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RADIONUCLIDES BY DOUBLE-RESONANCE
EXCITATION WITH CW LASERS

B. A. Bushaw
J. T. Munley

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Pacific Northwest Laboratory
Richland, Washington 99352

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Isotopically Selective RIMS of Rare Radionuclides by Double-Resonance Excitation with Single-Frequency cw Lasers

B. A. Bushaw and J. T. Munley

Pacific Northwest Laboratory, Richland, WA, 99352, USA

ABSTRACT: Double-resonance RIMS using two single-frequency dye lasers and a CO₂ laser for photoionization has been shown to be both extremely sensitive and highly selective. Measurements on the radioisotope ²¹⁰Pb have demonstrated optical selectivity in excess of 10⁹ and detection limits of less than 1 femtogram.

1. INTRODUCTION

There are a number of radionuclides that occur at relative abundances in the range of 10⁻⁸ to 10⁻¹³ with respect to other isotopes of the same element. Measurement of isotopes at these low abundances is generally beyond the capabilities of conventional RIMS with pulsed lasers because their broad linewidths and duty cycle constraints that limit sensitivity. Thus, we have been investigating the use of high-resolution cw dye lasers to obtain improved isotopic selectivity, beyond that which can be provided by a mass spectrometer, for the detection of these rare isotopes (Cannon 1985, Bushaw 1987, 1988, 1989). In this paper we will discuss, as an example, measurements on the isotope ²¹⁰Pb, which is of interest both as an indicator of radon exposure and in the microelectronics industry.

In our experiments, the analyte atoms of interest are generated with a vacuum-compatible graphite furnace and detected using the scheme depicted in Figure 1: a single-frequency cw dye laser is tuned to a resonance of the atom originating in the ground state, raising it to a low-lying excited state, a second single-frequency cw dye laser is tuned to promote the initially excited atom into a high-lying Rydberg state, the Rydberg state atom is ionized with a cw CO₂ laser, and the ions produced are then analyzed with a quadrupole mass spectrometer. There are several features of this scheme that make it attractive for the extremely low-level measurements being addressed. The graphite tube furnace is a self collimating beam source providing good transport of the atoms to the excitation region. All three steps of the excitation process can be saturated using cw lasers, leading to detection limits in the attogram range. The two dye lasers are counterpropagated to reduce residual Doppler broadening, and optical isotope selectivity can be realized in both resonance excitations. The Rydberg states are long-lived, providing a long access time for the CO₂ ionization laser as well as very narrow linewidths with small Lorentzian tails, enhancing selectivity. There is essentially no background ionization because the low photon energy of the CO₂ laser cannot ionize other materials that have not been specifically prepared in high-lying Rydberg states.

In previous studies on barium (Bushaw 1988), we have shown that this approach is capable of yielding detection limits of about 10⁻¹⁷ grams. However, Pb is a more difficult case and thus a more stringent test of the capabilities of the technique. First, one of the dye lasers must be frequency-doubled to reach the first step excitation wavelength of 283.3 nm. Second, the first excitation in barium involves a two-level system and any atoms not promoted to the Rydberg state will return to the ground state where reexcitation can occur, while in lead the first excitation is very susceptible to optical pumping: approximately 85% of the atoms excited to the 6p7s ³P₁ state will decay into the metastable ³P₁ and ³P₂ fine structure components of the ground state, where they are not accessible for further excitation.

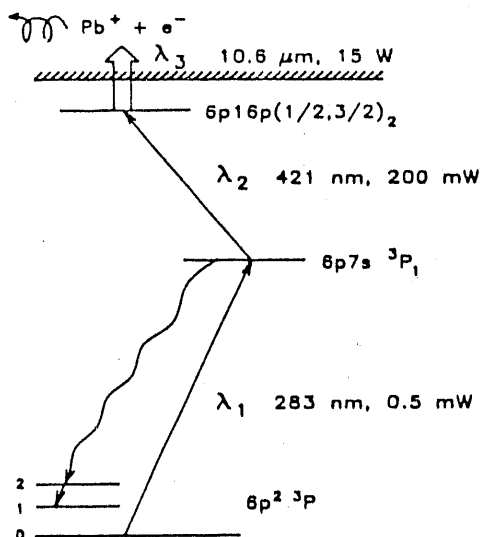


Fig. 1. Energy level diagram for double-resonance excitation of Pb isotopes, followed by photoionization with a CO₂ laser.

