

RESONANCE IONIZATION SPECTROSCOPY

A technique based on laser ionization allows researchers to attack an array of problems ranging from measuring fundamental physical parameters of atomic nuclei to understanding the extinction of the dinosaurs.

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More than two decades ago a laser-based spectroscopic technique was developed that has since proved effective in solving problems no other spectroscopic method, conventional or laser based, can tackle. Known as resonance ionization spectroscopy, it has become a very useful tool for pure and applied research in physics and chemistry (see an example in figure 1), and it has found application in many other fields, including microelectronics, the Earth sciences and biomedicine.

The basic science behind RIS is very simple, involving atomic, molecular and optical physics. First a laser pulse resonantly excites an electron in an atom or molecule from an initial ground state (sometimes a metastable state) to a higher discrete state. Then other photons, collisions or an electric field cause ionization of the excited neutral species. A proportional counter or secondary electron multiplier detects the photoion or photoelectron thus produced. Any type of mass spectrometer can achieve mass-selective detection of the species, which is already Z -selected (where Z is the atomic number) in the RIS process.

The resonant absorption of photons from the laser can begin when the neutral species is in its ground state or when the atom is already excited by some other means, such as a beam of charged particles. One can take advantage of the resonant transitions to detect excited atoms, such as metastable atoms, or ground-state atoms with quantum-state selectivity. (Of course, this selectivity requires some knowledge of the energy levels and other spectroscopic data for the species to be detected.) When the resonance ionization process is saturated, one electron is ejected from each of the "selected" neutral particles. This makes possible very *sensitive* as well as selective detection. Furthermore, the method is so general that one can apply it to all of the elements.

In the early 1970s much of the research on RIS was concentrated at the photophysics group of Oak Ridge National Laboratory and at the Institute of Spectroscopy of the USSR Academy of Sciences, in Troitsk. Because

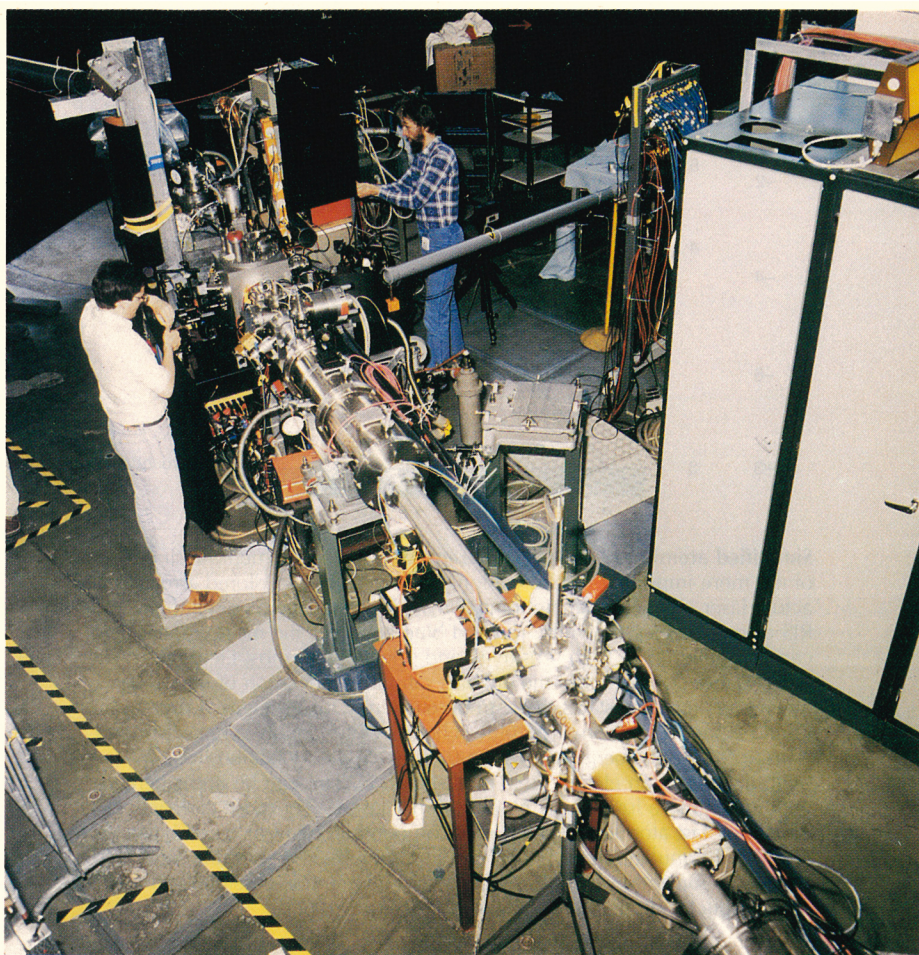
these two groups worked quite independently to develop the emerging technique, it is not surprising that each program had its own unique focus. Work in the Soviet Union concentrated on the use of atomic and molecular beams to serve that country's interests in isotope separation and sensitive elemental analysis. Early work at Oak Ridge explored sensitive devices for detecting the metastable states created through the interaction of fast particles with gases. Oak Ridge researchers also demonstrated that individual atoms in their ground states could be counted by introducing laser beams into proportional counters. In retrospect these independent efforts can be viewed as complementary, setting the stage for global interest in both the development and use of RIS.¹

