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# 超高純度試薬および海水中のニッケルの同位体希釈質量分析法

# Isotope Dilution Mass Spectrometry of Nickel in Some Ultra Pure Reagents and Seawater

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Isotope dilution surface ionization mass spectrometry has been successfully applied to the accurate determination of nickel in ultra pure reagents, ultra pure water and seawater. These reagents and water were purified by sub-boiling method. After spiked with a stable isotope of nickel $^{61}$Ni, the sample is heated to dryness and the residue obtained is dissolved in a mixture of a phosphoric acid and silica gel suspension. This solution is applied to the mass spectrometer equipped with a surface ionization device incorporating a rhenium single filament. On the basis of $^{58}$Ni$/^{61}$Ni ratio, the present method can determine ng amount of nickel with a relative error of 1%, the sensitivity limit of this determination for is about $10^{-13}$ g.

Keywords : Isotope Dilution Mass Spectrometry, Nickel, Ultra Pure Reagent, Ultra Pure Water, Seawater

## 1 Introduction

When nickel in a weighed amount of samples has reached isotopic equilibration with a known amount of a $^{61}$Ni enriched spike, a following relation holds for the molar amounts of the element and its isotopes;

$$\frac{^{58}\text{Ni}}{^{61}\text{Ni}} = \frac{^{58}\text{fNi-sample} \times X + {}^{58}\text{fNi-spike} \times Y}{^{61}\text{fNi-sample} \times X + {}^{61}\text{fNi-spike} \times Y} \quad \cdots \text{(1)}$$

where $^{58}$Ni and $^{61}$Ni represent the molar amounts of isotope $^{58}$Ni and $^{61}$Ni comprising nickel under measurement; X and Y are the molar amounts of the element in the sample and the added spike respectively, and also $^{58}$fNi-sample and $^{61}$fNi-spike are the isotopic abundance of the isotope $^{58}$Ni in the sample and $^{61}$Ni in the spike respectively. The amount
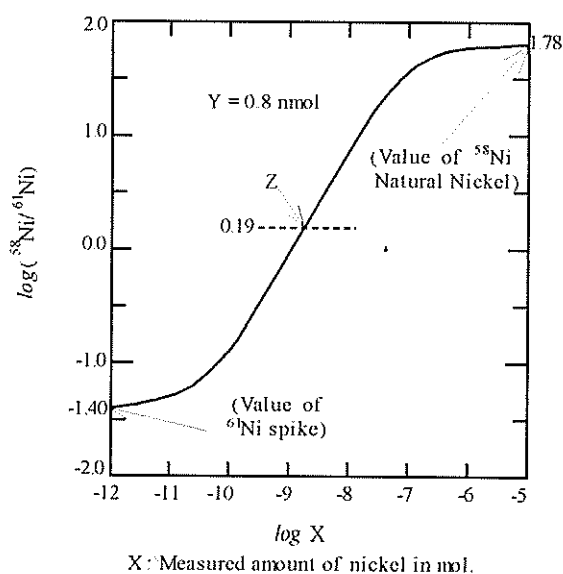
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Figure 1 Isotope dilution curve

of X can be determined on the basis of $^{58}Ni/^{61}Ni$ ratio, when the amount of Y is known. When a certain amount of Y is added to a sample, the resulting $^{58}Ni/^{61}Ni$ ratio moves along the isotope dilution curve according to the amount of X as shown in Figure 1. Different amounts Y will make shift corresponding curves parallel horizontally to that in Figure 1. Therefore, sample preparations must be carefully performed to make the $^{58}Ni/^{61}Ni$ ratio fall on close to the Z point in Figure 1, where the most accurate value of X is obtained[1]. The lack of purity in the isotopic abundance of the $^{61}Ni$ spike makes the tangent value of this isotope dilution curve smaller than those of cadmium, lead, silver, thallium, and so on. This means that unsuitable $^{58}Ni/^{61}Ni$ ratios will give large error to the analytical results of nickel.