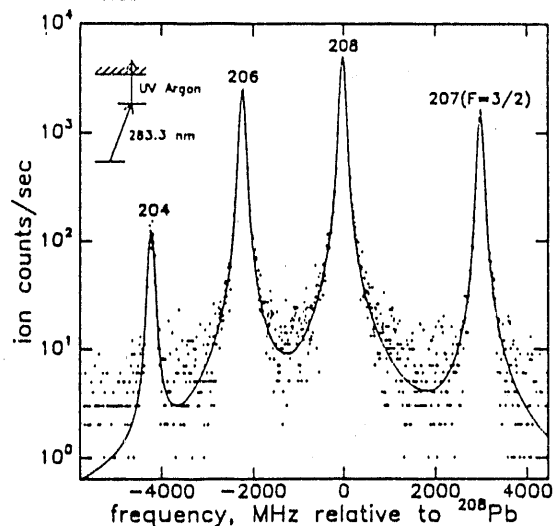


Fig. 2. Isotopic structure for the stable isotopes of Pb in the $6p7s\ ^3P_1 + 6p^2\ ^3P_0$ resonance transition.

2. OPTICAL ISOTOPE SHIFTS AND SELECTIVITY

Isotope shifts in the $6p7s\ ^3P_1 + 6p^2\ ^3P_0$ resonance for the stable, naturally occurring isotopes of Pb were determined using a $1+1$ photoionization scheme in which the frequency-doubled cw dye laser excited the resonance line (35287.26 cm^{-1}) and the atoms were then directly photoionized out of the $6p7s\ ^3P_1$ state with the ultraviolet output of an argon ion laser. For this measurement, the mass spectrometer was not used so that all the isotopes could be observed. The resulting spectrum is shown in Figure 2, where the points represent the actual data and the solid line is nonlinear least squares fit of a numerically generated Voigt line profile to the data. The fitted Gaussian component width of 99 MHz FWHM is consistent with a residual Doppler width for an atomic beam collimation factor of 14.7, provided by the tube furnace geometry. The Lorentzian component of 56 MHz FWHM corresponds to a 2.8 nanosecond lifetime for the $6p7s\ ^3P_1$ state. The second hyperfine component for ^{207}Pb , $F = 1/2$, is off scale at -10166 MHz. Our measured isotope shifts agree to within 0.3% with prior fluorescence measurements (Thompson 1983). Extrapolating the tails of one isotope to the position of its nearest neighbors, it can be seen that there is optical selectivity of about 10^4 in this transition. We did not measure the isotope shift for ^{210}Pb by this method since it has relatively low sensitivity and would require working with high level radioactive samples. Because of the excellent agreement for the stable isotopes, we have accepted and used Thompson's value of +3974 MHz for ^{210}Pb .

Measurement of the isotope shifts in Rydberg states used the full excitation scheme shown in Figure 1; however, the mass spectrometer is still not used. Figure 3 shows the results of these measurements for the $6p16p(1/2,3/2)_2$ Rydberg state. In each of the cases shown the dye laser pumping the first transition was tuned to resonance for a specific isotope, as labelled in the figure, while the second laser was scanned, but with an offset opposite to that of the first laser such that the total two-photon energy was the same in all four scans. While the positions of all the isotopic peaks remains constant, the intensity patterns vary greatly depending on the tuning of the first laser. For instance, the ^{208}Pb peak in (B), where the first laser is tuned for ^{206}Pb , is reduced by a factor of 500 from that in (D). These intensity patterns simply reflect the selectivity of the first excitation step.

