

# Comparison of alkaline fusion and acid digestion methods for the determination of rhenium in rock and soil samples by ICP-MS

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## Abstract

A simple acid digestion method was studied in order to analyze many samples at once to understand Re behavior in the terrestrial environment, because, under normal laboratory conditions, digestion methods generally used, such as Carius tube digestions, Teflon vessel digestions and alkaline fusions, can handle only a small number of samples at one time to ensure complete sample digestion. In this study, the Re results for reference materials (RMs) obtained by the acid digestion method were compared with those by the alkaline fusion digestion method to get applicability of the acid digestion method for Re determination in soil by inductively coupled plasma mass spectrometry. Alkaline fusion was chosen for the comparison because it is known to have the highest capability to dissolve Re in geological materials among digestion methods.

The average total Re recoveries measured using the <sup>185</sup>Re spike for RMs, such as rock, soil and sediment, were  $90.6 \pm 4.0\%$  for alkaline fusion and  $92.2 \pm 7.3\%$  for acid digestion, showing no differences between them. However, Re results obtained by the acid digestion method were usually slightly lower than those by the alkaline fusion (Student's *t*-test,  $P < 0.05$ ); the concentration ratio of acid digestion to alkaline fusion was 0.85 on average. When the total Re content was higher than  $0.2 \text{ ng g}^{-1}$ , the acid digestion method could dissolve about 80% of the sample Re. Although the acid digestion method is unable to dissolve all Re in the sample, however, the Re discharged to soils could be more extractable than the Re in the dissolution-resistant part; thus, the acid digestion method could be useful for obtaining Re levels in soil samples.

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## 1. Introduction

Rhenium (Re) is an interesting element from a geochemical viewpoint because of its sensitivity to redox potentials. However, because it is not an essential element for life and its concentration in environmental samples is not well known, Re behavior in the environment, especially in the terrestrial environment, has not been clarified yet. In seawater, the element seems to display conservative behavior [1], and to be enriched in anoxic sediments [2]. Only a small part of riverine Re is thought to be deposited on marine sediment and a missing sink for Re is unclear [3], although brown algae

[4] or anoxic sediments could play key roles. In the terrestrial environment, even less information has been reported for Re except for rivers [5], and almost no information has been published on its vertical and horizontal distributions in the soil environment. Re behavior is also of interest from the viewpoint of long-term environmental dose assessment. Re may be studied as a chemical analogue for fissionogenic Tc, for which the behavior is not well known; Tc is just above Re in the periodic table, and these two elements behave similarly in the environment [6].

To measure Re concentration in soil samples, the same methods as for rock samples are applicable. These days, inductively coupled plasma mass spectrometry (ICP-MS) is quite handy to measure Re at lower than several picogram per milliliter levels [7,8]. However, Re concentration in soil

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samples is expected to be very low since the concentration level in the earth's upper crust is low, e.g.  $0.39 \text{ ng g}^{-1}$  [9], so separation and concentration of the element from matrices are necessary before ICP-MS analysis. To dissolve the soil and rock matrix for platinum group and siderophile elements, fusions, including NiS fire assays [10–12] and alkaline fusions [13,14], and acid digestions, such as Teflon vessel digestions with microwave systems [5,15] and Carius tube digestions [7,16], are useful. Teflon vessel digestions cannot dissolve all phases in rock and soil, such as zircon, chromite and molybdenite. Fusions and Carius tube digestions are suitable extraction techniques, equally good at equilibrating spike and sample Re. However, as has been suggested [16], the Carius tube method, used alone, may not liberate all the Re.

It is necessary to obtain lots of Re data in soil samples to understand its behavior. Moreover, because Re contamination in soil along motorways has been reported [17], it is important to monitor the levels in surface soil. However, the methods widely used in geological sciences can usually handle only a few samples at one time which increases preparation time. Teflon vessel extractions and Carius tube methods are hazardous because they use high-pressure and high-temperature conditions which could lead to an explosion of the acid-added sample. In this study, we applied a simple acid digestion method using hot *aqua regia* under normal atmospheric pressure which allows us to handle a dozen or more samples at once. This relatively easy method is applicable for monitoring purpose. The method was compared with an alkaline fusion digestion method because alkaline fusion has the highest capability to dissolve Re in geological materials compared to other digestion methods as described above.