## 2 Experiments

### $^{61}Ni$ spike solution

A weighed amount of the $^{61}Ni$ enriched nickel metal was dissolved in a dilute nitric acid solution and stored in a tightly stoppered Teflon bottle. The isotopic abundance of this nickel was determined and listed together with that of a commercial Four-9 nickel metal and that of the certified value by the Oak Ridge National Laboratory, Tenn., U.S.A. in Table 1. The molar concentration of this spike solution was standardized to a reference nickel solution, which had been prepared from the Four-9 metal, and is shown in Table 2.

### Mass Spectrometer

A Hitachi RMU-6 mass spectrometer detected an emitter current of $10^{-19}A$ for the $Ni^+$ mass

spectrum and measures the isotopic ratio with an accuracy of 0.n % in the coefficient of variation.

### Cleanliness class in laboratory

. All chemical procedures were performed in a class 100 clean draft chamber and on class 100 clean benches set in a class 300 clean room.

### Sample preparation for mass spectrometry of nickel in ultra pure reagents

A weighed amount of $^{61}Ni$ spike solution, usually 0.8 nmol as $^{61}Ni$ was added to the addition of nitric acid, each 5 nmol of $^{61}Ni$ spike was added as indicated in Table 4. After setting stood for several days to reach the isotopic equilibrium, the spike sample was neutralized to a pH value of 9. Nickel was extracted into 10m$l$ of a 0.0013% dithizone chloroform solution. Then, the solution was rinsed several times with each 5.0 m$l$ of purified water to remove the aqueous emulsion containing the major components of seawater. A 5.0 m$l$ portion of 7 mol kg$^{-1}$ nitric acid was added to the dithizone chloroform solution for the back extraction of the element. The acid solution was rinsed twice with 5.0 m$l$ portions of chloroform solution. The acid solution was transferred to a Teflon beaker and 1.0 m$l$ of nitric acid and 0.25 m$l$ of perchloric acid were added. The contents were gently heated to dryness under a pure nitrogen atmosphere in an oven. Subsequently, 0.3 m$l$ of nitric acid and 0.1 m$l$ of perchloric acid were added to the residue and the contents were heated again to decompose completely the organic materials. The residue thus obtained was dissolved in the mixtur of phosopheric acid and water suspension of silica gel.

Table 1　Determination of isotopic abundance of natural nickel and $^{61}Ni$-enriched spike.

| Sample taken nmol | $^{58}Ni^+$ emitted | Isotopic abundance (%) | | | | |
|---|---|---|---|---|---|---|
| Natural Ni as $^{58}Ni$ | $10^{-14}$ A | $^{58}Ni$ | $^{60}Ni$ | $^{61}Ni$ | $^{62}Ni$ | $^{64}Ni$ |
| 13.4 | 2.30 | 68.3 | 26.2 | 1.12 | 3.55 | 0.88 |
| 3.15 | 5.90 | 68.3 | 26.1 | 1.12 | 3.56 | 0.88 |
| 0.580 | 0.85 | 68.4 | 26.1 | 1.12 | 3.53 | 0.89 |
| 0.123 | 0.17 | 68.4 | 26.1 | 1.13 | 3.53 | 0.89 |
| 0.062 | 0.16 | 68.4 | 26.0 | 1.12 | 3.55 | 0.90 |
| $^{61}Ni$ spike as $^{61}Ni$ | $^{61}Ni^+$ emitted | | | | | |
| 11.0 | 2.5 | 3.51 | 6.12 | 88.9 | 1.40 | 0.12 |
| 5.14 | 1.2 | 3.52 | 6.11 | 88.9 | 1.39 | 0.13 |
| 3.19 | 2.0 | 3.54 | 6.12 | 88.8 | 1.39 | 0.12 |
| 0.50 | 1.5 | 3.64 | 6.15 | 88.7 | 1.40 | 0.12 |
| 0.10 | 0.2 | 4.01 | 6.27 | 88.2 | 1.41 | 0.12 |
| 0.060 | 0.1 | 4.33 | 6.36 | 87.8 | 1.42 | 0.12 |
| Certified value by ORNL | | 3.45 | 6.12 | 88.8 | 1.10 | 0.20 |