Selectivity in the second step, excitation to the Rydberg state, can be estimated from the lineshapes shown in Figure 3. For example, in (D) the intensity in the tail of the ^{208}Pb peak at the ^{206}Pb position is reduced by a factor of

40,000. This implies an overall two-step laser selectivity of 2×10^9 , which may also be seen by overlaying the lineshape for ^{208}Pb from (D) with its intensity in (B) and extrapolating the tail intensity to under the ^{206}Pb position.

3. MASS SPECTROMETRY AND SENSITIVITY

Figure 4 compares mass spectra of the stable Pb isotopes obtained by conventional electron impact ionization, double-resonance excitation with the two cw dye lasers where absorption of an additional photon from the second laser causes photoionization, and double-resonance excitation with a cw CO_2 laser (15 watt) used for photoionization. In the case shown the lasers were tuned for the minor (1.5% abundance) ^{204}Pb . The dye lasers alone improve ionization efficiency by a factor of 60 over electron impact, while the CO_2 laser increases the signal by another factor of 670 to produce an overall increase in ionization efficiency over electron impact of about 40,000.

The isotopic selectivity of the laser approach is also apparent in Figure 4. Integrating the counts over each of the mass peaks and normalizing for abundances yields a nearly constant selectivity value of 2×10^7 for ^{204}Pb versus ^{206}Pb , ^{207}Pb , and ^{208}Pb . This is considerably less than the value of 2×10^9 predicted above from lineshape analyses. The fact that the selectivity remains constant for all isotopes suggests that the ^{206}Pb , ^{207}Pb , and ^{208}Pb ions observed are result from charge exchange, not a limitation of laser selectivity. Further, it should be noted that this charge exchange background will be inconsequential, less than the laser selectivity limit, when ionizing rarer isotopes at abundances of less than 0.01%.

It can be also seen from the shape of the high side of the mass 204 peak that, when measuring ^{210}Pb , the mass spectrometer will provide selectivity against the nearest stable isotope, ^{208}Pb , of greater than 10^7 . In conjunction with the laser selectivity, the overall isotopic selectivity is greater than 10^{16} ! It is apparent that actual measurements of ^{210}Pb will not be limited by the abundant Pb isotopes, but by other sources of background such as dark counts and nonresonant ionization of other materials such as residual pump oils in the vacuum system.

Absolute sensitivity was determined by holding the laser frequencies and mass spectrometer tuning constant, set for the isotope of interest, and evolving a small discrete sample by ramping up the temperature on the oven. Integrating the observed ion counts over the sample evolution period and subtracting the integrated counts for a blank sample load yields a measure of the absolute efficiency, conveniently expressed as observed ion counts per femtogram of the isotope placed in the furnace. This is shown in Figure 5, where a 2 microliter aqueous sample of 14.7 ppm total Pb, containing 432 picograms of ^{204}Pb , was placed in the furnace. The majority of the sample is evolved in a broad peak between 500 and 1300°C. This is attributed to the Pb on the graphite surface, while the continuing evolution and structure at higher temperatures is probably from Pb which has penetrated into the graphite matrix. Even though the furnace is

