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COLLECTORS FOR THE GENESIS DISCOVERY MISSION
BY RESONANCE IONIZATION MASS SPECTROMETRY

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W. F. Calaway¹, M. P. McCann^{1,2}, and M.J. Pellin¹

¹Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439

²Present Address: Department of Chemistry, Sam Houston State University, Huntsville, TX 77341

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IMPURITY CHARACTERIZATION OF SOLAR WIND COLLECTORS FOR THE GENESIS DISCOVERY MISSION BY RESONANCE IONIZATION MASS SPECTROMETRY

W. F. Calaway¹, M. P. McCann^{1,2} and M. J. Pellin¹

¹Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439

²Present address, Dept. of Chemistry, Sam Houston State University, Huntsville, TX 77341

ABSTRACT

NASA's Genesis Discovery Mission is designed to collect solar matter and return it to earth for analysis. The mission consists of launching a spacecraft that carries high purity collector materials, inserting the spacecraft into a halo orbit about the L1 sun-earth libration point, exposing the collectors to the solar wind for two years, and then returning the collectors to earth. The collectors will then be made available for analysis by various methods to determine the elemental and isotopic abundance of the solar wind. In preparation for this mission, potential collector materials are being characterized to determine baseline impurity levels and to assess detection limits for various analysis techniques. As part of the effort, potential solar wind collector materials have been analyzed using resonance ionization mass spectrometry (RIMS). RIMS is a particularly sensitivity variation of secondary neutral mass spectrometry that employs resonantly enhanced multiphoton ionization (REMPI) to selectively postionize an element of interest, and thus discriminates between low levels of that element and the bulk material. The high sensitivity and selectivity of RIMS allow detection of very low concentrations while consuming only small amounts of sample. Thus, RIMS is well suited for detection of many heavy elements in the solar wind, since metals heavier than Fe are expected to range in concentrations from 1 ppm to 0.2 ppt. In addition, RIMS will be able to determine concentration profiles as a function of depth for these implanted solar wind elements effectively separating them from terrestrial contaminants. RIMS analyses to determine Ti concentrations in Si and Ge samples have been measured. Results indicate that the detection limit for RIMS analysis of Ti is below 100 ppt for 10^6 averages. Background analyses of the mass spectra indicate that detection limits for heavier elements will be similar. Furthermore, detection limits near 1 ppt are possible with higher repetition rate lasers where it will be possible to increase signal averaging to 10^8 laser shots.

INTRODUCTION

Last year NASA selected the Genesis mission as its fifth Discovery mission. The intent of the Discovery program is to fund highly focused science projects that meet the "faster, better, cheaper" criteria under which NASA now operates. The purpose of the Genesis Discovery mission is to collect solar matter and return it to earth for analysis.[1] This will be accomplished by equipping a spacecraft with an array of ultra-clean and -pure solar wind collectors. The spacecraft will be inserted into a halo orbit about the L1 libration point where the collectors will be exposed to the solar wind for a period of two years. Afterwards, the collector array will be stowed into a contamination-tight canister within a sample return capsule and returned to earth for mid-air recovery. A key consideration of the Genesis Discovery mission is that the collectors are returned to earth. This allows sophisticated analytical instruments, that are too bulky and complex for onboard spacecraft operation, to be used for the solar wind collector analyses. In addition, some of the collector material will be archived for future analyses when new instruments and new scientific questions arise.