Standard reference materials (RMs; rock, soil and sediment) were used in this study because of their uniformity. They were dissolved by both alkaline fusion and acid digestion methods and Re in each dissolved sample was separated with an extraction chromatographic resin for ICP-MS measurement. The measured Re concentrations in the RMs were then compared. Also, through this study, we could obtain Re content information for these RMs, which is very important since there are no suitable soil RMs for Re.

## 2. Experimental

### 2.1. Samples

Rock RMs were standard igneous rocks found in Japan and prepared by the National Institute of Advanced Industrial Science and Technology (formerly Geological Survey of Japan, GSI). The details of their compositions were reported elsewhere [18]. The RMs had provisional Re values which were measured by radiochemical neutron activation analysis (RNAA), determined only 1–3 times per sample (personal communication with Dr. N. Imai). The sample codes were JG-1 (granodiorite), JB-1 (basalt), JB-3 (basalt), JA-1 (andesite), JA-2 (andesite) and JR-2 (rhyolite).

One sediment and three soil RMs were also analyzed; SRM-4350b (river sediment) and SRM-4355 (Peruvian soil) were provided by National Institute of Standards and Technology, and NDG-7 (Gray lowland soil) and NDG-8 (Gray lowland soil) were provided by the Japanese Society of Soil Science and Plant Nutrition. Gray lowland soil is a typical paddy field soil found throughout Japan. Both of the Gray lowland soil samples used were silty clay, with water contents of about 4.3% on a dry weight basis.

### 2.2. Reagents and standards

Water ( $>18 \text{ M}\Omega$ ) which was treated using a Milli-Q water system (Millipore Co.) was used for analysis and also to rinse all beakers and vials. Sodium carbonate anhydrous and sodium hydroxide were guaranteed reagent grade (Merck KGaA). Super-pure grade 68% nitric acid and 30% hydrochloric acid (TAMAPURE-AA-100, Tama Chemicals Co. Ltd.) were used. A prepacked TEVA resin column, which was charged with 2 mL TEVA resin (Eichrom Technologies Inc.), was pretreated with 5 mL of 8 M  $\text{HNO}_3$  and 5 mL of 0.1 M  $\text{HNO}_3$ . The TEVA resin is an aliphatic quaternary amine sorbed on Amberchrom CG71. The properties are similar to those of typical strong base anion exchange resins, however, because the functional groups are in a liquid form, rather than fixed to a polymer backbone, these groups have greater flexibility to coordinate around target anions.

An enriched  $^{185}\text{Re}$  spike solution was obtained by dissolving  $^{185}\text{Re}$  metal (Oak Ridge National Laboratory) in a known amount of Milli-Q water with addition of concentrated  $\text{HNO}_3$ . Rhenium-185 and -187 abundances in the solution were 96.74 and 3.26%, respectively. The Re concentration of the enriched  $^{185}\text{Re}$  solution was  $2.7 \text{ ng mL}^{-1}$ , from which a 0.2 mL portion was taken for each sample. Re solutions of known concentrations ( $0\text{--}100 \text{ pg mL}^{-1}$ ) were prepared by diluting a multi-element standard solution (XSTC-8, SPEX Industry Inc.) with 2%  $\text{HNO}_3$ .

### 2.3. Sample dissolution methods

Two methods were used to dissolve about 1 g of the rock or soil sample. Because of the low Re concentration, 1 g or more samples are necessary to obtain good quality Re data, although ICP-MS has high sensitivity and a low background level. For each digestion method, RMs were analyzed at least five times. A microwave digestion method was not employed because it can digest only 0.5 g amounts of soil or rock sample per vessel (and in practice usually 0.1–0.2 g), which means that two or more vessels are necessary to dissolve 1 g amount of rock or soil sample, which is time consuming.

For the alkaline fusion method, a known weight of the rock or soil sample (ca. 1 g dry) was placed in a platinum crucible and Re spike (0.1 mL) was mixed thoroughly with the sample. Next, about 5–7 g of  $\text{Na}_2\text{CO}_3$  (about 5–6 times the sample volume) were added with thorough mixing. The mixture was fused for 1 h in a molten state over a Bunsen burner flame

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