & Goering 1988). Several recent reviews detail the technique (Pellin *et al.* 1988). Although this SNMS technique is often complex and time consuming due to the low repetition rates of commercially available lasers, there are many important advantages associated with the technique. The useful yield can, in contradistinction to SIMS, be extraordinarily high, approaching 10% for the surface analysis by resonant ionization of sputtered atoms (SARISA) apparatus (Young *et al.* 1986, 1987, 1988; Gruen 1986; Gruen *et al.* 1988; Pellin *et al.* 1988; Parks *et al.* 1988). Moreover, the detection sensitivity of resonant laser ionization SNMS represents a substantial improvement over SIMS. Detection sensitivities below 100 p.p.t. have been achieved (Pellin 1990; Becker & Gillen 1986; Pappas *et al.* 1989). Here, we demonstrate that these sensitivities can be achieved even in the presence of intense isobaric overlaps.

Trace surface analysis requires by its very nature analysis of an extremely limited number of atoms. The key to the sensitivity achieved by resonant laser ionization SNMS is the elimination of noise signal from the vast excess of other target atoms and molecules. The use of resonance ionization spectroscopy (RIS) combines both extreme selectivity and high efficiency in a single step. In this manner, measurements can be made for the first time which combine both high useful yields and high sensitivity. As measurements move from well-characterized test samples to more difficult practical samples, the selectivity of the RIS process is being tested more and more severely. This is particularly true when isobaric interferences exist in the sample of interest. Here we demonstrate the power and selectivity of the SARISA technique with two examples.

2. Experimental

There are presently two SNMS instruments (designated SARISA III and SARISA IV) in operation at Argonne National Laboratory. For the purposes of this publication, these units will be used as examples of laser SNMS instruments. Alternative designs have also been successful and can be found in the literature (Pellin 1990; Parks *et al.* 1983, 1988; Blum *et al.* 1990*a–c*; Pellin *et al.* 1987, 1988; Harrison *et al.* 1986; Young *et al.* 1986, 1988; Gruen 1986; Becker & Gillen 1984*a*,*b*, 1985*a*,*b*, 1986; Pappas *et al.* 1989; Winograd *et al.* 1982; Kimock *et al.* 1984; Donahue *et al.* 1985; Gruen *et al.* 1988). The SARISA instrument consists of five major subunits: the ion source, the sample vacuum chamber, the energy and angle-refocusing time-of-flight spectrometer/detector, the ionizing lasers, and a computer system for control and data acquisition. The first three subunits are depicted in figure 1.

2.1. *Ion source*

The pulsed ion source for the SARISA system can be operated with any of the standard sputtering gases using kilovolt extraction potentials (0.5–5 keV). Typically, noble gases are used to reduce sample compositional changes associated with the use of reactive gases such as oxygen. The source is differentially pumped in two separate chambers and mass filtered using a Wien filter in the first differential stage. Deflection plates allow the beam to be centred on each differential pumping aperture. These deflection plates are also used to electrically pulse the ion beam for use in resonance ionization SNMS analysis. The pulsing of the ion beam is produced with the use of two sets of deflection plates which sweep the beam past the two differential pumping apertures. By varying the phase of the two deflections, ion pulse widths ranging from less than 100 ns to 5 μs are produced.