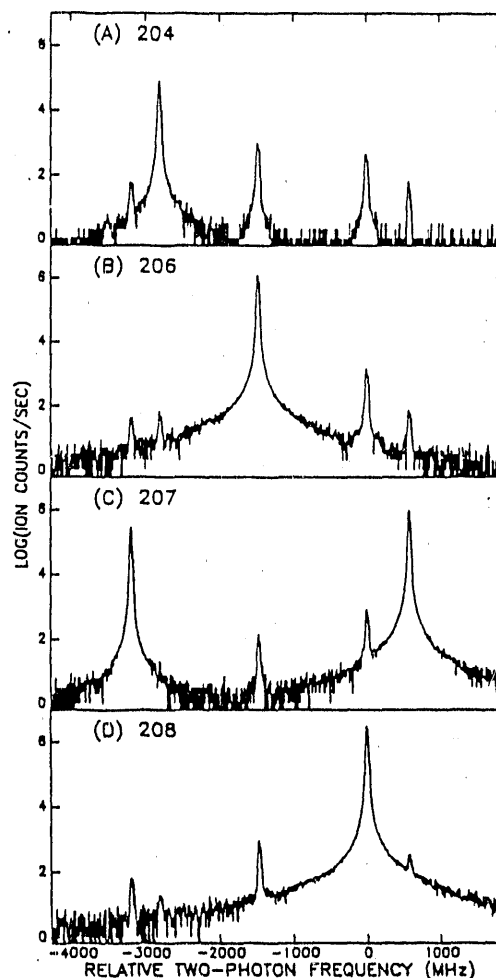


Fig. 3. Isotope shifts of the stable Pb isotopes in the $6p16p(1/2,3/2)_2$ Rydberg state. Details of the measurements are given in the text.

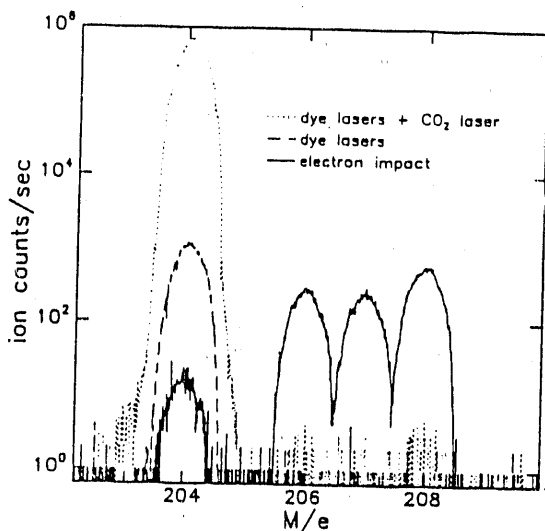


Fig. 4. Mass spectra of Pb with electron impact ionization and laser ionization tuned for ²⁰⁴Pb, with and without a CO₂ laser.

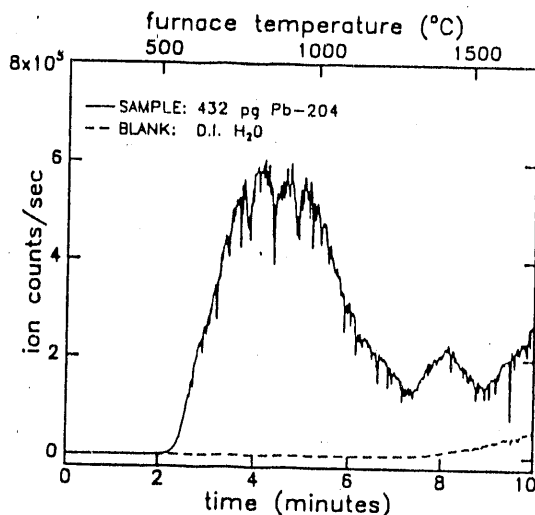


Fig. 5. Measurement of absolute sensitivity by evolution of a small discrete sample during temperature ramp of the graphite furnace.

"cleaned" by heating to 2100°C for one minute between runs, some of this deep matrix contamination is always present, as can be seen in the blank signal. Fortunately, the temperature profile for the matrix contamination is quite different from that of the sample and does not significantly interfere with the measurements. Integrating the main peak over the 500–1300°C range yields 1.06×10^8 ion counts, while a deionized water blank produces 1.5×10^5 counts over the same region. The net counts from the sample yields a sensitivity figure of 244 counts per femtogram, or an absolute efficiency of 1 of every 12,000 atoms placed in the furnace detected as an ion.