For a more detailed description of the principles and applications of RIS than we can give in this article, we refer the reader to two monographs.^{2,3}

Underlying principles

There are many possible resonance ionization pathways. (See figure 2.) In an atom having a low ionization potential a single resonant excitation can raise the atom to a level at which ionization is possible by absorption of another photon of the same wavelength. In most cases, however, the arrangement of the energy levels makes it more convenient to use successive resonant excitation to two discrete levels (two resonance steps) with two laser pulses at properly tuned wavelengths. These excited atoms can then be ionized in several ways. For example, one can use another photon absorption to take the atom to the ionization continuum. Such nonresonant transitions typically have comparatively small cross sections for ionization by a photon (10^{-17} – 10^{-16} cm²) and wide absorption bands. Atoms with multielectron optical shells often feature narrow autoionization levels (discrete states higher in energy than the ionization potential). One can take advantage of those excited states to produce resonance ionization with a greater cross section (10^{-15} – 10^{-16} cm²). A convenient and versatile alternative technique is to excite a Rydberg atomic level (a bound state close to the ionization continuum with a high principal quantum number n^* around 15), which can be ionized with an electric field pulse of moderate strength (10–20 kV/cm). These various resonance ionization pathways enable one

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Resonance ionization spectroscopy facility at CERN used for research in nuclear physics. **Figure 1**

to select an optimum RIS scheme for the atom of interest using ordinary lasers that are financially and technically within reach of most laboratories.

To maximize the sensitivity and selectivity of RIS, the laser pulses used must meet certain requirements. Their duration must be shorter than or commensurate with the lifetimes of the intermediate states (for atomic transitions, usually a few tens of nanoseconds) to avoid the "optical pumping" effect, which causes the excited atom to drop spontaneously back to an intermediate level out of resonance with the light field and thus escape ionization. Also, the energy fluence (photon energy per unit area) of each laser pulse must be high enough to saturate the quantum transition involved, that is, to raise the atom to the next excited state with a probability of 50–100%. This requirement is actually quite modest: Allowed atomic transitions require laser pulse fluences of 10^{-6} – 10^{-3} J/cm². Some 0.1–1 J/cm² is necessary to complete the transition to the ionization continuum with high efficiency. Because no nonlaser light source can meet the requirement that the quantum transitions must be saturated, RIS was invented and successfully applied only after the advent of the tunable pulsed laser.

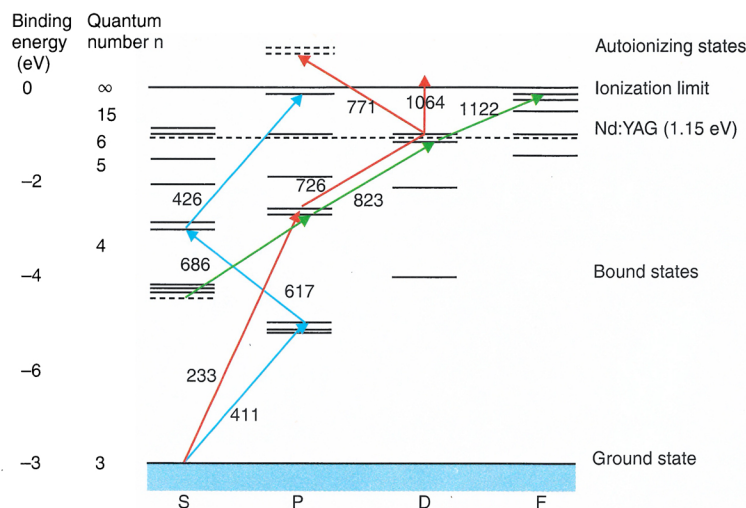
Under optimum conditions an atom can be ionized with an ionization yield approaching 100%. One can detect the photoion produced with a probability close to 100% and simultaneously use a mass spectrometer to

identify its mass (or mass spectrum when, for example, several isotopic species are being ionized). This technique, known as resonance ion mass spectroscopy, or RIMS, combines high detection sensitivity with the ability to select species according to atomic number *and* mass.