The overall purpose of the Genesis Discovery mission is to determine the isotopic and elemental abundances of the solar wind and thus the sun. These results will be used (1) to expand the present isotopic and elemental abundance data base for the sun, (2) to obtain more precise values for those isotopic and elemental abundances that have already been determined by other methods, and (3) to produce a set of consistent isotopic and elemental abundances for comparison with other objects in the solar system. The goal of the mission would be to use the wealth of new data to improve our understanding of how the highly diverse objects of our solar

system originate from a relatively homogeneous solar nebula and to test theories of the origins of the solar system. To accomplish these tasks, solar wind collector samples will be analyzed in Advanced Analytical Instrument Facilities developed as part of the Genesis Discovery mission. A number of state-of-the-art analytical techniques will be brought to bear on the problem including, gas source mass spectrometry (GSMS), secondary ion mass spectrometry (SIMS), resonance ionization mass spectrometry (RIMS), radiochemical neutron activation analysis (RNAA), synchrotron x-ray fluorescence, thermal ionization mass spectrometry (TIMS), and inductively coupled plasma mass spectrometry (ICPMS). This paper presents a discussion of RIMS and how it will contribute to the overall objectives of the Genesis Discovery mission.

Resonance ionization mass spectrometry is a surface analytical method that has a unique combination of capabilities no other single analytical instrument can match, namely unambiguous identification of elemental impurities at trace levels with single monolayer resolution. These features allow a RIMS instrument to produce concentration versus depth profiles of solid materials at levels below 1 ppb. The RIMS instrument capabilities match well the needs of NASA's Genesis Discovery Mission where solar wind constituents will be implanted in collector arrays at levels down to 0.1 ppt and at depths no greater than 100 nm.[2] As part of the Genesis Discovery mission, RIMS instrument development and sample analyzes of collector materials are being conducted at Argonne National Laboratory (ANL). The goal is to improve detection limits for the RIMS technique to the levels required for accurate quantification of the least abundant elements present in the solar wind while contributing to the collector materials selection and verification processes. Recent progress toward this goal is presented in this paper.

EXPERIMENTAL

The RIMS instrument used in this study is referred to as SARISA (surface analysis by resonance ionization of sputtered atoms). It was developed and built at ANL and has been previously describe in detail elsewhere.[3] The basic instrument consists of an ion source for sputtering samples, a laser system for photoionization of elements, a time-of-flight mass spectrometer (TOF MS) housed in an ultra-high vacuum chamber for detection, and a computer system for instrument control and data collection. In a typical measurement, a 500 ns pulse of 5 keV Ar^+ ions (300 μm spot diameter) strikes a sample target causing material to be ejected via sputtering. Approximately 300 ns later, light from as many as three tunable dye lasers simultaneously pass through the plume of sputtered material photoionizing neutral ground state atoms of a specific element. (The number of lasers and their frequencies are determined by the ionization scheme for the element of interest.) The photoions are extracted into the TOF MS and detected by a pair of microchannel plates arranged in a chevron configuration.

RIMS is a variation of secondary neutral mass spectrometry (SNMS) that employs resonantly enhanced multiphoton ionization (REMPI) to maximized selectivity and sensitivity. The use of REMPI is a key feature of the RIMS technique. REMPI can photoionize ground state atoms with an efficiency near unity facilitating the detection of a large fraction of the sputtered material. In fact, useful yields (atoms detected/atom sputtered) between 1 and 5% have been measured for SARISA.[4] Particularly important for trace analysis is the fact that REMPI is an efficient way to separate an element of interest from the large number of neutral bulk atoms and to identify unambiguously that specific element.

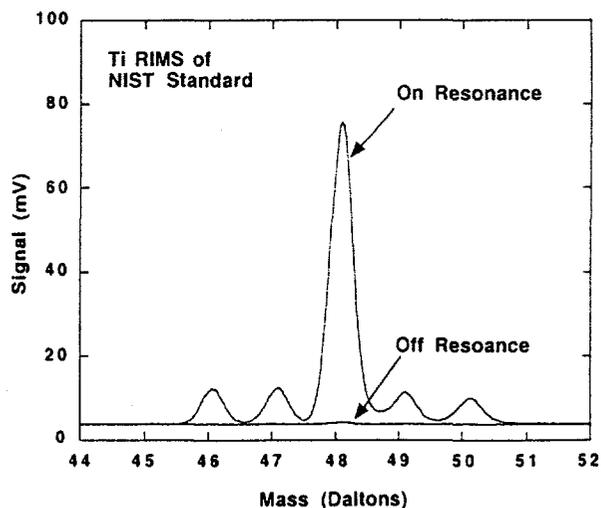


Figure 1. RIMS of Ti in a low alloy steel showing the on resonance signal and the off resonance background.