4. MEASUREMENTS ON ²¹⁰Pb

The first task in applying the method to the actual measurement of the radioisotope ²¹⁰Pb is to determine the isotope shift of the selected Rydberg state. Fortunately, for the even isotopes without nuclear spin, the shift can be predicted with reasonable accuracy from the simple proportionality: $S_R(210)/S_R(i) \approx S_1(210)/S_1(i)$, where $S_R(210)$ is the unknown shift for ²¹⁰Pb with respect to ²⁰⁸Pb in the Rydberg state, $S_R(i)$ is the known shift for the other even isotopes, either ²⁰⁴Pb or ²⁰⁶Pb, and $S_1(210)$ and $S_1(i)$ are the known shifts in the $6p7s\ 3P_1$ state. The average of the values of the shift for ²¹⁰Pb in the $6p16p(1/2, 3/2)_2$ Rydberg state predicted from the known ²⁰⁴Pb and ²⁰⁶Pb shifts is +2653 MHz. Thus we were able to constrain our search for the actual resonance to a limited range in this vicinity. The measurement was accomplished by tuning the first dye laser to the known ²¹⁰Pb frequency, setting the mass spectrometer for mass 210, and then repeatedly scanning the second dye laser over the predicted region while a sample containing 203 femtograms of ²¹⁰Pb slowly evolved from the furnace. These

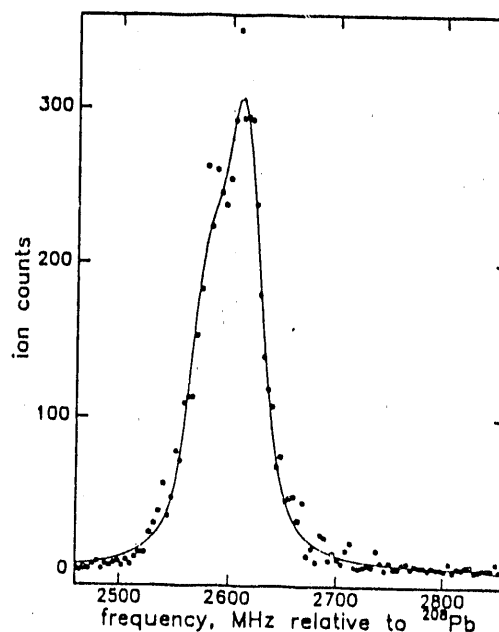


Fig. 6. Isotope shift for ²¹⁰Pb measured with a sample containing 203 femtograms. Sum of 20 laser scans repeated during sample evolution.

repeated scans were then summed to yield the spectrum shown in Figure 6. The observed isotope shift is $+2622 \pm 4$ MHz, in excellent agreement with the predicted value. The slight asymmetry in the peak is caused by the AC stark effect and a slight detuning (60 MHz) of the first dye laser, which is used to reduce metastable state trapping.

With the isotope shift known, all the information necessary for test analytical measurements is available. These were performed in a manner analogous to that described previously for the absolute sensitivity measurements with ^{204}Pb : both dye lasers were tuned for excitation of ^{210}Pb , the mass spectrometer was set at mass 210, and ion counts were recorded as the furnace temperature was ramped. Figure 7A shows the result for a prepared sample which contained 18.4 femtograms of ^{210}Pb in the presence of 2.95 micrograms of the stable Pb isotopes. This was compared to a "blank" that contained only the 2.95 micrograms of the stable isotopes. The ^{210}Pb signal is clearly observed, producing about 15 counts per second at the peak of the temperature profile, while the blank produces no observable increase in the count rate above the constant background of approximately 0.3 counts per second. The rapid increase in signal above 1400°C is present without laser excitation and thus is not the matrix contamination discussed earlier. It is attributed to the onset of blackbody ultraviolet photons generated by the furnace, which can be detected with the channeltron detector. Figure 7B shows the result for a sample having an even lower ^{210}Pb content of 1.6 femtograms, but still containing 2.95 micrograms of the stable isotopes: a relative ^{210}Pb concentration of 5.6×10^{-10} with respect to the stable isotopes. Because the expected count rate at the peak of the temperature profile is less than 2 per second, the signal has been summed over one minute intervals. The signal from the 1.6 femtograms of ^{210}Pb is still clearly observable, and with the blank sample there is still no observable increase in signal from the stable isotopes above the constant background. The results appear to be statistically limited: over the period including the fourth through seventh minutes 200 total ion counts were recorded for the sample containing ^{210}Pb , while 64 counts were recorded for the sample without ^{210}Pb . This corresponds to a net signal of 136 ion counts from the 1.6 fg of ^{210}Pb and a signal-to-background noise ratio $[(S-B)/\sqrt{B}]$ of 17. Thus the 3σ detection limits are slightly less than 3×10^{-16} grams.