Measurement limits

A remarkable feature of RIS is its potential to attain very rigorous measurement limits. (See the table on page 40.) Its *sensitivity* is high enough to permit detection, during a single laser pulse, of a single atom or molecule of a certain type and in a certain initial quantum state. The *spectral resolution* of RIS is governed by the multistep resonance excitation linewidth of the atom under study, which in turn depends on the individual linewidths at each excitation step. The exciting store of laser spectroscopy methods make it possible to eliminate Doppler broadening, so that ultimately the spectral resolution of the RIS technique will be defined by Γ_{hom} , the homogeneous linewidth. This possibility was demonstrated in the well-known experiments on the Doppler-free two-photon RIS of positronium.⁴ Maximum possible values of the *time resolution* of the RIS technique are determined by the inverse of the homogeneous linewidth, Γ_{hom}^{-1} . Subpicosecond resolution has been attained in RIS experiments with molecules.⁵

A unique feature of RIS with multistep resonance



Simplified atomic energy-level diagram for a typical element illustrates some of the more important resonance ionization schemes. Colored arrows (not actual laser colors) designate transitions, with wavelengths in nanometers. RIS using schemes shown by red and blue arrows is the most versatile and can be applied with high sensitivity and selectivity to most elements. With a Nd:YAG laser, the red scheme enables saturated ionization of elements having autoionizing states that can be efficiently ionized with a third bound-bound transition. The blue scheme, which involves bound-bound transitions to a Rydberg state within 0.05 eV of the ionization limit, followed by ionization in an electric field of about 10 kV/cm, can be implemented with inexpensive low-power N₂ or excimer lasers. For those elements in which, by fast atomic collisions, electron bombardment or recombination, a significant population can be trapped in a long-lived metastable state, resonance ionization by the scheme shown in green is possible with tunable semiconductor diode lasers. **Figure 2**

excitation is its exceptionally high *selectivity*. Selectivity is the number of background (nonselected) atoms required to produce a signal equal to that produced by one atom of the selected type. In conventional optical spectroscopy, we are accustomed to selectivity's being limited by the overlapping of wings of close atomic or molecular lines. For this reason, it is in principle impossible to detect optically a radiocarbon atom (¹⁴C, for example) against the background of the abundant carbon isotope ¹²C. (Natural terrestrial ¹⁴C/¹²C concentration ratios run between 10⁻¹² and 10⁻¹⁶.) By contrast, in, for example, a three-step RIS excitation of an isotopic atom, the total selectivity *S* is the product *S*₁*S*₂*S*₃ of the excitation selec-

tivities of the individual steps and so can exceed 10¹⁵–10²⁰.

The resonance ionization of an atom or molecule gives rise to charged particles at the point of interaction. In principle it is quite possible to locate the point where a photoelectron and a photoion are formed with an accuracy much better than the photoionizing radiation wavelength. This positional accuracy forms the basis for potential detection by RIS of absorbing centers, impurities and chromophores on surfaces with spatial resolution on a nanometer scale, that is, for the development of resonance ionization microspectroscopy, or RISM. A key step toward the realization of the RISM concept has been the recent observation of laser resonant photoionization of absorbing centers (F₂ color centers) on the surface of LiF crystals.⁶

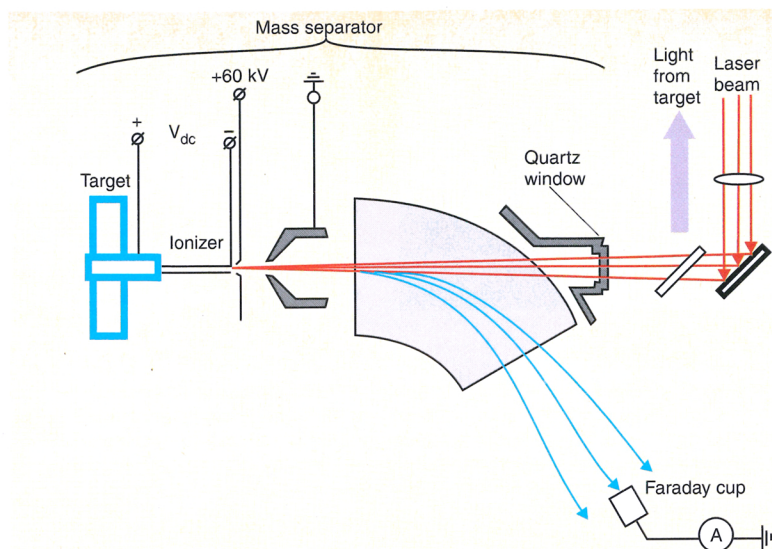
To select the optimum RIS pathway for a given atom or molecule, it is necessary to know not only the wavelength of the quantum transition from the ground state but also the wavelengths of the transitions between excited states, the lifetimes of these transitions and the transition cross sections. This information is scattered among various handbooks and the periodical literature. Researchers at the National Institute of Standards and Technology in Gaithersburg, Maryland, also gather such data.⁷

Because the RIS technique is itself a convenient means for studying highly excited states, one can use it to obtain spectroscopic information on atoms and molecules directly. By varying the delay time between laser pulses one can measure the lifetimes of intermediate excited states, and by changing the ionizing laser wavelengths (λ_2 or λ_3) one can detect and measure the positions

Ultimate characteristics of RIS

Characteristic	Theoretical limit
Sensitivity	Single atom or molecule
Spectral resolution	$\Gamma_{\text{hom}} = 10^{-6} - 10^{-13} \text{ sec}^{-1}$
Time resolution	$1/\Gamma_{\text{hom}} = 10^{-6} - 10^{-13} \text{ sec}$
Selectivity	$S = S_1 S_2 \dots S_n = 10^{10} - 10^{20}$
Spatial resolution	De Broglie wavelength of electron or ion
Versatility	Any atom or molecule

Characteristics based on using modern lasers. Γ_{hom} is the homogeneous linewidth.