Figure 1

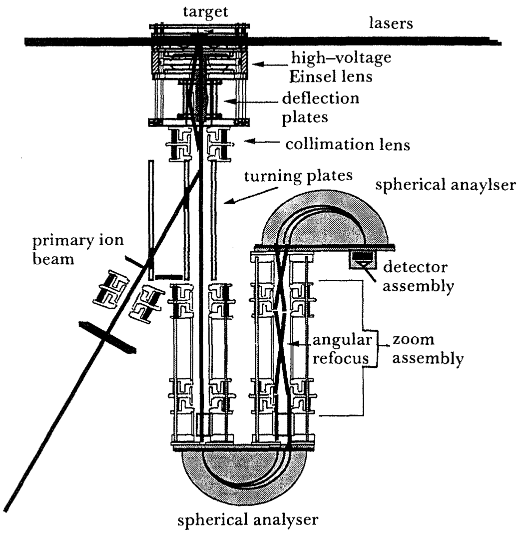

Figure 2

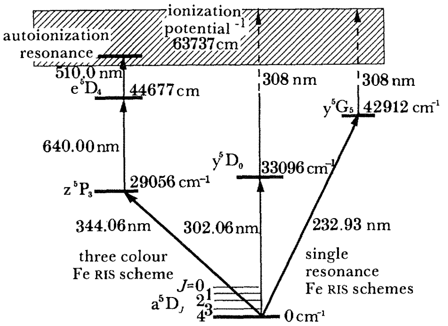

Figure 1. The SARISA IV energy- and angle-refocusing time-of-flight system for detection of sputtered neutral atoms.

Figure 2. Several ionization pathways for the Fe atom. The single resonance schemes have been used previously (Becker & Gillen 1984*a*, *b*). The three-colour resonance scheme shown on the left has recently demonstrated superior performance.

Lateral resolution for SARISA measurement is determined by the ion source spot size. The Colutron ion source used produces an average current of 2 μA in a 100 μm spot size. With appropriate aperturing spot sizes as small as 10 μm can be produced at reduced average current. Clearly, any commercially available ion source, including the VG liquid gallium ion source (which would allow submicrometre resolution), may be incorporated into this system in the future. When contemplating smaller ion spot sizes, however, it is important to consider the inevitable trade-off between current to the target and precision.

2.2. *Vacuum chamber*

The vacuum chamber holding the sample is cryogenically pumped (Varian UHV-8) with an operating pressure of 2×10^{-11} Torr (1 Torr ≈ 133 Pa). Included in the system is an Auger electron spectrometer for surface characterization of the sample before analysis, and an UTI no. 100C quadrupole mass spectrometer for residual gas analysis. The ultrahigh vacuum system is necessary to prevent residual gas contamination of samples during the measurement. The consequence of residual gas contamination depends on the details of the particular surface under study. Often, however, a changing sample surface during measurements leads to a reduction in the measurement precision.

2.3. *Laser system*

High laser intensity and precise tuning are required to achieve high photo-ionization efficiency. Excimer pumped, tunable dye lasers have been used for the SARISA instrument. These lasers have the advantage of good reliability, high repetition rate (less than 100 Hz) and the convenience of broadly tunable outputs.

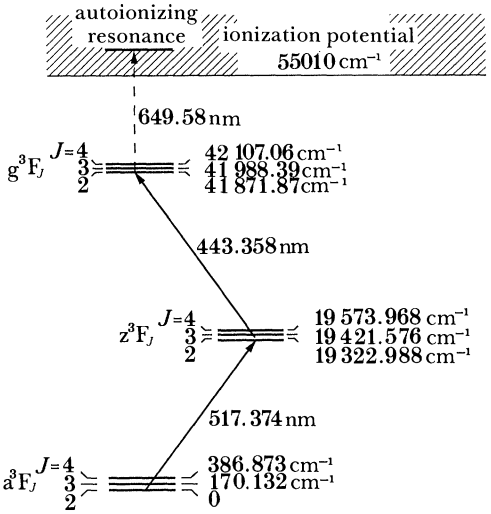

Figure 3. The 3-colour resonance scheme used to photoionize Ti.

The intensity of the excimer pump laser allows the use of as many as three dye lasers. We have used this property to resonantly tune to not just one but rather three separate resonances of the desired atom.

A typical resonance ionization scheme is shown in figure 2 for the Fe atom. Several excitation schemes are possible and have been tested. In each case, laser intensities can easily achieve saturation of the resonant transition. The ionizing transition may be saturated using an intense fixed-frequency pump laser. The diversity of laser excitation paths available to the investigator virtually insures that accidental ionization of other species due to absorption frequency overlaps can be avoided.