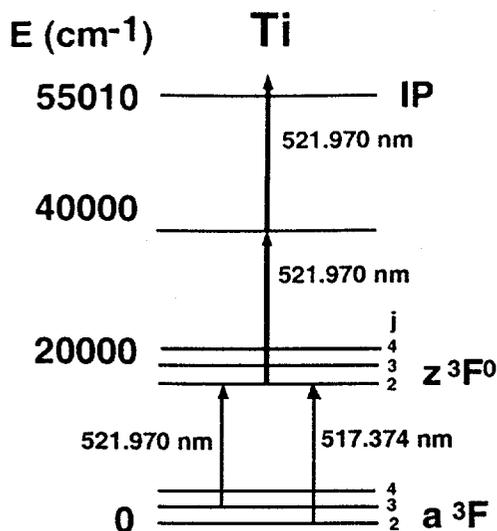


Figure 2. Resonance ionization scheme used for detecting Ti.

Because atomic transitions are very narrow and have large cross sections, tunable lasers can be used to photoionize a specific element without photoionizing other species. Further, a small detuning of the laser allows the background to be measured directly.

Shown in Fig. 1 is a mass spectrum of Ti from a low alloy steel (NIST Standard #1264a; 0.27 at.% Ti) used to calibrate the SARISA instrument. Figure 1 also shows the background level when the ionizing lasers are tuned off the Ti resonance transitions by only 0.1 nm. The resonance ionization scheme used in these measurements was developed at ANL and is rather special.[5] Only two green lasers are needed to ionize Ti from its ground state (a^3F_2) and a multiplet level of the ground state (a^3F_3) 170 cm^{-1} above the ground state. This ionization scheme is shown in Fig. 2.

The two major noise sources in a RIMS measurement are photoionized molecules and secondary ions. Photoionized molecules can be virtually

eliminated as a noise source by the proper selection of an ionization scheme and maintaining appropriate laser intensities.[6] Secondary ions are eliminated in the SARISA instrument by imparting different energies to the secondary ions and photoions then using the energy filtering, which is part of the TOF MS, to block the secondary ions.[3] This is accomplished by applying a high voltage pulse to the sample while the primary ion beam strikes the sample. Once the primary ion beam is pulsed off, the target voltage is restored to its normal potential for extraction of photoions (+1100 V) before the lasers are triggered. Employing these techniques, background count rates for SARISA have been previously demonstrated to be near 2 counts in 1000 averages (2×10^{-3} counts/average), corresponding to a detection limit of 1 ppb for 10^6 averages.[7]

Two separate studies were conducted and are reported herein. The first study was aimed at improving the detection limit of the SARISA instrument. In this study, measurements of the background levels from a Si target as a function of various instrument parameters were obtained. Measurements were conducted either with the lasers tuned off their resonance frequencies or turned off altogether. Count rates were determined by summing the total counts over a large mass range (typically, 40 to 100 Daltons) and dividing the result by the mass range and number of averages. In the second study, samples from Si and Ge wafers supplied by various vendors have been analyzed to determine baseline levels of Ti. In these measurements, data was collected with lasers tuned on and off the Ti resonance frequencies. Count rates for Ti^{48} were integrated and converted to concentrations using standard calibration procedures.[6] Depth versus Ti concentration profiles were constructed by ion milling into the samples between measurements. Combining background measurements with the Ti analysis results allows a detection limit to be calculated as discussed below.

