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TRACE ANALYSIS OF OSMIUM AND RHENIUM BY RESONANCE IONIZATION MASS SPECTROMETRY OF SPUTTERED ATOMS

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1. INTRODUCTION

The quantitative trace analysis of Os and Re was investigated using the surface analysis by resonance ionization of sputtered atoms (SARISA) apparatus developed at Argonne National Laboratory [1]. SARISA samples the large fraction of sputtered neutral atoms and utilizes multiphoton resonance ionization to suppress atomic and molecular interferences. Matrix effects are considerably reduced for high ionization potential elements compared to secondary ion mass spectrometry because ionization occurs in the gas phase and is independent of the physical properties of the substrate. Synthetic metal standards and iron meteorites of known bulk Os concentration were used to establish a calibration curve for Os to test the linearity of the Os⁺ signal over a large range in concentration.

2. EXPERIMENTAL

A mass analyzed 5 keV Ar⁺ primary beam with a current of 2.0 μ A and a fwhm diameter of <100 μ m is produced by a Colutron ion gun. During analyses, the primary ion beam is chopped into 200 nsec pulses and is synchronized with lasers operating at a 40 Hz repetition rate. The Ar⁺ ion pulses strike the target in a UHV chamber pumped to a base pressure of 5×10^{-10} torr. During sputtering, the target is held at a 1.5 kV potential; incoming Ar⁺ ions are decelerated to 3.5 keV and positive secondary ions produced by sputtering are accelerated to 1.5 keV. The secondary ions are not transmitted through the mass spectrometer which is designed to accept ions with 1.0 ± 0.1 keV energy.

Three hundred nsec after the end of each ion pulse a XeCl excimer laser is fired producing a ~ 10 nsec, 200 mJ UV pulse. The excimer output is used to pump three tunable dye lasers (loaded with Rhodamine 590, Coumarin 480, and DCM dyes). The Rhodamine dye laser's visible light output is frequency doubled in a non-linear crystal to produce UV pulses. The three laser beams are overlapped in a volume that extends from about 0.5 to 1.5 mm above the target surface and has a diameter of ~ 1 mm. Photoionization of sputtered neutrals occurs within this volume following a three photon ionization scheme which utilizes resonant energy levels at 34365 and 55402 cm^{-1} and an autoionizing resonant energy level at 71032

cm⁻¹. The photoion beam is accelerated away from the target and is focussed and shaped in a time-of-flight mass spectrometer by a series of einzel lenses, deflection plates, and two hemispherical energy analyzers, after which it strikes a chevron-type microchannel plate electron multiplier. The resulting electron pulse is measured by a pulse-counting system which records counts per 5 nsec channel.

Synthetic and meteoritic samples of Fe-Ni solid solutions were analysed in this study. The synthetic samples consist of equal atom fractions of Os and Re (1000, 100, and 10 ppm) dissolved in a Ni matrix. The meteoritic samples are the metallic Fe-Ni kamacite phase (4 to 7% Ni) from iron meteorites which range in bulk Os concentration from 0.33 to 25 ppm. Prior to each analysis a 2.0 μ A direct current Ar⁺ beam was rastered across the sample for 2 min in a 2.5 x 2.5 mm pattern to remove surface contaminants. Each analysis consisted of summing the counts in each 5 nsec channel for a period of 125 sec at a repetition rate of 40 Hz (5000 pulses). The total counts in the channels between mass 185.5 to 192.5 were summed to collect Os⁺ counts from all of the major Os isotopes and the average background was subtracted from the total. The background was determined by detuning the ultraviolet dye laser 12 cm⁻¹ from the center of the first resonant energy level and collecting an analysis. The average background was 18 counts per 125 sec analysis. The absence of interferences resonant with the UV frequency was verified by analyzing stainless steel for Os and recording only 19 counts. The background intensities are assumed to represent instrumental background for a sample containing no Os. Each sample was analyzed at least twice and the total counts were averaged. The 1000 ppm Os standard was analyzed prior to each analysis session and served as an internal standard to correct for variations in operating conditions.

3. RESULTS AND DISCUSSION

The Os⁺ signal (relative to the 1000 ppm standard) is plotted versus the known Os concentration for each sample on a logarithmic scale in Fig. 1. The bulk Os concentration of the synthetic samples was determined by weighing of powdered metals before sample synthesis [2] and the bulk Os content of the meteorites was determined by radiochemical neutron activation analysis (RNAA) [3,4]. Replicate SARISA analyses vary from the mean for each sample by 1 to 13%, which may be used as an estimate of the precision. Uncertainties due to counting statistics range from less than $\pm 1\%$ up to $\pm 11\%$ in the lowest concentration sample. The data fall along a calibration line of slope one indicating a simple linear proportionality. The deviation from the line ranges from 6 to 25% of the concentration. We have no independent check of the compositions of the synthetic samples but the 1000 ppm sample has the smallest uncertainties due to weighing during preparation of the standards. The RNAA concentrations have reported precisions of 12 to 14% with accuracies as low as $\pm 30\%$ [3,4]. Iron meteorites may be inhomogeneous with respect to Os concentration [5], but the magnitude of this effect is unknown. The $\pm 25\%$ deviation of the data from the calibration line contains contributions from uncertainties in the Os⁺ signal intensities, the RNAA data, and possible heterogeneities in the samples. The magnitude of the various contributions to the uncertainty is unclear but the data show that unknown Os concentrations can be determined to at least $\pm 25\%$ using SARISA.