Mass separator and laser ion source developed at CERN based on the principles of resonance ion spectroscopy. This instrument can produce beams of atoms that are isotopically, isobarically or isomerically pure. **Figure 3**

of Rydberg levels, ionization limits and autoionization levels. This capability was successfully demonstrated in early experiments on uranium and the lanthanides at the Lawrence Livermore National Laboratory and in experiments with radioactive francium atoms, which are only available in infinitesimal amounts (around 10^5 atoms in a sample).⁸ By varying the wavelength of the first resonance transition (λ_1) one can obtain with high sensitivity and spectral resolution information about the hyperfine structures of various isotopes and about the isomer shifts of atomic energy levels. These characteristics of RIS are especially important in experiments with short-lived radioactive isotopes produced in the course of nuclear reactions. The RIS method can also be used to measure populations and lifetimes of excited states produced in complex collision processes in gases, as demonstrated for helium in some of the early RIS work.⁹

Nuclear physics applications

Laser spectroscopic techniques are being used for studies of long chains of short-lived radioactive isotopes far from β stability. The high resolution and sensitivity of these techniques make it possible to measure the hyperfine structure and isotope shifts of atomic spectral lines and from these data to gather information on the nuclear spins I , magnetic moments μ_I , quadrupole moments Q_s , changes in the mean-square charge radii $\delta\langle r^2 \rangle$ and the deformation parameters $\langle \beta^2 \rangle$ of nuclei in ground and isomeric states. One obtains short-lived isotopes of many elements in accelerators where protons (of some 1 GeV in energy) or heavy ions bombard suitable targets. The resulting isotopes are then mass-separated under on-line conditions by the so-called isotope separation on-line, or ISOL, method. An ISOL facility has operated successfully at CERN for many years.¹⁰

Because of its high sensitivity and versatility RIS is a valuable method for running experiments on ISOL facilities. It is natural to combine RIS with a mass spectrometer for the purpose of identifying the masses of isotopes. The resulting RIMS technique features both Z and A selectivity (where A is the sum of protons and neutrons, $Z + N$). That combination is very important for nuclear experiments conducted in the presence of numerous isobars (atomic species with the same A but different Z).

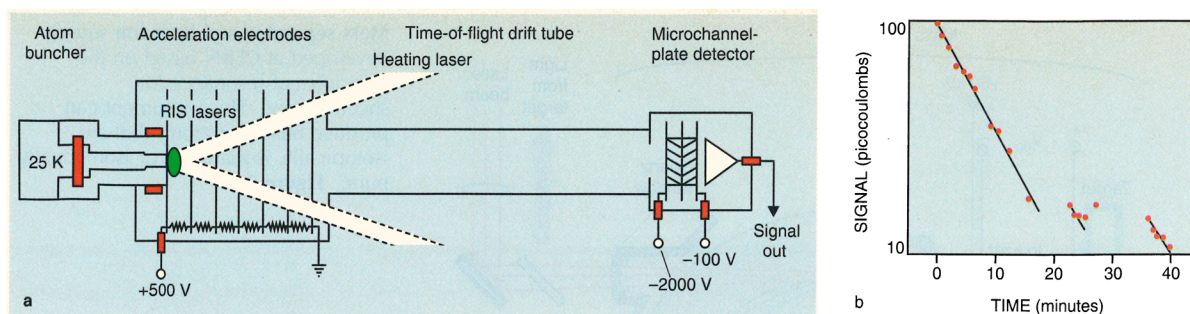
Researchers at the Leningrad (now Saint Petersburg)

Institute of Nuclear Physics, in collaboration with researchers from the Institute of Spectroscopy, ran the first successful on-line RIS experiments with the chain of radioactive isotopes $^{141-145}\text{Eu}$ on the proton accelerator at the Institute of Nuclear Physics.¹¹ In those experiments, researchers also managed to carry out the resonance ionization of the metastable nuclear isomer ^{142m}Eu . The RIS technique was further developed on the ISOLDE facility at CERN by Jürgen Kluge from the University of Mainz. Figure 1 is a photograph of the laser portion of that facility. Researchers ran the first successful on-line RIS experiments on ISOLDE with chains of the radioactive isotopes of the noble metals Au and Pt. Meanwhile Jonathan Lee and John Crawford directed early work at McGill University to study Pt atoms that were the decay products of accelerator-implanted Au atoms.¹²

RIS also has made its way to the front end of accelerators. One of the main problems connected with ion sources used at on-line separators for radioactive beam production has been the need to obtain chemically pure beams of the various elements. The ion sources most widely used for this purpose are based on non- Z -selective surface ionization or ionization in gas-discharge plasma. The resonance ionization idea has proven useful for the development of a highly efficient, Z -selective and often N -selective ion source at the entrance to an ISOL facility, solving the difficult problem of obtaining ion beams of single isobars for nuclear physics experiments.¹³ The efficiency of photoionization is high enough that the ion yield may reach tens of percent, even for elements with high ionization potentials. Figure 3 is a schematic diagram of the mass separator with a laser ion source developed at CERN. The test measurement performed under on-line conditions at the mass separator ISOLDE-3 at CERN showed the strength of the laser ion-source principle for efficient and selective ionization of short-lived isotopes, and especially the selective laser ionization of isobars.