Here we demonstrate that the selectivity of REMPI, and thus the sensitivity of SNMS, can be greatly enhanced using resonant excitation schemes involving multiply resonant processes. Of particular interest is the accessing of autoionizing resonances with energies in excess of the ionization potential of the atom. The use of autoionizing resonances can reduce the laser intensity required to saturate the ionization process by more than an order of magnitude. In this way, non-resonant ionization of the interfering constituents of the sputtered flux can be substantially decreased, thus greatly enhancing the signal to noise of the SNMS measurement. This approach to laser ionization SNMS is quite generally applicable.

Three-colour resonant ionization schemes have also been identified and tested by us for Ti, Os and Re. The resonant ionization scheme for Ti is shown in figure 3; the Os and Re energy level pathways are displayed in figure 4. The use of three-colour resonant ionization is particularly important for complex samples. In planetary samples, the ubiquitous presence of interfering isobaric atoms and molecules requires the use of extremely discriminative ionization techniques. Any facility without the flexibility to use a variety of ionization schemes and ionize atoms using multiple resonant steps will often fail due to concomitant non-resonant ionization of isobaric species.

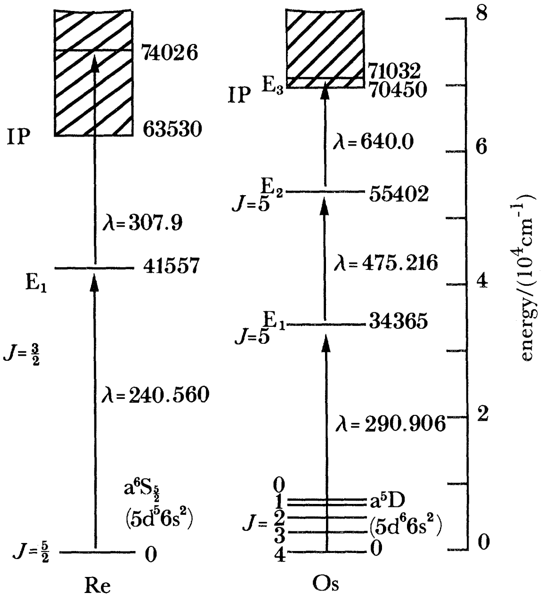

Figure 4. Resonance ionization schemes for Re and Os.

2.4. *Energy- and angle-refocusing time-of-flight mass spectrometer*

The final and most complex part of the SARISA apparatus is the time-of-flight detection system. The essential features of the energy- and angle-refocusing time-of-flight (EARTOF) mass spectrometer design are depicted schematically in figure 1. A description of the operation of the apparatus requires reference to the experimental timing sequence displayed in figure 5. It is the pulsed nature of the experiment that allows the combination of high throughput and high noise suppression. The data collection sequence is initiated when a 500 ns long primary ion pulse enters from the bottom left through the second differential pumping aperture. The ion pulse traverses a set of ion turning plates that merge the primary ion beam onto the EARTOF axis by means of electrostatic deflection. The beam is then focused onto the target by the high-voltage Einzel lens. The spot size produced is *ca.* 150 μm in diameter with up to 2 μA peak current.

As can be seen in figure 5, the primary ion pulse strikes the sample target during a time when the sample is held at +1400 V. Secondary ions and backscattered primary ions are ejected away from the target at high energy by this potential. The target potential is lowered to +1100 V and the lasers are triggered 300 ns after the end of the primary ion pulse. The photoions created leave the target region with an average energy of 1000 V. The combination of the high-voltage lens and the collimation lens images the photoions on the spherical energy analyser slits. The two spherical analysers are constructed to have large angular and energy acceptance windows. This is accomplished with unique boundary matching fields, using a design developed at Argonne. The boundary fields are established by screen printing a resistive paste onto a ceramic substrate; subsequent firing of this film at 950 °C completes the process and ensures good ultrahigh vacuum compatibility.