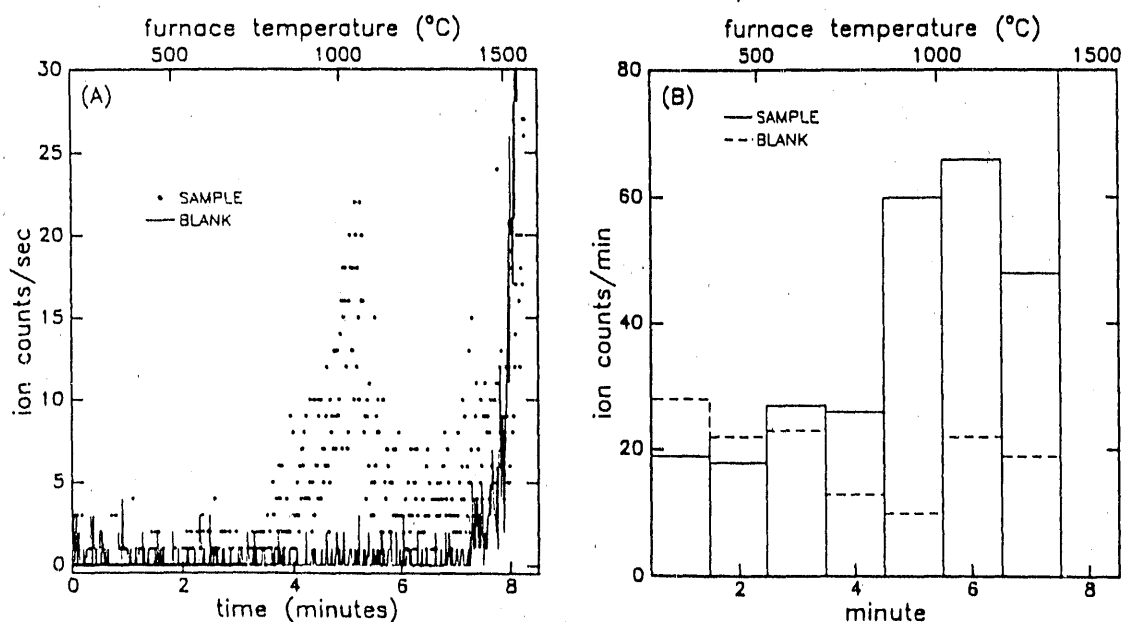


Fig. 7. Analytical measurements on prepared samples containing traces of ^{210}Pb in the presence of a large excess of the stable isotopes. The sample in (A) contained 18.4 femtograms of ^{210}Pb while (B) contained 1.6 femtograms. Both samples and the blanks contained 2.95 micrograms of the stable isotopes. The relative isotopic concentration of ^{210}Pb in (B) is 5.6×10^{-10} .

5. CONCLUSIONS

We have shown that double-resonance RIMS, using single-frequency dye lasers and an auxiliary cw CO₂ laser for photoionization, can effectively measure extremely rare isotopes at relative abundances of 10⁻¹⁰ or less. Detection limits for ²¹⁰Pb of 0.3 femtograms have been demonstrated with actual sample measurements made at levels within a factor of 5 of this detection limit. It is expected that these detection limits can still be improved by another factor of about 10 with continued work and a cleaner vacuum system to reduce nonresonant background ionization. Further, it has been shown that these techniques are applicable even for complicated spectroscopic systems where optical pumping and metastable trapping occur, and where ultraviolet wavelengths are required for the excitation scheme. Thus it should be possible to make measurements for most of the elements in the periodic table (Bushaw 1989) with similar isotopic selectivity and subfemtogram detection limits.

6. ACKNOWLEDGEMENT

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