It is possible to achieve not only isotopically or isobarically but also *isomerically* selective excitation of atoms. Hence isomeric nuclei can also be detected and separated by laser resonance ionization.

Thus RIS detection and separation are powerful tools, useful not only for elements (Z selectivity) but also for isotopes (Z and N selectivity), isobars (A and Z selectivity)



Atom counter depicted schematically in **a** can detect as few as 100 noble gas atoms with isotopic selectivity. Graph **b** shows the counting of ^{81}Kr atoms. This signal decays rapidly as atoms are removed from the system once they are ionized, accelerated and implanted. Gaps in the data result from the RIS laser beams having been blocked for 5 and 10 minutes to illustrate that the signal decrease is due to ionization and to demonstrate that interference is negligible. Counting the atoms directly rather than waiting for half of them to decay in 213 000 years reduces the "effective" half-life of ^{81}Kr by a factor of 2×10^{10} , to 5 minutes. **Figure 4**

and isomers (Z , N and E selectivity, where E is the energy of excited nuclei). The capabilities are much more powerful than those of mass separation alone, which allows detection and separation only of A -selected species and cannot distinguish among the nuclear isomers.

Counting noble gas atoms

Decay counting of radioactive atoms has been and continues to be an important measurement method in a number of basic and applied sciences. When the half-life of an isotope is reasonably short (compared with the measurement time available) decay counting stands alone as a selective and sensitive technique. For any isotope with a very long half-life, however, decay counting requires a large number of atoms. Consequently it has long been of interest to develop methods for direct counting of atoms that do not depend on radioactive decay.

The RIS method for counting atoms in their free state is most easily illustrated by considering the detection of noble gas atoms. Envision a closed system in which noble gas atoms are free to move hither and thither without sticking to walls, thus always remaining in the gas phase. Imagine that a laser is pulsed into the compartment and ionizes just one of the chemically inert atoms. If the ion is accelerated to a surface and in the process is given enough energy to implant itself into the surface, the atom will be removed from the gas phase. When bombarded by ions with energies in the 10–20-keV range, some materials will emit a pulse of a few electrons at low energy. Detection of such an electron pulse would provide a sure method of counting each implanted atom, and one could continue the process until there were no more counts, that is, until no atom had escaped detection.

The above ideal has only partially been realized. Nevertheless researchers clearly have demonstrated that the method can work as an atom counter.¹⁴ This technique for counting noble gas atoms was inspired by the solar neutrino problem: Since 1984 we have known that RIS could be used¹⁵ to count ^{81}Kr atoms produced by the interaction of intermediate-energy neutrinos from the Sun in a target rich with ^{81}Br .

Figure 4 is a schematic rendering of the atom counter currently used by Norbert Thonnard and others for counting ^{81}Kr atoms.¹ The system uses a laser for resonance ionization of Kr, based on the rather difficult four-wave mixing scheme developed by Marvin Payne, Chung-Hsuan (Winston) Chen, Steven Kramer and others at Oak Ridge.

A time-of-flight mass spectrometer selects the isotope, for example, ^{81}Kr or ^{85}Kr . An atom buncher increases the likelihood that the atom of interest will be in the small ionization volume when the laser is pulsed into the system. To avoid excessive outgassing of the stable isotopes of Kr from the chamber, which could interfere with the counting, special precautions are taken; for example, the volume of the vacuum enclosure is kept as small as possible. Samples with as few as 100 atoms of ^{81}Kr or ^{85}Kr can be counted in a matter of minutes with this technique. Because the half-lives of ^{85}Kr and ^{81}Kr are, respectively, 10.7 and 213 000 years, it is clearly impossible to analyze that small a sample by decay counting.

Applications of these sensitive measurements on Kr atom populations include groundwater and polar ice-cap dating, measuring the cosmic-ray-exposure age of meteorites and potentially performing a solar neutrino experiment using a Br target. All of these applications require atom counting with good sensitivity: For example, 1 kg of modern ice contains only 1400 atoms of ^{81}Kr . For further information on these applications we refer the reader to a summary by Bernhard Lehmann,¹⁶ who, with his colleagues at the University of Bern, Switzerland, has used noble gas isotopes for geophysical applications and has reported on the use of RIS to date water from the Milk River source in Canada.