The purpose of the spherical energy analysers is twofold. First, the secondary ions (a major noise source) produced during the sputtering process and ejected at high

Figure 5

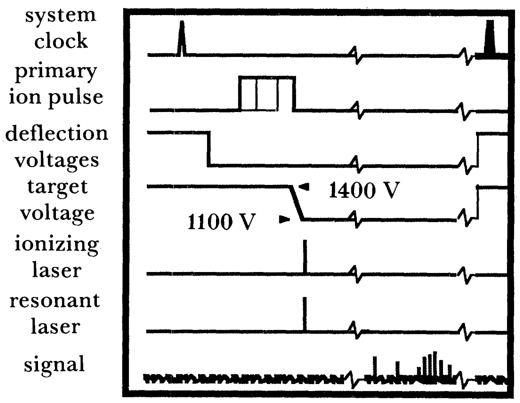

Figure 6

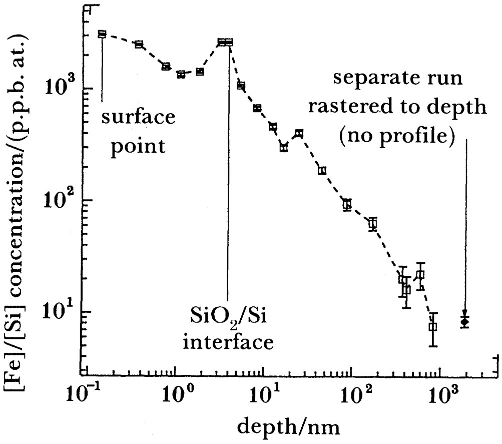

Figure 5. SARISA timing diagram. The labels refer to elements displayed in figure 2.

Figure 6. Fe depth profile in a Si wafer. Following a standard treatment (Ziebold 1967), we calculated from Poisson statistics a detection limit of 240 p.p.t. for ^{56}Fe and 70 p.p.t. for ^{54}Fe.

potential cannot pass the first analyser. Rather, they exit through a high-transmission screen which doubles as the outer hemisphere of Analyser 1. Second, the combination of two energy analysers provides time refocusing properties, allowing this instrument to achieve both reasonable mass resolution and high transmission.

The basic principle of using spherical energy analysers for time refocusing in TOF apparatuses has been discussed at length elsewhere (Grasserbauer *et al.* 1985). Spherical analysers were chosen rather than the simpler reflectron for energy refocusing for three reasons. First, the imaging properties of spherical energy analysers enhance the total machine throughput. Second, the noise reduction properties of this system are superior since there are no grids in the beam path and there are two separate reflecting stages. Third, slits can be inserted to increase the TOF mass resolution with a penalty in throughput by reducing either the energy spread or the angular spread in the photoion beam. The photoions, following traversal of the EARTOF, are then detected by a chevron microchannel plate arrangement. Data collection is accomplished either by gated pulse-counting electronics or with a LeCroy 8828C transient digitizer system.

2.5. *Computer control and analysis*

As noted above, SARISA IV is completely under computer control. Using Microsoft Windows, an integrated software package has been developed which allows the user to conveniently operate the instrument from the computer keyboard. All aspects of the experiment including operation, data collection, display, storage, and manipulation are incorporated into the software. All data are available on a network (TOPS) that can be addressed either by IBM or Macintosh platforms. This software package represents a significant advantage for users of the SARISA microprobe facility, since data from collaborative users can easily be transferred among the many groups involved, expediting cooperation among many users with diverse computer backgrounds.

3. Results

3.1. *Iron impurities in silicon*

An example of the power of the SARISA apparatus is shown in figure 6. The graph tracks the concentration of Fe in a Si sample as a function of depth. Fe impurity atoms form deep level traps in Si, changing bulk electrical properties even at concentrations approaching 1 p.p.t. In this case, normal mass spectrometry of Fe impurity atoms is complicated by the isobaric interference of ^{56}Fe by ^{28}Si$_2$ molecules. The mass resolution of greater than 10^4 required to separate these two species exceeds the capabilities of most mass spectrometers. Even for instruments with sufficient mass resolution, the concomitant reduction in useful yield limits detection sensitivity in the near-surface region to 1 p.p.m. (M. Anthony, personal communication). In these experiments, resonantly enhanced multiphoton ionization (REMPI) was successfully used to separately ionize the Fe atoms of interest. Three-colour REMPI dramatically reduces the residual non-resonant ionization of isobarically interfering Si$_2$ allowing SNMS measurements at levels below 100 p.p.t. This result is accomplished without significant reduction in the fraction of Fe atoms ionized and, therefore, in useful yield. Lateral resolution for these measurements was 150 μm. Each analysis was accomplished with removal of only a few atoms. Even at the highest sensitivity level, only 2.5 nm of sample surface was removed during measurement. For the depth profile shown in figure 6, each point represents a measurement. The ion beam pulsing was then stopped and the sample ion milled with a 2.3 mm × 2.3 mm raster pattern to the next desired depth. The solid line is only to aid the reader.