RESULTS AND DISCUSSION

Noise Suppression

The background for a RIMS analysis is the measured count rate when the laser is detuned from the resonant wavelength of that element. As such, it is the sum of all ions reaching the detector at the appropriate mass that are not resonantly photoionized atoms of the element of interest. To improve the detection limit of SARISA below present value, a detailed study of the sources that cause background counts during RIMS measurements was undertaken. In addition to secondary ions and nonresonant photoions, four other noise sources have been identified. The sum of these four noise sources corresponds to the background count rate of 2×10^{-3} counts/average mentioned above. An important feature of all four noise sources is that, for

the most part, they do not exhibit a mass signature, but rather are distributed in time fairly uniformly. Each noise source was isolated by monitoring background levels as various sections of the instrument were turned off. From this it was possible to characterize the four noise sources as follows: (1) ions that evolve after primary ion bombardment ends, (2) ions originating from the sample without primary ion bombardment, (3) stray ions striking the detector that have not traveled down the TOF path, and (4) dark counts from the microchannel plate detector. Of the four identified sources, the first contributes most to the background and is the least understood. The second noise source is likely electron stimulated desorption of atoms or molecules. The sample receives a constant flux of high voltage electrons from electrostatic lens elements in the TOF MS that could possibly produce ions that reach the detector. The stray ions striking the detector has been eliminated as a noise source by shielding the detector and TOF path from stray ions and electrons in the vacuum chamber. The detector dark count rate, last noise source, is sufficiently small as not to be important, although it is possible to purchase special "low dark noise" microchannel plates if the need arises.

While the causes of the first two noise sources are different, both are present only when the target potential is set to transmit photoions. The difference is that the latter noise source is constant with time while the former noise source is was found to decrease with time after the ion pulse. Thus, it is possible to fully suppressed the first two noise sources only if the target is held at a nontransmitting potential (e.g., +2500 V) for all times. It is important to note that the background that is observed is from ions that are forming at times after the primary ion pulse in the extraction region of the mass spectrometer. The most likely explanation for the observed phenomenon is delayed formation of ions above the target. The source of these ions while not known could likely be neutral clusters ejected during ion bombardment that fragment to ions or that ionize by some mechanism such as electron bombardment. Neutral clusters are known to sputter from clean metal surfaces and are thought to possess substantial internal energy.[8]

Since ions are forming continuously throughout the time when extraction of photoions must occur, this residual noise source can not be total eliminated by any target pulsing scheme. It can be suppressed, however, by minimizing the length of time that the transmitting target potential is on. In addition, during this study it has been discovered that a negative target potential is better at suppressing noise than a positive potential. A new noise suppression scheme that uses these two observations has been implemented by designing a fast bipolar target pulser with variable width. Using this circuit, the target can remain at a negative nontransmitting potential at all times except for the short time need to extract the photoions. The results of this new design are shown in Fig. 3 where the photoion signal and noise level are plotted as a function of the length of time the target remains in photoion transmitting mode after

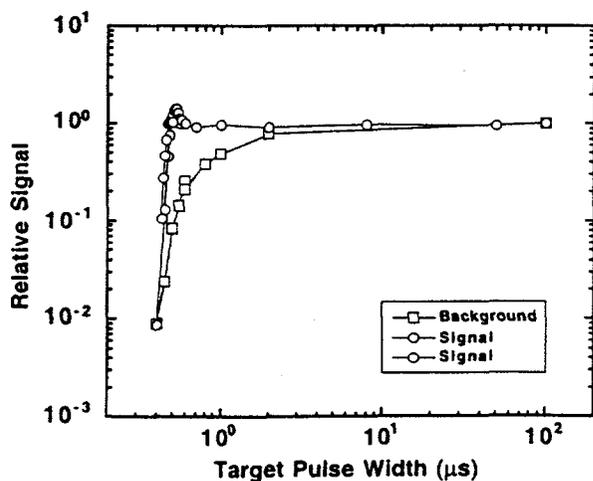


Figure 3. Observed signal and noise for the newly designed target pulsing scheme as a function of target pulse width.