ORNL : Oak Ridge National Laboratory

Table 2  Standardization of a $^{61}$Ni spike solution to a standard solution prepared from four-9 natural meta

| $^{61}$Ni spike solution taken, g | Natural nickel added. $\mu$ mol | $^{61}$Ni emitted $10^{-11}$A | $^{58}$Ni / $^{61}$Ni | C.V.* % | Spike nickel found $\mu$ mol | $\mu$ mol/g |
|---|---|---|---|---|---|---|
| 0.7020 | 0.7002 | 0.6 | 0.5520 | 0.2 | 1.037 | 1.478 |
| 0.7465 | 2.517 | 1.5 | 1.739 | 0.1 | 1.103 | 1.477 |
| 0.7831 | 2.584 | 1.0 | 1.704 | 0.1 | 1.156 | 1.476 |
| 0.7515 | 6.237 | 1.3 | 4.06 | 0.1 | 1.090 | 1.477 |
| | | | | | Ave | 1.477 |

* Coefficient of variation as to $^{58}$Ni/$^{61}$Ni

Table 3  Determination of nickel in reagents, water and seawater

| Sample | | Sample taken g | Spike added as total spike nmol | $^{58}$Ni / $^{61}$Ni | C.V.* % | Nickel found in sample p mol | ng kg$^{-1}$ |
|---|---|---|---|---|---|---|---|
| A | HNO$_3$ | 45.15 | 0.7614 | 0.156 | 0.2 | 117 | 152 |
| | HClO$_4$ | 31.01 | 0.7543 | 0.134 | 0.5 | 93.8 | 177 |
| | HF | 45.40 | 0.7601 | 0.143 | 0.4 | 103 | 133 |
| | CHCl$_3$ | 71.92 | 0.7607 | 0.0583 | 0.7 | 18.5 | 15.2 |
| | NH$_3$aq | 42.25 | 0.7857 | 0.140 | 0.2 | 104 | 144 |
| B | HNO$_3$ | 45.07 | 0.7779 | 0.0628 | 0.4 | 23.7 | 30.9 |
| | HClO$_4$ | 74.70 | 0.7827 | 0.0770 | 0.3 | 37.0 | 29.1 |
| | HF | 48.60 | 0.8256 | 0.0647 | 0.6 | 27.1 | 32.8 |
| | CHCl$_3$ | 83.97 | 0.7820 | 0.0490 | 0.5 | 9.36 | 6.54 |
| | NH$_3$aq | 50.56 | 0.7827 | 0.0742 | 0.5 | 34.3 | 39.7 |
| | water | 706.1 | 0.7909 | 0.102 | 0.5 | 62.4 | 5.18 |
| Seawater | | 623.2 | 5.063 | 0.654 | 0.2 | $4.11 \times 10^3$ | 385 |
| | | 620.6 | 5.032 | 0.652 | 0.2 | $4.03 \times 10^3$ | 383 |
| | | 1239.5 | 5.203 | 1.208 | 0.1 | $8.09 \times 10^3$ | 382 |
| | | 1240.3 | 5.109 | 1.227 | 0.1 | $8.08 \times 10^3$ | 381 |

A: Ultra pure grade,  B: Purified by sub boiling distillation,  * Coefficient of variation as to $^{58}$Ni/$^{61}$Ni

Table 4 Blank for a sample preparation,

| Sample | Reagents used g | Ni contamination from each reagent ng |
|---|---|---|
| Seawater | HNO$_3$  9.6 | 0.4 |
| | NH$_3$aq.  10.0 | 0.4 |
| | HClO$_4$  0.4 | 0.01 |
| | CHCl$_3$  45.0 | 0.3 |
| | water  33.0 | 0.2 |
| | room environments | 0.06 |
| | Total  1.4 | |