The sample examined here was prepared at Siemens by Dr H. Zieninger. The wafer was determined by DLTS measurement to have a bulk Fe impurity concentration of 3 ± 3 p.p.b. The point labelled 'surface' is an Fe determination made with less than one monolayer sample removal. Note the smooth transition across the Si–SiO$_2$ interface. The final measurement was made on an adjacent location on the Si wafer. The measurement was made a week later and demonstrates the measurement reproducibility. The time-of-flight nature of these measurements allows isotopic determination of the Fe concentration. The concentration of ^{54}Fe at 2 μm, for instance, was determined to be 155 ± 55 p.p.t. The measurement time was 30 min.

3.2. *Osmium and rhenium impurities in nickel*

A second example illustrating the selectivity of SARISA involves the mass spectrometric analysis of Os and Re, which has constituted a long-standing and important problem in geochemistry. The concentrations and isotopic compositions of these elements must be determined to utilize the radioactive decay of ^{187}Re to ^{187}Os ($t_{\frac{1}{2}} = 4.23\times10^{10}$ years) to trace the nature and cause of complex chemical processes in the solar nebula. Three features have limited the analysis of Os and Re. First, the concentrations of Os and Re in naturally occurring samples are extremely low, ranging from less than 1 p.p.b. to 60 p.p.m. Second, the high IP of Os (8.7 eV) and Re (7.9 eV) has precluded the use of thermal ionization and limited the sensitivity of SIMS measurement to parts per thousand. Finally, the mass difference between ^{187}Re and ^{187}Os is about 1 p.p.m., making conventional mass analysis (without complex chemical separation) impossible. In figure 7*a*, *b*, we show mass spectra obtained via resonant ionization of Re and Os respectively, using the ionization schemes depicted in figure 4. These spectra were taken using a synthetic sample consisting of 95.2%

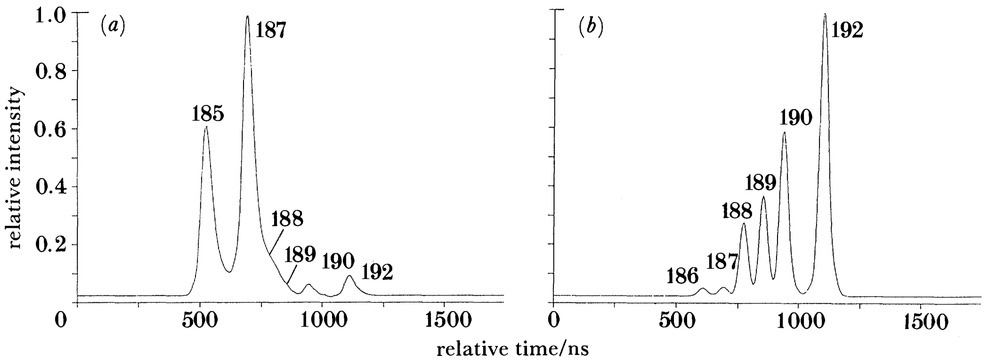

Figure 7. (*a*) Re spectrum taken at low mass resolution and (*b*) Os spectrum taken at higher mass resolution for the same synthetic sample (2.3 % Re; 2.5 % Os).