the primary ion pulse (defined as target pulse width in Fig. 3). As can be seen from Fig. 3, the noise level and signal level are constant for long target pulse widths. As the target pulse width is shortened, the noise is reduced as ions that are formed long after the primary ion pulse are suppressed. The noise rate falls rapidly as the more abundant ions formed at shorter times are suppressed. Finally, as the target pulse is shortened further, photoion extraction efficiency falls off and no further noise suppression can be accomplished without loss of signal. Even so, as can be seen in Fig. 3, noise can be suppressed by a factor of >100 compared the previous method. This background reduction substantially reduces elemental detection limits as discussed below.

Trace Measurements

Pieces of Si and Ge wafers have been analyzed to determine baseline levels of Ti using SARISA. High Ti levels (between 1000 and 100 ppb) were detected on the surface of all samples. Sputter cleaning the sample surface reduced these levels. However, concentration versus depth profiles show a leveling off of the Ti concentration at about 1 ppb at a depth of 1 μm . A series of measurements was conducted that proved memory effects in the instrument were not responsible. Conversely, a correlation between the sputter cleaning spot size and the amount of Ti contaminating the surface suggesting that the wings of the primary ion beam were limiting the dynamic range of the instrument. These problems are presently being addressed with the introduction of a high quality primary ion source. Procedures to minimize contamination during sample preparation are being developed. In addition, a new ion source with substantially shaper wings has been purchased. A new ion optics design for SARISA that incorporates the improved ion gun has begun.

Detection Limits

The background reduction that has been achieved results in a significant reduction of detection limit for the SARISA instrument. For a signal-to-noise ratio of 3, the detection limit, D , (for counting ions when a background is subtracted) is derived from Poisson statistics as

$$D = S \cdot \frac{9 + \sqrt{81 + 72nB}}{2n}, \quad (1)$$

where S is the instrument sensitivity, n is the number of averages, and B is the background count rate (counts/average).[10] As can be seen from eq. 1, for a large number of averages and a fixed instrument sensitivity, the detection limit goes as the square root of the background count rate. Figure 3 shows that the new noise suppression scheme reduces the background count rate nearly 100 fold leading to a reduction in D of more than an order of magnitude. This is shown in Fig. 4 where the detection limit for Ti is plotted as a function of the number of averages for past and present measured backgrounds. It should be noted that RIMS instrument sensitivities for most metals differ by only a factor of two to three. Therefore, the detection limits plotted in Fig. 4 are approximately valid for any metal where a REMPI scheme can be found that does not cause a measurable photoionization background.

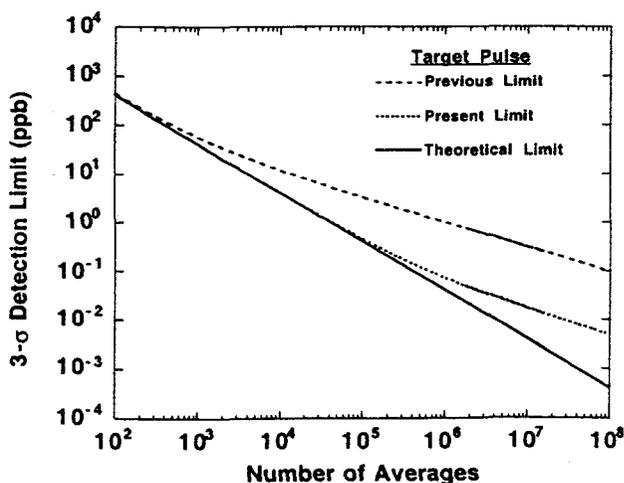


Figure 4. Calculated detection limit for the new noise suppression method compared to the previous detection limit and the theoretical detection limit.