Thermal atomization

Most of this article deals with the use of pulsed lasers to implement RIS. However, some very impressive work has been done with continuous-wave lasers in combination with simple mass spectrometers to detect small numbers of atoms in medical and environmental samples. In most such cw-RIMS applications atoms are evaporated from hot crucibles into laser beams situated above an opening. Tom Whitaker, while at the Pacific Northwest Laboratory, initiated a program in which cw-RIMS was used to detect ^{210}Pb and ^{90}Sr in various samples. Bruce Bushaw, also at PNL, is largely responsible for impressive work¹ in which 3000 atoms of ^{210}Pb were detected with an isotopic selectivity exceeding 10^{10} . For ^{90}Sr the experimental detection limit is about 14 000 atoms with an isotopic selectivity exceeding 10^9 . Researchers have applied this technique to detect in human hair ^{210}Pb resulting from the decay of radon in residences where the radon concentration was only 0.3 picocuries per liter of air. Other applications include the detection of the same isotope in brain

tissues of patients with Alzheimer's disease. Kluge's group has used collinear RIS, a related technique, to detect as few as 5×10^8 atoms of environmental ^{90}Sr , but with a more useful isotopic selectivity, exceeding 10^{11} .

Implementation of the pulsed-laser RIS technique in analytical applications involves first slowly heating the sample in an evacuated crucible to a temperature of 2000–3000 °C (depending on the trace element species and sample type). This heating protocol ensures that the trace element is released from the sample in the form of a beam of neutral atoms. Laser pulses of appropriate wavelength then resonantly ionize, out of all the atoms in the neutral atomic beam, only the trace element to be detected. This technique is sometimes referred to as RIS with thermal atomization, or TARIS. TARIS enables one to handle complex samples and elements that are difficult to detect, such as platinum-group elements, at detection limits between parts per billion and parts per trillion.

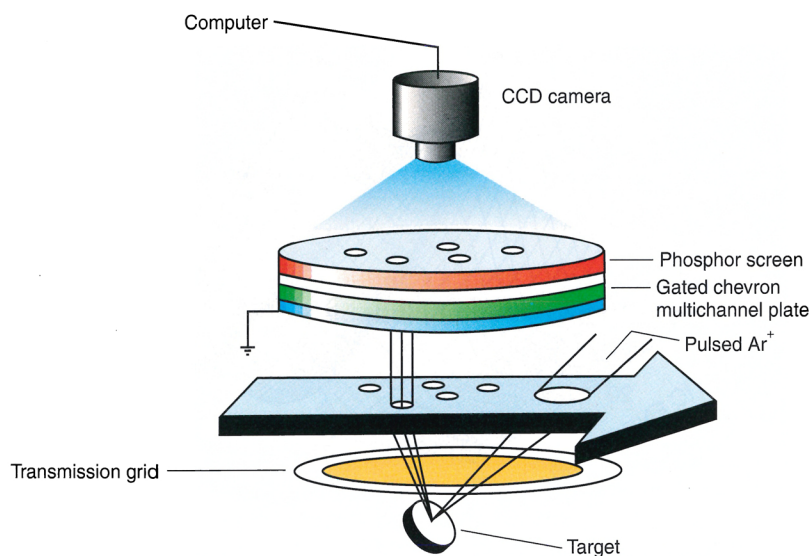
Measurement of the rhodium distribution at the Cretaceous–Tertiary geological boundary exemplifies the successful application of TARIS. There is evidence of an unusual event at that boundary, which corresponds to the extinction, some 65 million years ago, of a great many species of the Mesozoic era, including the dinosaurs. Luis Alvarez and coworkers evaluated the rate of accumulation of sediments at the boundary by studying the concentration of the platinum-group element iridium in sedimentary rock.¹⁷ Because extraterrestrial material is rich in iridium and its concentration in surface terrestrial rock is several orders of magnitude lower, this element is a convenient indicator for cosmic matter. The Ir concentration at the Cretaceous–Tertiary boundary turned out to be so high that it could not be explained by the gradual accumulation of extraterrestrial material in the form of micrometeorites and cosmic dust. Alvarez and others interpreted this anomaly as the result of the impact of a large cosmic body with the Earth, which produced a terrific cloud of dust. Climatic effects of this cloud then presumably caused the mass extinction. Alternative models attempt to explain the elemental anomaly as resulting from concentration by sedimentation or by volcanic activity.

To gain a better understanding of the Cretaceous–

Tertiary event, it is important to establish the proportions of many elements and their isotopes in the boundary deposits of that age, especially the proportions of platinum-group elements whose concentrations are high in extraterrestrial material and low in terrestrial rocks. Iridium traces can be detected in concentrations up to 10 ppt by neutron-activation analysis. But the rest of the platinum-group elements are very difficult to detect in low concentration with that technique. TARIS is ideally suited to this purpose, as demonstrated by George Bekov and coworkers, who measured the distributions of iridium and rhodium in Cretaceous–Tertiary sedimentary rocks from the Sumbar-SM4 section in Turkmenistan.¹⁸ They determined the Ir content by neutron-activation analysis and the Rh content by the TARIS technique. The boundary between the geologic periods was clearly marked by a sharp rise in the concentrations of *both* elements. The Rh/Ir concentration ratio determined for a section through the boundary correlated well with that in meteorites. The data point unambiguously to an extraterrestrial origin of the Cretaceous–Tertiary anomaly and support the hypothesis of a large cosmic body colliding with the Earth. Determination of the proportions of other platinum-group elements could allow further classification of that body.