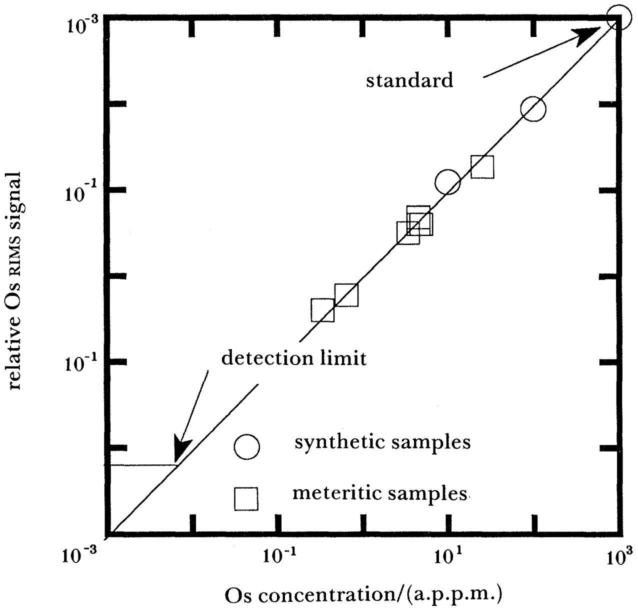

Figure 8. Logarithmic plot of normalized Os^+ signal intensity in parts per million atomic (p.p.m.a.) against Os concentration determined gravimetrically for synthetic samples or by RNAA for meteoritic samples. Circles are synthetic metals measured during analysis session 1, triangles are meteorites analysed during session 2, and diamonds are meteorites analysed during session 3. Signal intensities for each analysis session were normalized to the 1000 p.p.m.a. synthetic standard.

Ni, 2.5 % Os, and 2.3 % Re. The selectivity of Os over Re using the three-colour, triple-resonance Os-ionization scheme is far superior to the selectivity of Re over Os using the two-colour, single resonance Re-ionization scheme, as evidenced by the presence of non-resonantly ionized ^{188}Os and ^{192}Os in figure 7*a*. In fact, we have demonstrated the ability of three-colour resonant SNMS to detect Os in the presence of Re in Ni samples at the 4 p.p.b. level (Blum *et al.* 1990*a–c*). *In situ* analysis of Os in iron meteorites demonstrates an elemental selectivity of Os over Re of greater than 10^3 without prior chemical separation.

It is important to address the linearity of measurement when considering any analytical technique. We have measured the SARISA signal as a function of atomic Os concentration in the range of 0.33 to 1000 p.p.m. Both synthetic and meteoritic samples were used. The synthetic samples consisted of equal pre-weighed fractions of Os and Re dissolved in a Ni matrix at 1000, 100, and 10 p.p.m., with estimated uncertainties due to weighing of ±4%, ±25%, and ±35%, respectively. The meteoritic samples were taken from iron meteorites, and had bulk Os concentrations, as determined by radiochemical neutron activation analysis (RNAA), ranging from 0.33 to 25 p.p.m. The reported RNAA precision range between ±12% and ±14%. Before each SARISA analysis, a 2.0 μA continuous Ar^+ beam was rastered across a 2.5×2.5 mm^2 portion of the sample to remove surface contaminants. Each analysis consisted of summing the total counts in 24 channels, each 5 ns wide, for a period of 125 s at a repetition rate of 40 Hz (5000 pulses). These channels corresponded to a mass range of 185.5 to 192.5, so that the Os^+ counts from all major Os isotopes were collected simultaneously. A background nonresonant ionization correction was determined by detuning the ultraviolet laser 12 cm^{-1} from the first resonant transition wavelength (see figure 4) and collecting an analysis. Errors due to counting statistics were small (less than 2% 2σ) and the best indicator of the analytical precision is provided by the reproducibility of replicate analyses. Replicate SARISA analyses vary from the mean for each sample by 1% to 13%. The 1000 p.p.m. Os standard was analysed before each analysis session and served as an internal standard to correct for variation in the operating conditions. The results of the analysis are presented in figure 8 on a log–log scale. The data fall along a calibration line of slope 1, indicating a simple linear proportionality with the deviation from the line ranging between 6% and 25% of the concentration.

4. Conclusion

Here we have demonstrated the use of three-colour resonant ionization to enhance the sensitivity and the selectivity of resonant laser ionization SNMS. This technique reduced the interference of isobaric ions allowing measurements at the p.p.b. level even for complex matricies without a loss in useful yield. A second significant advantage of the technique is its potential to detect and selectively ionize most high ionization potential elements, including all of the Pt group elements, with good sensitivity and precision.