As seen in Fig. 4, the detection limit for Ti has dropped from about 1 ppb to less than 100 ppt for 10^6 averages. For 10^8 averages the $3\text{-}\sigma$ detection limit is near 5 ppt. With the present low repetition rate (<50 Hz) laser system, it is not possible to achieve 10^8 averages in a reasonable amount of time. (Presently, 10^6 averages require 5.6 hours.) However, a new laser system that can produce the desired tunable light at 5 kHz will allow such low detection limits to be reached. It thus appears possible to achieve the desired detection limits for most heavy metals in the Genesis Discovery mission collectors with only small improvements in instrument sensitivity and background suppression.

CONCLUSIONS

A systematic study of noise sources in the ANL RIMS instrument (SARISA) has led to a substantial improvement in the attainable detection limit. Complete elimination of the two dominant sources of background counts, secondary ions and nonresonant photoions, allowed identification of four residual sources. The most substantial of these is ions formed in the mass spectrometer extraction volume after ion bombardment of the sample has ceased. It is proposed that this noise source is derived from neutral clusters that are fragmenting and/or ionizing. Concentration versus depth measurements of Ti in Si and Ge samples were undertaken to test a new noise suppression method and to assess the cleanliness of potential solar wind collector materials. Concentrations near 1 ppb were measured indicating that surface contamination was limiting the dynamic range of the instrument. However, backgrounds were found to be below 5×10^{-5} counts/average. Combining the measured sensitivity for Ti with the measured background, a detection limit for Ti in Si was found to be below 100 ppt for 10^6 averages and near 5 ppt for 10^8 averages.

ACKNOWLEDGMENTS

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REFERENCES

1. A detailed discussion of the Genesis Discovery mission can be found on the Internet at www.gps.caltech.edu/genesis/.
2. A. H. Treiman, *Curation of Solar Wind Collector Plates from a Solar Wind Sample Return (SWSR) Spacecraft Mission*, NASA Report No. JSC 26406 (October, 1993).
3. C. E. Young, M. J. Pellin, W. F. Calaway, B. Jörgensen, E. L. Schweitzer, and D. M. Gruen, *Nucl. Inst. Method.* **B27**, 119-129 (1987).
4. M. J. Pellin, C. E. Young, W. F. Calaway, J. E. Whitten, D. G. Gruen, J. D. Blum, I. D. Hutcheon, and G. J. Wasserburg, *Phil Trans. R. Soc. Lond. A* **333**, 133-146 (1990).
5. Z. Ma, R. N. Thompson, K. R. Lykke, M. J. Pellin, and A. M. Davis, *Rev. Sci. Instrum.* **66**, 3168-3176 (1995).
6. W. F. Calaway, R. C. Coon, M. J. Pellin, C. E. Young, J. E. Whitten, R. C. Wiens, D. M. Gruen, G. Stinger, V. Penka, M. Grasserbauer, and D. S. Burnett, *RIS 92*, *Inst. Phys. Conf. Ser. No. 128*, pp. 271-274 (IOP Publishing, 1992).
7. C. S. Hansen, W. F. Calaway, M. J. Pellin, R. C. Wiens, and D. S. Burnett, *RIS 96*, AIP Conference Proceeding No. 338, pp. 215-218 (AIP Press, 1997).
8. W. F. Calaway, R. C. Coon, M. J. Pellin, D. M. Gruen, M. Gordon, A. C. Diebold, P. Maillot, J. C. Banks, and J. A. Knapp, *Surf Interface Anal.* **21**, 131-137 (1994).
9. G. Betz and K. Wien, *Int. J. Mass. Spec. and Ion Proc.* **140**, 1-110 (1994).
10. W. F. Calaway, D. R. Spiegel, A. H. Marshall, S. W. Downey, and M. J. Pellin, *CARRI 96*, AIP Conference Proceeding No. 392, pp. 739-742 (AIP Press, 1997).