## 3  Results and Discussion

### Emission of Ni$^+$ ion beam current

As shown in Table 1, the use of silica gel and phosphoric acid permits 0.50 nmol of nickel to emit $1.5 \times 10^{-14}$A of $^{61}$Ni$^+$ beam current for a long time and sometimes 0.025 nmol of nickel to do $10^{-15}$A of $^{61}$Ni$^+$. The mass spectrometer can detect $10^{-19}$A of ion beam current due to Ni$^+$ mass spectrum, accordingly the present method can secure to measure

the presence of $10^{-13}$~$10^{-12}$g of nickel on the ionization filament. As for Y in Equation(1), 0.8 nmol of the spike is enough for the present method.

### Isotopic abundance of natural and spike nickel

In Table 1, the isotopic abundance measured by loading 11.0 nmol is used as substitute for $^{58}$fNi-spike and $^{61}$fNi-spike in Equation(1). They are in good accordance with those determined by the Oak Ridge National Laboratory, within the analytical error as shown in Table 1. However, measured isotopic abundance of the $^{61}$Ni spike has ·a certain variation with decreasing amount of loaded spike as shown in Table 2. The lesser the loaded amount, the smaller the isotopic abundance of $^{61}$Ni. This tendency tells us that the present method suffers contaminations amounting to $0.06 \pm 0.02$ ng of nickel from laboratory environments. For $^{58}$fNi and $^{61}$Ni, 68.3 and 1.12 are substituted respectively.

### Determination of nickel in reagents

The data in Table 3 show the applicability of the present method to the determination of nickel at the level of ng·kg$^{-1}$ concentration with an error of

1%, samples taken being lesser than $10^{-7}$g. Sub boiling distillation effectively works to decrease nickel contaminant from the 0.1 ppb level in commercial reagents to one third of those in purified ones.

**Application to seawater samples**

　　　Dithizone chloroform extraction is used to develop the present method to the simultaneous determination method for silver, cadmium, copper, nickel, lead, zinc and thallium in seawater[1]. A sample solution is shown in Table 3. The spiked solution is heated to dryness under a nitrogen atmosphere in a Teflon oven. The residue is dissolved in a mixture solution of $65\mu l$ of 0.2% silica gel suspension aqueous solution and $5\mu l$ of 2.0% phosphoric acid solution for the mass spectrometry.

**Sample preparation for mass spectrometry of nickel in seawater samples**

　　　Four aliquots of a seawater sample which had been kept at a pH value of 1 is prepared. Sample preparations require the use of several reagents and apparatus from which samples suffer contamination as listed in Table 4, i.e., 1.4 ng of nickel for seawater analysis. Amount of contaminant corresponds to 1% of measured values.

　　　The isotope dilution mass spectrometry of nickel has following inherent advantages. All chemical manipulations are done on a weight basis and involve straight-forward stoichiometric separations to determine amounts of nickel in samples and the $^{61}$Ni spike solution, and the mass spectrometric determinations involve only ratios but not absolute determinations of the isotopes. Furthermore, instrumental sensitivity and accuracy are essentially high, no instrumental corrections being necessary. Thus, the present method can detect $10^{-12}$ ~ $10^{-13}$g of nickel and measure pmol level of nickel with a relative error of 1%.

### References

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超高純度試薬および海水中のニッケルの同位体希釈質量分析法

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概　要

同位体希釈質量分析法は超純度試薬と超純度水および海水中のニッケルの正確な量の決定を可能にした。超純度の試薬や水はサブボイリング法によって精製した。安定同位体のニッケル$^{61}$Niスパイクを添加後、試料を蒸発乾固し、この得られた残滓をりん酸とシリカゲルけん濁液に溶解させた。この溶液をシングルレジウムフィラメントの質量計で分析した。本法による$^{61}$Ni／$^{61}$Ni比を基にして、相対誤差1%でngオーダーのニッケル量を検出でき、その検出限界は$10^{-13}$gである。

キーワード：同位体希釈質量分析法、ニッケル、超高純度試薬、超高純度水、海水

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