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Discussion

L. de Galan (*Unilever Research Laboratory, The Netherlands*). How easily can isotopes of one element be ionized with a single wavelength?

M. J. Pellin. Wavelength shifts in the electronic absorption spectrum for differing isotopes of the same element are generally small when compared with the Doppler line broadening which we encounter and the effective power broadened laser bandwidth used. Thus in general ionization is accomplished for all isotopes of a given element. Presently we are exploring the fine details of this interaction. The literature details problems with hyperfine interactions which alter the yield of odd isotopes with respect to even isotopes. Presently, we feel that to within ±10% we can accurately determine the isotope ratios present in any sample. The precision of these measurements is better than ±1%. Thus by using standards the accuracy of these measurements can be improved by at least one order of magnitude.

L. de Galan. How does laser ionization compare with non-resonant techniques, e.g. electron impact ionization?

M. J. Pellin. Resonant laser ionization is an efficient (*ca.* 10^{-1}), but pulsed method of ionization. Thus when properly used very high useful yields may be achieved. Moreover, nearly all elements are ionized with near unit probability. An additional benefit of RIS is its selectivity; thus isobaric interferences are all but eliminated.

Electron impact ionization is at least three orders of magnitude less efficient. Thus the sample utilization is relatively poor. However, it can be operated in a continuous mode. Therefore, the signal acquisition rate may even be higher than for RIS. Since the ultimate detection limit of a technique is limited by background noise, interferences typically limit the detection limit of EI ionization. This is in part balanced by the fact that all masses are ionized (with widely varying sensitivities) and by the ease of operation of an EI unit.

Cracking of molecular species in general occurs for both cases. In the case of RIS, however, some control is available through the use of low laser intensities and favourable non-dissociative intermediate spectroscopic states.

L. de Galan. What vacuum is used?

M. J. Pellin. The SARISA instrument's base vacuum is 1×10^{-10} Torr. Since the measurements we make are 'static' in nature residual gas contamination is undesirable. The system has an entry lock for sample insertion to minimize down time.

M. Grasserbauer (*University of Vienna, Austria*). Could Dr Pellin compare the relative advantages or disadvantages of resonant and non-resonant ionization?

M. J. Pellin. There really are three cases of laser ionization which I would like to compare: resonant ionization, near-resonant ionization, and non-resonant ionization. Resonant ionization is characterized by the use of one or more tunable laser sources to precisely match the absorption spectra of an atom or molecule of interest. Near-resonant ionization involves the use of a fixed frequency laser source which has been carefully chosen to utilize an enhanced cross section of a particular component of the sputtered flux. So-called 'soft', or utilizing one-photon intermediate near-resonances in multiphoton ionization (MPI) is an example of near-resonant ionization. Finally non-resonant ionization utilizes a fixed frequency, intense laser source in an attempt to ionize all species in the sputtered flux, almost always in MPI without intermediate state enhancements.

There really isn't enough space to do justice to a complete comparison of all the aspects of these three different methods of ionization. At the risk of offending knowledgeable practitioners here are several salient points versus SIMS. Non-resonant ionization reduces substrate matrix effects, has a range of element-specific useful yields which can vary by two orders of magnitude, has useful yields as high as 10^{-4}, detects all species in the flux but as a consequence often suffers from isobaric interferences (although these may be reduced from the SIMS case by laser induced fragmentation of molecular species). Lasers are required and so an additional level of complexity (when compared with SIMS) is present. Near-resonant ionization is particularly suitable for the detection of molecular species. The laser equipment required is often only moderately more complicated than in the non-resonant case, the benefit derived is an increased useful yield and specificity. Resonant ionization has the most complex apparatus, it detects only one species at a time. A benefit of this is a high useful yield (approaching 10^{-1}), high specificity, a 10–100 p.p.t. detection sensitivity at full useful yield and a virtual elimination of isobaric overlaps.

