



Research Article

Evaluation of Uncertainties in Measurement of Isotopic Abundance by Semi-quantitative Analysis with TOF-SIMS

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Abstract

In *Condensed Matter Nuclear Science*, an anomaly in isotopic abundances of the sample components is often considered as an evidence of a nuclear transmutation. TOF-SIMS is one of the popular tools to investigate the isotopic composition in the research, and it is known that a measured abundance possibly has a certain uncertainty due to unique effects of the device. In this study, we measured isotopic abundances for some types of metal foil samples with various surface conditions by a semi-quantitative analysis with TOF-SIMS, and evaluated the uncertainties.

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1. Introduction

In *Condensed Matter Nuclear Science* (CMNS), an anomaly in the isotopic abundances on the sample components is often referred as an evidence of a low-energy nuclear transmutation. Iwamura et al. performed a deuterium permeation experiment and they found that the ratios of signals on the masses corresponding to Mo isotopes were quite similar to natural abundances of Sr isotopes, which were deposited onto the sample surface [1]. This result was considered to be an evidence of the selective transmutation from Sr to Mo. Omori et al. found that the abundance of Pd isotopes on the

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surface layers of the Pd cathode can change from natural abundance in light water critical electrolysis [2]. They also found an isotopic anomaly of potassium in plasma electrolysis in K_2CO_3/H_2O and K_2CO_3/D_2O solutions [3]. These results suggested an occurrence of a nuclear transmutation. In these experiments, Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to analyze the isotope compositions.

The TOF-SIMS is capable of analyzing all the elements including their isotopes as well as good sensitivity for detecting a small amount of elements on a sample with high mass resolution, and it is widely used in various fields such as physics, chemistry, biology, and medical researches [4–6]. In CMNS experiments, it is used as one of the most popular tools to identify a small amount of nuclear products on the sample. In addition, it provides us information on isotopic composition to discuss an occurrence of a nuclear transmutation. Once a significant difference between the measured and natural isotopic abundances, it is referred as a strong evidence of an occurrence of a nuclear transmutation. However, a signal intensity of existing elements/isotopes depends on various effects such as surface sputtering, surface scattering, thermo-diffusion by external source, and so on [7,8]. Then, appreciable changes from the natural isotopic composition can happen for an element at near-surface layer even for a sample not subjected to an experiment. Therefore, it is really important to make out the uncertainty for the signal intensity in the TOF-SIMS measurement to justify the results of a low energy nuclear transmutation if we discuss an anomaly in the isotopic abundance.

In this study, we measured isotopic abundances for some types of metal foil with various surface conditions by a semi-quantitative analysis with TOF-SIMS. Then, the varieties of the isotopic abundances were evaluated for those samples and the uncertainties in the measurements were discussed quantitatively.

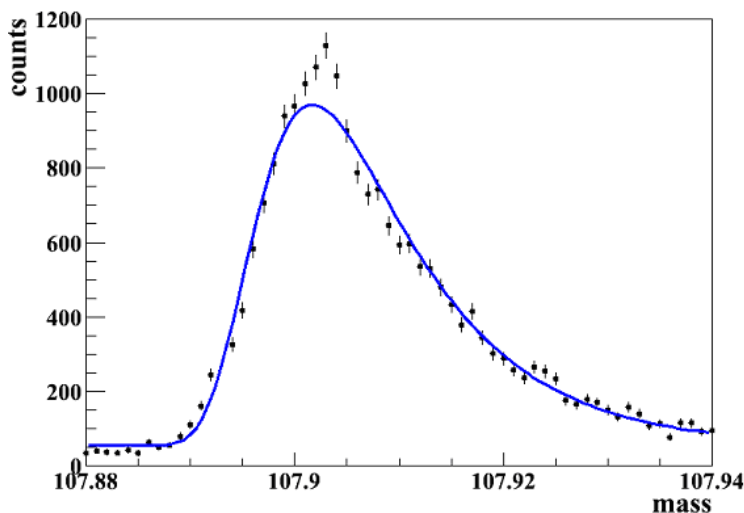


Figure 1. Signal of ^{108}Pd in TOF-SIMS mass spectrum with a fitted function; $f(x) = 54.79 + 1508.47 \times \exp\left[-\frac{1}{2} \left\{ \frac{x-107.90}{0.0050} + \exp\left(-\frac{x-107.90}{0.0050}\right) \right\}^2\right]$.

