

RESONANCE IONIZATION: POTENTIAL APPLICATION OF FEW-ATOM DETECTION TECHNIQUES TO INTER-PLANETARY DUST PARTICLE AND "STARDUST" STUDIES.
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Resonance ionization, an emerging laser-based element analysis technique, is being harnessed to a wide variety of problems in which minute quantities of a particular element need to be measured efficiently in the presence of an overwhelmingly larger background of other materials. By utilizing lasers tuned to specific atomic energy levels of the analyte element, ions are produced selectively in a mass spectrometer with much higher efficiency than possible using conventional methods, such as electron bombardment, thermal ionization, or ion sputtering. Pioneered in the 1970s at the Oak Ridge National Laboratory [1,2] and the Institute of Spectroscopy of the Russian Academy of Sciences [3], resonance ionization has brought detection limits down to the single-atom-level, which was first demonstrated by detecting single Cs atoms in the presence of 10^{19} Ar atoms and 10^{18} CH₄ molecules [4]. Research now ranges from basic atomic physics studies and new implementations of the principle, to applications in particle physics, biology, the environment and cosmochemistry [5]. The salient characteristics of resonance ionization, its implementation emphasizing applications to studies of interplanetary dust and microscopic refractory grains from meteorites, and preliminary data illustrating its unique capabilities, are presented.

For many applications, resonance ionization is coupled to mass spectrometry (RIMS), an approach that has been reviewed recently [6]. A RIMS system consists of: (1) a sample atomizer, as the excitation process requires isolated atoms or molecules, (2) tunable laser(s) to promote the valence electron through one or more excited states to ionization, (3) a filter to separate the different ion masses (primarily isotopes) and reject interfering ions, and (4) an ion detection and data collection system. Atomizers for spatially resolved solids measurements and for noble gases are shown in the RIMS schematic of Figure 1. Both utilize pulsed atomization and ionization to optimize sample utilization efficiency and element accessibility.

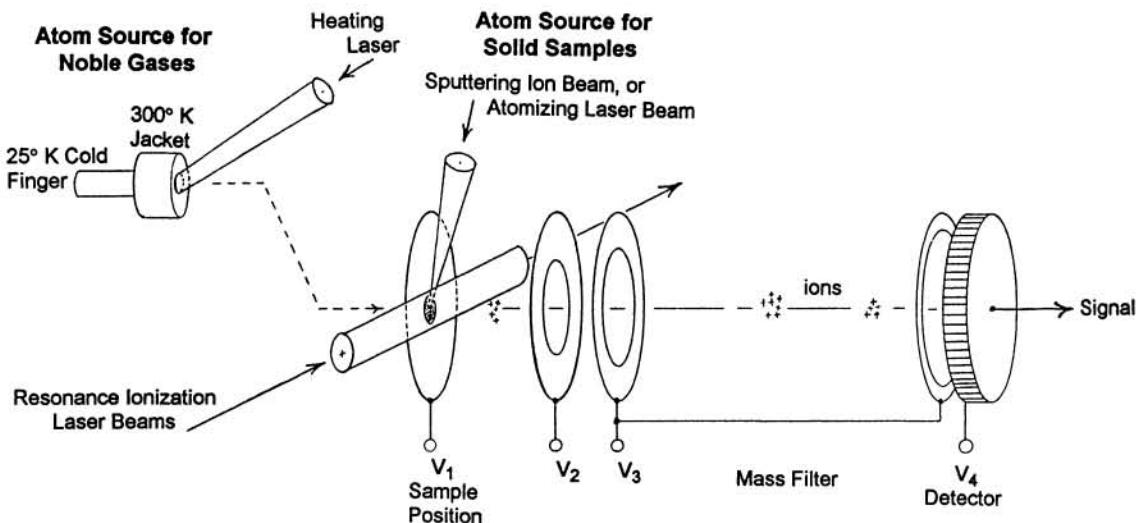


Figure 1. Resonance ionization mass spectrometry (RIMS) system. By rastering the sputtering ion beam or atomizing laser beam, the spatial distribution of the analyte can be determined. Ion sputtering yields better spatial resolution, while laser atomization provides faster analyses. Locating the cold finger at the sample position in a static mass spectrometer, allows noble gases to freeze and be concentrated at a specific location, and subsequently released simultaneously by gently heating with a pulsed laser. Careful selection of atomization and ionization beam overlap result in detecting 2 to 20% of the atoms released; in the case of noble gases, atoms that did not become ionized, continue returning to the cold finger until all have been detected.