M. GRASSERBAUER. What determines the useful yield of resonant postionization SNMS?

M. J. PELLIN. Useful yield, defined as (atoms detected)/(atoms removed), is determined by several parameters. First, one must consider the fraction of sputtered species in the ground electronic state. This fraction typically ranges from 0.5 to 1 and varies only slightly from matrix to matrix. Second, the length of the primary ion pulse, the velocity distribution of the sputtered atoms, the angular distribution of sputtered atoms, and the laser firing time after the primary ion pulse strikes the target determines the spatial extent of the sputtered flux. Third, the useful part of the laser volume (that part which the mass spectrometer can extract and transmit to the detector) must be large. Finally the laser intensity must be sufficient to saturate the ionization transition in this relatively large spot size.

J. C. VICKERMAN. (*UMIST*, *U.K.*). Has Dr Pellin studied resonant ionization of organic molecules? Does he see a future for the quantification of these species using this approach?

M. J. PELLIN. We have used 'resonant' ionization spectroscopy (RIS) on a variety of organic molecules ranging from tryptophane and tryptophan-containing biopolymers to small polymer additives. Saturating intensities can certainly be achieved. Several complications arise for molecules which are not present for atoms. First, the rotational and vibrational distribution of sputtered molecules make purely resonant ionization much less efficient. In general, we have found near resonant ionization to be a useful tool for ionization of a reasonable fraction of the ejected molecules. In this method the intensity of the laser is increased until the absorption band is power broadened sufficiently to excite most of the molecular flux. Second, molecules may fragment during or immediately following the ionization process. This fragmentation is common for many ionization techniques such as electron impact ionization. Since the photon energies may be adjusted to leave a minimum of excess energy in the molecular ion, often photo-ionization produces a minimum of fragmentation.

The use of resonant ionization can eliminate one of the uncertainties associated with quantitative molecular analysis – the matrix-dependent ionization fraction. True quantization requires a knowledge of molecular sputtering yields and the molecule-dependent fragmentation channels. Thus, while this approach has several advantages for quantification, it does not represent a complete solution.

J. C. VICKERMAN. Dr Pellin does not think non-resonant ionization is any better than TOF-SIMS due to the lower useful yield. Is there a benefit in greatly reduced or eliminated matrix effects for multimatrix samples? There are also elements such as As or Au where the yield compared with SIMS will certainly be higher.

M. J. PELLIN. Non-resonant ionization SNMS for the analysis of Si samples is not I think, in general, worth the added expense and difficulty versus TOF-SIMS. Certainly there are instances when its performance is superior to TOF-SIMS. The positive ion yield of As is certainly low and a NRIS experiment will have an increased useful yield (although perhaps not as high as the negative ion yield).

Multimatrix samples are another good example of a system where the better quantification available in a NRIS measurement is of use. However, the best detection limits demonstrated for NRIS so far have been disappointing, generally inferior to TOF-SIMS. Thus overall one must carefully examine the experimental goals before choosing the added expense and complication of a NRIS experimental system.

D. T. BURNS (*The Queen's University of Belfast, U.K.*). Could Dr Pellin comment on the problems of running dye lasers for the long periods necessary for analysis?

M. J. PELLIN. Dye laser operation has in recent years become more or less routine. For these experiments we use relatively broad band, unsophisticated dye laser sources. Since we run strongly into the laser saturation intensity region, intensity fluxuations do not significantly affect our signals. During analysis, dye interchange is required each day (2 l of 10^{-3} molar solutions) and half an hour of alignment is required. Pump laser gases must be changed every two or three days and their optics cleaned each week.

In the near future solid-state tunable lasers will become routinely available. These systems will be much more robust, requiring little daily maintenance.

R. F. C. MANTOURA (*Plymouth Marine Laboratory, U.K.*). Can laser ionization MS systems be used to determine $^{13}C/^{12}C$ and $^{15}N/^{14}N$ isotope ratios in 1–10 μm sized cells trapped on glan fibre filters? Can Dr Pellin suggest key references on this topic?

M. J. PELLIN. Isotope ratio measurements in laser ionization MS systems have been investigated for a variety of different elements. Typically with the use of standards 1% precisions can be obtained. For C, in particular, you might look at the paper by Gelin *et al.* (1990).

Additional reference

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