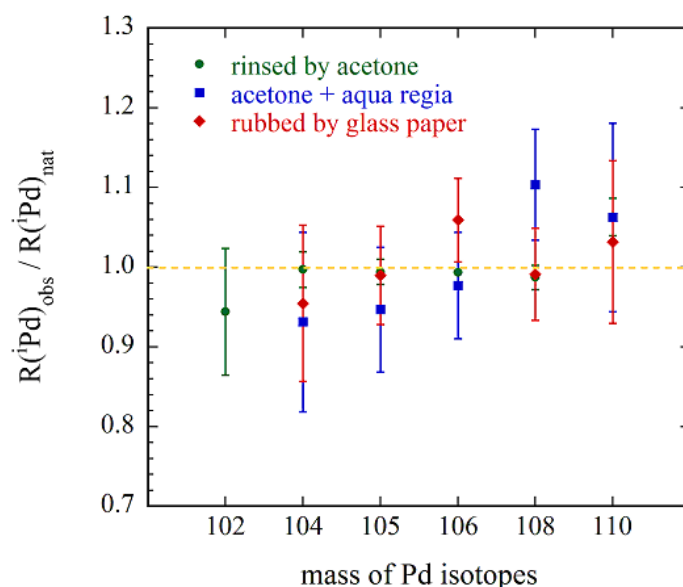


Figure 2. Ratio of measured and natural abundances of Pd isotopes for surface processed Pd foils.

2. Experiment

2.1. Sample preparation

In the experiments for CMNS study, a metal sample is often used as a host material for inducing a nuclear reaction. The metal sample is usually rinsed with acetone and soaked into acid to remove possible impurities in the preparation process, so that the surface condition of the metal can be affected [1,9]. Considering the treatments in the experiment, we prepared Pd, Ni, and Cu foil samples subjected to rinsing by acetone and soaking into aqua regia, and investigated how much the isotopic abundance changed by TOF-SIMS analysis. We also prepared samples rubbed with a glass paper (No. 1000) for making the surface much more rough to examine the effects. Moreover, a metal sample is exposed to hydrogen isotope in most of CMNS experiments, so that a condition of the sample surface can change by sorption of hydrogen atoms. So, we prepared a Pd foil exposed to 5 atm deuterium gases for 23 h, and analyzed the surface of the deuterium loaded Pd.

The surface morphology of these samples was analyzed by AFM to investigate the surface condition, and roughness was found to be 0.05–1 μm for the sample processed by aqua regia and 0.5–1.5 μm for the sample rubbed with a glass paper, typically. Even in the case of showing almost same roughness values, the morphology is indeed different in sample by sample. For example, the mesh pattern on the surface of the sample rubbed with a glass paper is finer and shallower in comparison with that of the sample processed with aqua regia.

2.2. TOF-SIMS measurement

The TRIFT V nano-ToF (ULVAC Phi) equipped with Bi liquid metal ion source was employed in this study. The primary ion beam was 30 keV Bi^+ with a 8400 Hz repetition rate and a pulse width of 10 ns. The current on the target

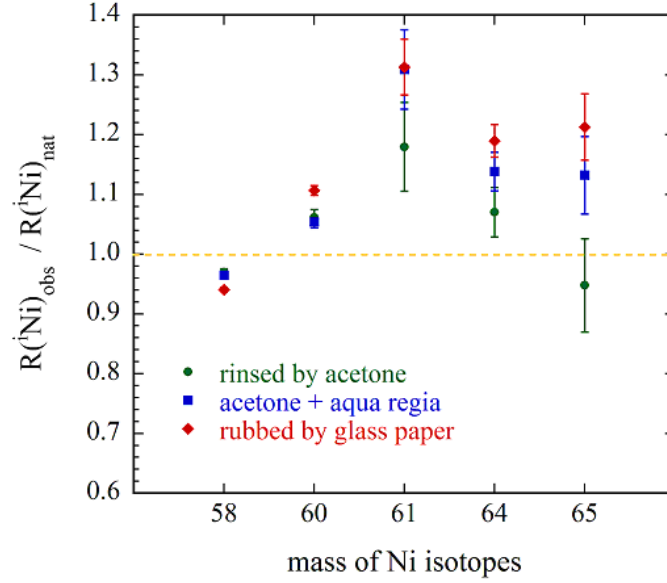


Figure 3. Ratio of measured and natural abundances of Ni isotopes for surface processed Ni foils.