Materials science

One of the more practical applications of RIS is the bulk and surface analysis of very low levels of elements in solid materials. The method is based on the fact that the sputtering of condensed materials by beams of ions such as Ar^+ is a very efficient and well-characterized process for putting neutral species in the vapor phase. One would like to present to the RIS beam a cloud of atoms that faithfully represents the concentrations of impurity atoms in the condensed material itself. We know, for example, that the secondary-ion mass spectrometer method, which looks directly at the mass spectrum of the sputtered ions themselves, is a powerful one, having good sensitivity for some species, but it is limited by the so-called matrix effect, in which the yield of sputtered ions depends on the host material. In contrast, the copious literature on sputtering suggests that the neutral atoms emitted are orders



Laser RIS apparatus can obtain basic information on the sputtering process. This technique permits measurement of the energy- and angle-resolved spectra, or EARN maps, of the neutral species emitted from a solid target bombarded by Ar^+ . Atom Sciences Inc uses a somewhat simplified approach in its sputter-initiated RIS apparatus. (Courtesy of Nicholas Winograd, Penn State University.) **Figure 5**

of magnitude more abundant than the ions. Furthermore, the resulting vapor plume should be far more characteristic of the solid material; that is, the matrix effect should be much smaller. These facts were the inspiration behind the development of the sputter-initiated RIS, or SIRIS, method at Atom Sciences Inc, in Oak Ridge, Tennessee.¹⁹

Nicholas Winograd²⁰ and his group at Penn State University pioneered the use of RIS for basic research in materials science. Figure 5 illustrates Winograd's approach for obtaining the fundamental characteristics of the sputtering process. The method is capable of recording the energy- and angle-resolved spectrum—called an EARN map—of the neutral atoms emitted when the sputtering beam strikes a selected spot on the surface of a material. Figure 6 shows such a map of rhodium atoms sputtered from single-crystal Rh(111). Information of this type helps us to understand the angular anisotropic effects in the yields of desorbed species and has applications to, for example, the chemical modification of electronics materials by ion etching and ion implantation.

The development and use of SIRIS by Heinrich Arlinghaus and coworkers at Atom Sciences has taken the use of RIS for the analysis of materials to new levels of sophistication. As shown in figure 7a, the apparatus can be used for depth profiling with excellent depth resolution. One may also image the impurity concentrations on surfaces, either by rastering the ion beam over the surface or by changing the X and Y target positions while the ion and RIS beam positions remain fixed. This kind of imaging is illustrated by figure 7b, a map of boron atoms implanted at four locations on a silicon sample. These capabilities for depth and lateral characterization of very low levels of atoms in materials have opened up a host

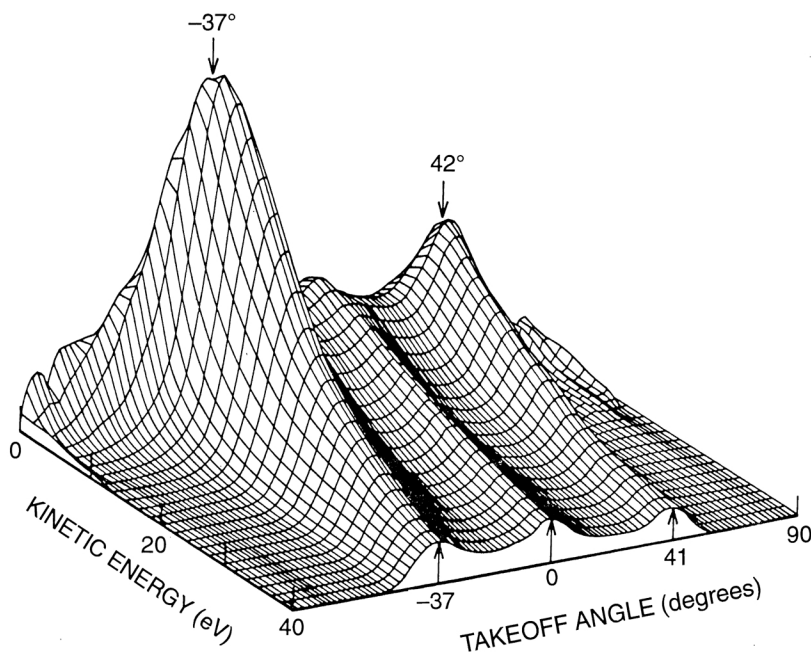
of applications in the geosciences, biology and medicine as well as in the electronics industry.¹⁹ Several other laboratories are making use of the SIRIS method. A recent collaboration between Argonne National Laboratory and the Enrico Fermi Institute of the University of Chicago dealt with a cosmochemical application.²¹ Researchers at AT&T Bell Laboratories made a state-of-the-art application of SIRIS to the analysis of exceedingly complex device substrates.²²