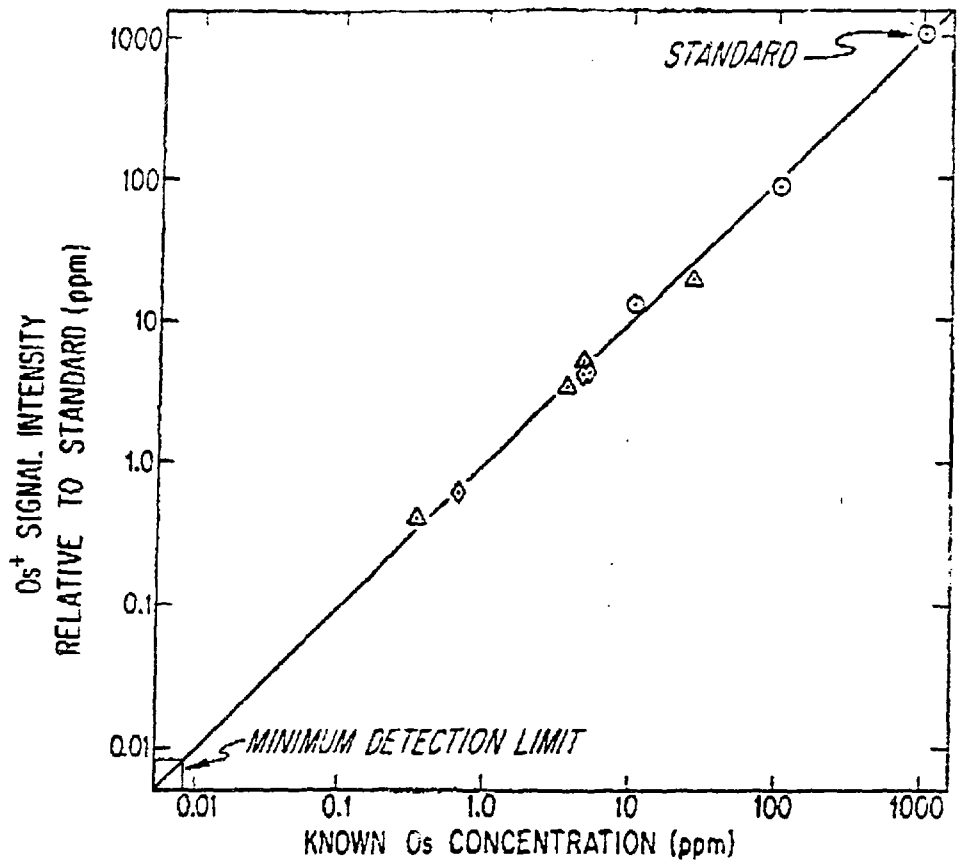


Fig. 1. The SARISA Os⁺ signal intensity relative to the 1000 ppm standard plotted versus known bulk Os concentration for synthetic samples and iron meteorites. A line with a slope of one is plotted for reference. The 8 ppb detection limit is for a 3600 sec analysis.

The relative ion yield and the maximum background count rate were used to calculate the detection limit for Os from Poisson statistics at the 95% confidence level following the approximation derived by Ziebold [6]. Following this treatment we calculate that the detection limit for Os is 40 ppb for a 125 sec analysis and 8 ppb for a 3600 sec analysis. We note that the 40 Hz pulsed sputter rate is so low that a 3600 sec analysis consumes only ~6 monolayers of the sample.

The useful yield is defined as the ratio of ions detected to atoms present in the ion source and is determined from the ratio of Os⁺ ions detected per laser shot to the number of Os atoms sputtered from the sample per primary ion pulse. The mean relative Os⁺ ion yield corresponds to 0.069 counts per ppm per laser shot. The amount of target material sputtered per primary ion pulse can be estimated from the sputter yield of pure Fe under bombardment by 3.5 keV Ar⁺ ions, which is 2.5 Fe atoms per Ar⁺ ion [7]. With a primary ion current of 2.0 μ A and a pulse width of 0.20 μ sec, 2.5×10^6 ions strike the target per pulse and, therefore, approximately 6.3×10^6 Fe atoms are sputtered. Assuming that trace levels of Os are sputtered at the same rate as the Fe matrix, 6.3 Os atoms will be

sputtered per ppm of Os in the sample during a single primary ion pulse. Dividing the Os counts per laser shot by the number of sputtered Os atoms per primary ion pulse gives a useful yield of 1.1×10^{-2} .

4. SUMMARY

We have demonstrated that SARISA can be used for quantitative geochemical microanalysis of Os with a spatial resolution of $< 100 \mu\text{m}$. The measurement of Os concentrations in metal standards and iron meteorites was used to demonstrate the analytical capabilities of the technique. A linear correlation between Os⁺ signal intensity and the known Os concentration has been demonstrated over a nearly 10^4 spread in Os concentration with a precision of $< \pm 13\%$, a minimum detection limit of 8 ppb, and a useful yield of 1%. We do not know the exact accuracy of these SARISA measurements because we are limited by uncertainties in the Os concentration of our standards and samples, but it is *at least* $\pm 25\%$. SARISA can be calibrated and applied to *in situ* analysis of Os and most other elements in virtually any composition of matrix material.

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