surface was 1–2 nA. The raster size was set to be $40 \mu\text{m} \times 40 \mu\text{m}$. The mass resolution, $m/\Delta m$, was typically ~ 5000 at $m/z = 27$. These conditions are the same in our typical analysis for CMNS study [10]. The depth profile of the abundance was obtained by sputtering with DC Bi^+ for 30, 60, 180, 300 s. The raster size of the DC beam was $200 \mu\text{m} \times 200 \mu\text{m}$ which covers wholly the analysis area. In our typical measurements, no significant variation could be seen in the measured mass spectra for different areas on a sample, so far. Then, we only analyzed an area selected randomly for each sample in this study.

3. Results and Discussion

In order to obtain the intensity of a specific signal, we fitted a function to the corresponding peak on the mass spectrum. Since a secondary ion sputtered by a primary ion has a variety of the initial kinetic energy, especially for metal elements, the signal in the mass spectrum shows a tail [11,12]. In order to determine the signal intensity for an objective isotope, the Moyal function was fitted to the signal distribution with parameters, p_1 , p_2 , p_3 , and p_4 [13],

$$f(x) = p_1 + p_2 \times \exp \left[-\frac{1}{2} \left\{ \frac{x-p_3}{p_4} + \exp \left(-\frac{x-p_3}{p_4} \right) \right\} \right].$$

Then, we obtained the number of contained events by integral of the fitted function. Figure 1 shows the signal of ^{108}Pd isotope for the Pd foil rinsed by acetone. A fitted function was also shown in the figure.

Table 1. Natural isotopic abundance of Pd, Ni, and Cu.

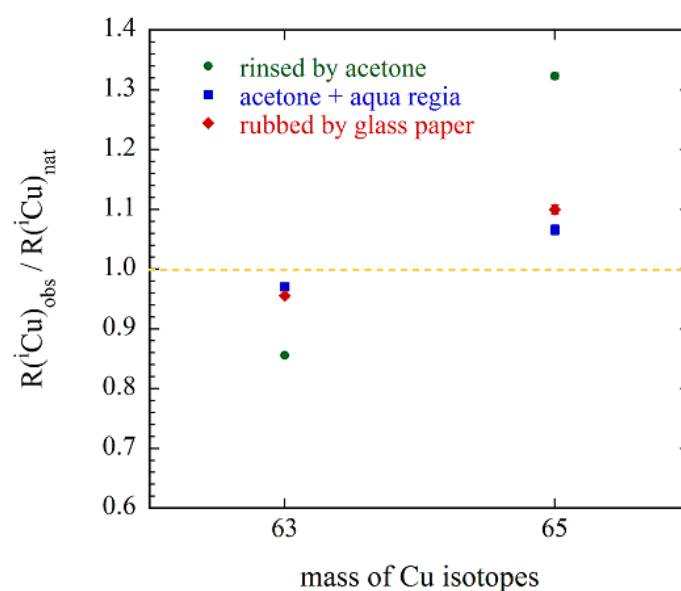
Pd	Mass	102	104	105	106	108	110
	Abundance (%)	1.0	11.1	22.3	27.3	26.5	11.7
Ni	Mass	58	60	61	62	64	
	Abundance (%)	68.1	26.2	1.1	3.6	0.9	
Cu	Mass	63	65				
	Abundance (%)	69.2	30.8				

In evaluation of the change in the abundance, we took into account for the ratio of observed abundance to natural one with the following equation,

$$\frac{(N_{M_i} / \sum N_{M_i})_{\text{observed}}}{(N_{M_i} / \sum N_{M_i})_{\text{natural}}} = \frac{R(M_i)_{\text{obs}}}{R(M_i)_{\text{nat}}}.$$

Here, N_{M_i} is the intensity of the TOF-SIMS on the mass of i -th isotope of metal M. Sets of natural abundances for the metals investigated in this study are shown in Table 1 [14].