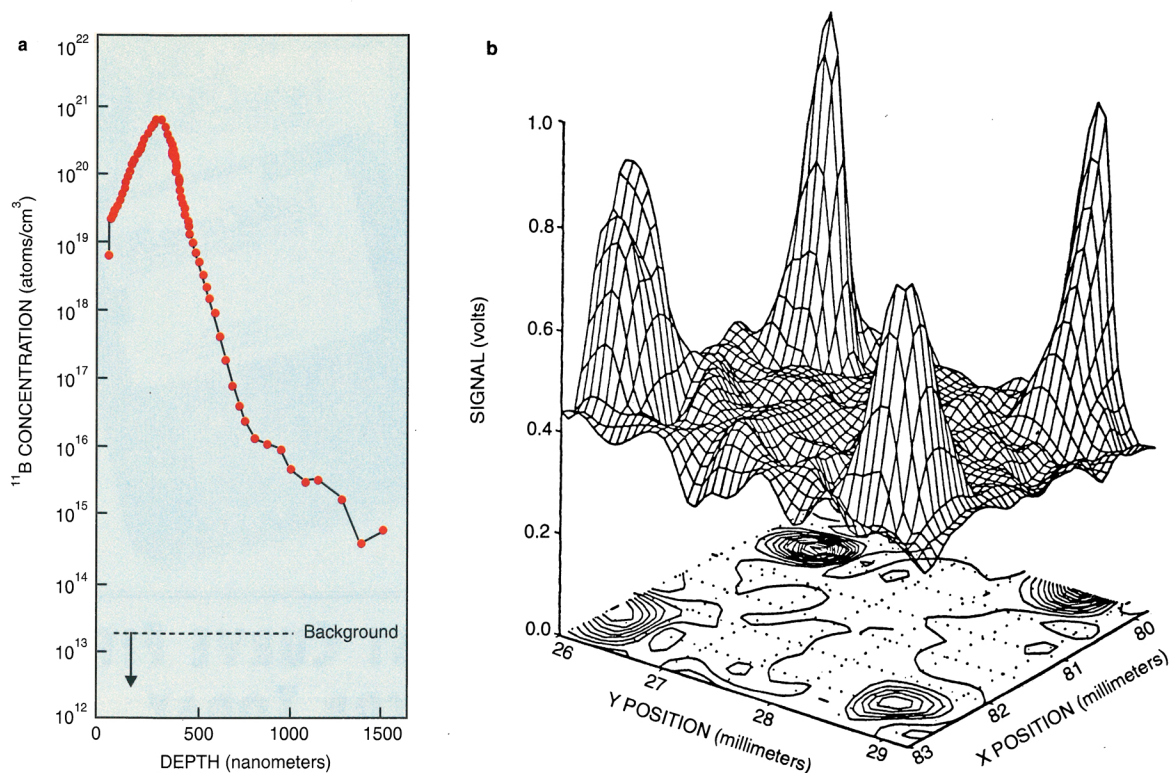
Remaining hurdles

In the early days of RIS, we and the many others who contributed to its development believed that all of the problems of implementing the technique would be solved by this time. While the numerous successes we have described have gone far toward fulfilling our expectations, our optimism was not entirely warranted: Many technical problems still need attention. Chief among those problems are the need for better laser sources and more effective atomizers for putting atoms from solids into laser beams. Small, tunable solid-state lasers are becoming available to meet some of the laser needs, and these could even help solve a current problem, namely that essentially only one element can be analyzed at any one time. Atomization of solid samples for analytical purposes has a long history and has evolved into two classes of methods: continuous and pulsed. Some are based on heating the sample; others on sputtering atoms with an ion beam; and still others on laser ablation. A recent review article describes atomization, as well as many other technical aspects of RIS, in more detail.²³

In spite of its limitations, RIS is beginning to fill a role as an analytical method with enormous sensitivity

EARN map for a clean, single-crystal Rh(111) surface. The takeoff angle of the emitted neutral is measured with respect to the surface normal. **Figure 6**





Sputter-initiated RIS results. **a:** Depth profile of ^{11}B atoms implanted (with an energy of 70 keV) in a silicon crystal. The background is zero counts in 33 000 shots, or less than 2×10^{13} atoms/cm³. The SIRIS method permits depth resolution of 2 nm with bombardment by low-energy (500 eV) Ar^+ ions. **b:** Lateral characterization of B atoms implanted at four locations on a Si crystal. One can achieve lateral resolution of 100 nm using a liquid-metal ion gun for sputtering. **Figure 7**

and selectivity. The examples we have discussed are only a small representation of the many applications being pursued. And as illustrated abundantly at the recent international symposium on the technique in Bernkastle-Kues, Germany, resonance ionization spectroscopy continues to make fundamental contributions to many basic and applied sciences.

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