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The most notable characteristics of the RIMS technique are greatly reduced background and isobaric interferences, efficiency, few-atom detection limit, and applicability to most elements in the periodic table [7]. Efficiencies (ions detected/atoms removed from sample) of 30 to 50% in semiconductor analyses using sputter atomization have been reported [8,9] although 5% is more typical under most circumstances. Note that within the laser beam(s), ionization efficiency is usually close to 100%. The achievable efficiency is limited by the geometric and temporal overlap of the atomized sample with the ionizing laser beam, the transmission through the mass filter, and the detector efficiency. In RIMS analyses for traces of Ga in Si, the ionization efficiency for the Si matrix was $<2 \times 10^{-9}$ of that for Ga [10], highlighting the very large selectivity possible in the ionization process. This element-specific selectivity depends on the resonance ionization scheme (multiple longer-wavelength, lower-intensity laser beams are better than a single high-intensity, short-wavelength beam) and the composition and complexity of the matrix, but usually provides many orders of magnitude reduction in interference from isobars, hydrides and molecules, permitting use of simpler (and higher transmission) mass filters, such as time-of-flight mass spectrometers. The benefits of RIMS need to be evaluated for each specific application against the added complexity and cost of the ionizing laser system. The high selectivity, of course, makes RIMS unsuitable in surveys requiring simultaneous determination of the overall element composition of an unknown sample.

The ion microprobe (or, secondary ion mass spectrometry, SIMS) has become a very valuable tool for element and isotopic analyses of extraterrestrial samples with spatial resolution down to few μm . Although some work has been attempted with probe resolution as low as ~ 50 nm, the typical SIMS ion yield of 10^{-3} , 10^{-4} , or less, limits its usefulness. This is where resonance ionization can provide a tremendous improvement, and a number of researchers have been applying the technique to a wide variety of solid samples [11,12,13], including extraterrestrial samples [14]. Using a laser beam for atomization [15,16] can significantly increase the speed of analyses (and lower detection limits) as much higher atomization rates are possible, but resolution is limited to $\sim 0.5 \mu\text{m}$.

In a static RIMS system for noble gases, the combination of high ionization efficiency and sample concentrator (Figure 1) results in an extremely fast (~ 3 min. detection half-life vs. ~ 60 min. for conventional systems) analyzer with a detection limit of ~ 100 ^{85}Kr atoms, Figure 2 [16]. In addition to the almost complete absence of interferences, the short analysis time significantly reduces the background contribution of outgassing in the mass spectrometer. Although using a less efficient laser scheme resulting in slower analyses, a similar system has recently been completed and dedicated to extraterrestrial Xe measurements [17]. At the newly formed Institute for Rare Isotope Measurements, IRIM [18], the noble gas equipment that had previously been at Atom Sciences [6,16] is being re-installed and upgraded to provide routine noble gas measurements from terrestrial and extraterrestrial samples. An early application will be Kr and Xe isotopic measurements from single microscopic interstellar SiC grains.

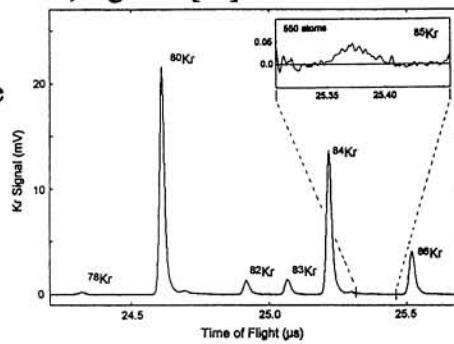


Figure 2. RIMS signal from 550 atom sample.

- References:** [1] Hurst G.S. et al. (1975) *Phys. Rev. Lett.*, 35, 82. [2] Payne M.G. et al. (1975) *Phys. Rev. Lett.*, 35, 1154. [3] Ambartsumian R.V. and Letokhov V.S. (1972) *Appl. Optics*, 11, 354. [4] Hurst G.S. et al. (1977) *Appl. Phys. Lett.*, 30, 229. [5] Miller C.M. and Parks J.E., eds. (1992) *Resonance Ionization Spectroscopy 1992*, *Inst. Phys. Conf. Series*, 128, (IOP, Bristol). [6] Payne M.G., Deng L. and Thonnard N. (1994) *Rev. Sci. Instrum.*, 65, 2433. [7] Hurst G.S. et al. (1979) *Rev. Mod. Phys.*, 51, 767. [8] Pappas D.L. et al. (1989) *Science*, 243, 64. [9] Arlinghaus H.F. et al. (1990) *J. Vac. Sci. Technol. A*, 8, 2318. [10] Thonnard N. et al. (1989) *Surf. Interf. Anal.*, 18, 751. [11] Arlinghaus H.F. et al. (1993) *J. Vac. Sci. Technol. A*, 11, 2317. [12] Winograd N. (1993) *Anal. Chem.*, 65, 622. [13] Arlinghaus H.F. et al. (1992) *Inst. Phys. Conf. Ser.*, 128, 275. [14] Blum J.D. (1990) *Geochim. Cosmochim. Acta* 54, 875. [15] Arlinghaus H.F. and Thonnard N. (1991) in *Laser Ablation Mechanisms and Applications*, Miller J.C. and Haglund R.F. Jr., eds., (Springer, Berlin), 165. [16] Thonnard N. et al. (1992) *Inst. Phys. Conf. Ser.*, 128, 27. [17] Gilmour J.D. et al. (1994) *Rev. Sci. Instrum.*, 65, 617. [18] Thonnard N. and Lehmann B.L. (1995) in *RIS'94, AIP Conf. Ser.*, in press.