Figure 2 shows the ratios of measured and natural abundances of the Pd isotopes for the samples rinsed by acetone, soaked in aqua regia, and rubbed with a glass paper. These data were taken after 30 s surface sputtering in the TOF-SIMS measurement. Since the yields of secondary ions for Pd isotopes are relatively low, the statistic errors were large. The measured abundances show reasonably good agreement with the natural ones within the errors for every sample

**Figure 4.** Ratio of measured and natural abundances of Cu isotopes for surface processed Cu foils..

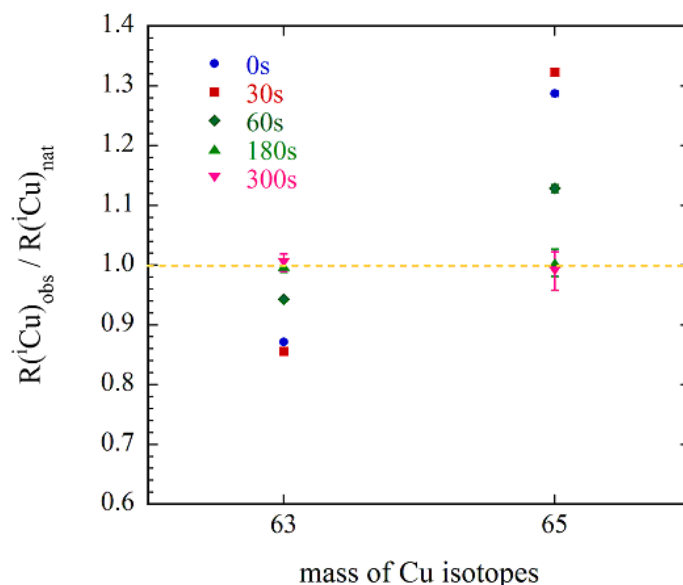


Figure 5. Ratio of measured and natural abundances of Cu isotopes for the sample washed by acetone, for each etching time.

condition except for the isotope ^{102}Pd , which has a small natural abundance. The abundance of an isotope with a small number of counts may have a large fluctuation.

Figure 3 shows the ratios of measured and natural abundances of the Ni samples with the same conditions as the Pd ones. We found up to 20 % discrepancies between measured and natural abundances. They seem to be larger for an isotope with a small abundance, as observed for Pd isotopes. In addition, we found larger differences for the surface processed samples.

Figure 4 shows the results for the Cu samples. Even for the sample just rinsed by acetone, the measured abundance is more than 20% different from natural one. In principle, relative yield of a light isotope in comparison to a heavy one is likely to become larger than natural isotopic ratio because a lighter atom is easy to be sputtered by an incident primary ion. However, our result showed a larger ratio in the heavier isotope. This shift is not due to such a mass effect, but supposed to be a kind of systematic uncertainty in our analysis conditions. Figure 5 shows a comparison for the data taken with a different sputtering time for the sample rinsed by acetone. We found that the abundances get close to natural ones increasing the sputtering time. Since there is more contaminant on the layer such as molecular ion of hydro-carbon so that the secondary ion signal may overlap the original signal and its intensity becomes larger. We should take really care for this effect in estimating isotopic abundances.

Figure 6 shows the results for the Pd sample before and after exposing to deuterium gas. The sample surface condition was apparently different between before and after exposing deuterium according to the AFM images. We observed formation of many small protrusions and change in the surface pattern for the sample after exposing deuterium, as shown in Fig. 7. These changes are supposed to be due to hydrogen embrittlement. However, we did not observe a significant change in the isotopic abundances and the difference of abundance in each isotope was less than 10%. In the case of analyzing the metal sample (X) exposed to the hydrogen isotopes, we should be careful about the interference of the molecular ion of $\text{X}+\text{H}/\text{D}$. The signal of the molecular ion can overlap the signal for an isotope with corresponding

$$\begin{aligned}
\text{Mass 102:} \quad & N(^{102}\text{Pd}) - N(\text{PdD}) \times R(^{102}\text{Pd}), \\
\text{Mass 104:} \quad & N(^{104}\text{Pd}) - N(\text{PdD}) \times \{R(^{104}\text{Pd}) - R(^{102}\text{Pd})\}, \\
\text{Mass 105:} \quad & N(^{105}\text{Pd}) - N(\text{PdD}) \times R(^{105}\text{Pd}), \\
\text{Mass 106:} \quad & N(^{106}\text{Pd}) - N(\text{PdD}) \times \{R(^{106}\text{Pd}) - R(^{104}\text{Pd})\}, \\
\text{Mass 108:} \quad & N(^{108}\text{Pd}) - N(\text{PdD}) \times \{R(^{108}\text{Pd}) - R(^{106}\text{Pd})\}, \\
\text{Mass 110:} \quad & N(^{110}\text{Pd}) - N(\text{PdD}) \times \{R(^{110}\text{Pd}) - R(^{108}\text{Pd})\},
\end{aligned}$$

mass, and we cannot distinguish them usually because their masses are very close. Now, we considered the effect of formation of PdD for an identified signal. Assuming that the probabilities of the formation of PdD molecule for every Pd isotopes are same, the signal intensity of the mass corresponding to the Pd isotopes can be expressed as follows;

where $N(^i\text{Pd})$ and $N(\text{PdD})$ are the number of the ^iPd isotopes and the Pd+D compound, respectively, and $R(^i\text{Pd})$ is the natural abundance of ^iPd isotope. Substituting the values of the natural abundance (Table 2) into the equations above, the abundances of ^{102}Pd , ^{104}Pd and ^{105}Pd should get smaller, while the abundances of ^{106}Pd , ^{108}Pd and ^{110}Pd

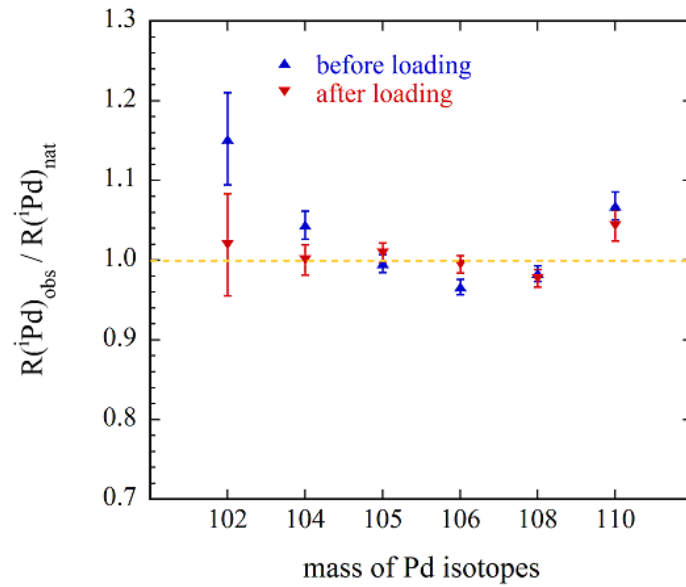


Figure 6. Ratio of measured and natural abundances of Pd before and after exposing high pressure deuterium gas.

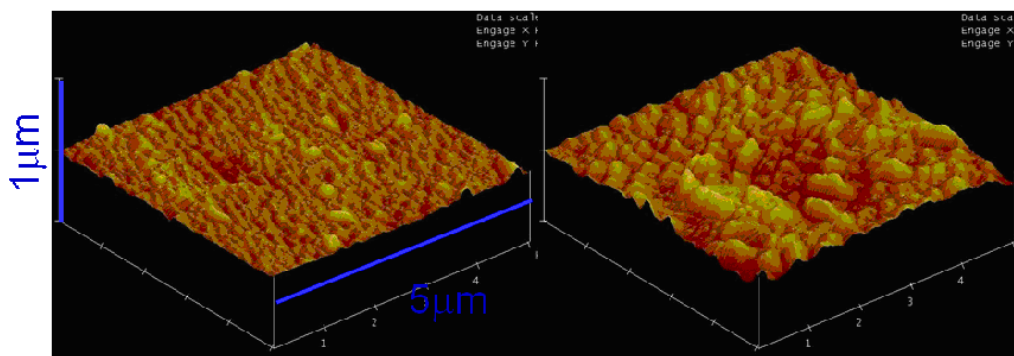


Figure 7. AFM images of Pd surface before (*left*) and after (*right*) exposing to deuterium.

should get larger. We have not seen such a tendency clearly in our results. Thus, the effect of the PdD compound is smaller than that of other effects.

4. Conclusion

We measured the isotopic abundance for the samples with various surface conditions by the semi-quantitative analysis with TOF-SIMS. We found uncertainties in determining the abundance is a range of 10–30%. No clear dependence on the surface morphology but the sample material. We also found that the abundance of the isotope with small intensity is likely to shift from natural one. We should consider these results when we discuss the anomaly in isotopic abundance in the CMNS study.

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