

Improvement of pre-treatment method for $^{36}\text{Cl}/\text{Cl}$ measurement of Cl in natural groundwater by AMS

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ABSTRACT

Estimation of $^{36}\text{Cl}/\text{Cl}$ by accelerator mass spectrometry (AMS) is a useful method to trace hydrological processes in groundwater. For accurate estimation, separation of SO_4^{2-} from Cl^- in groundwater is required because ^{36}S affects AMS measurement of ^{36}Cl . Previous studies utilized the difference in solubility between BaSO_4 and BaCl_2 (BaSO_4 method) to chemically separate SO_4^{2-} from Cl^- . However, the accuracy of the BaSO_4 method largely depends on operator skill, and consequently Cl^- recovery is typically incomplete (70–80%). In addition, the method is time consuming (>1 week), and cannot be applied directly to dilute solutions. In this study, a method based on ion-exchange column chromatography (column method) was developed for separation of Cl^- and SO_4^{2-} . Optimum conditions were determined for the diameter and height of column, type and amount of resin, type and concentration of eluent, and flow rate. The recovery of Cl^- was almost 100%, which allowed complete separation from SO_4^{2-} . The separation procedure was short (<6 h), and was successfully applied to dilute (1 mg/L Cl) solution. Extracted pore water and diluted seawater samples were processed by the column and BaSO_4 methods, and then analyzed by AMS to estimate ^{36}S counts and $^{36}\text{Cl}/\text{Cl}$ values. ^{36}S counts in samples processed by the column method were stable and lower than those from the BaSO_4 method. The column method has the following advantages over the BaSO_4 method: (1) complete and stable separation of Cl^- and SO_4^{2-} , (2) less operator influence on results, (3) short processing time (<6 h), (4) high (almost 100%) recovery of Cl^- , and (5) concentration of Cl^- and separation from SO_4^{2-} in the one system for dilute solutions.

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1. Introduction

^{36}Cl is one of the most useful natural tracers for hydrological processes because of its long half-life and the conservative properties of the chloride ion. It can be used to date groundwater [1–3] or to estimate the sources of salinity in groundwater [4–6].

^{36}Cl in groundwater is usually measured by accelerator mass spectrometry (AMS). For mass-36, there are two stable isotopes ^{36}S and ^{36}Ar . ^{36}S largely affects ^{36}Cl measurement by AMS because sulfur forms stable negative ions almost as easily as chlorine during AMS measurement [7–9]. Only 1 ppm of sulfur in AgCl can result in a detector counting rate 10^3 times higher than the ^{36}Cl rate for samples with $^{36}\text{Cl}/\text{Cl} = 10^{-13}$ [10]. For samples with low $^{36}\text{Cl}/\text{Cl}$ (e.g., 10^{-14}) it is desirable to reduce S contamination below 1 ppm, so that the gas filled magnet in the AMS system can effectively separate ^{36}Cl and ^{36}S [10,11]. Treatment of samples is required to remove or reduce the S present as SO_4^{2-} ion from in groundwater, river water and rainwater.

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In previous studies [12–14] chemical treatment utilizing the difference in solubility between BaSO_4 and BaCl_2 (BaSO_4 method) has been adopted (BaSO_4 method). The BaSO_4 method (Fig. 1) is lengthy procedure. It involves acidification of groundwater samples with concentrated HNO_3 , which is followed by addition of AgNO_3 solution to precipitate AgCl . The precipitate is separated from solution by centrifugation, and washed with distilled and de-ionized water. The AgCl is then re-dissolved in NH_4OH solution and $\text{Ba}(\text{NO}_3)_2$ solution is added to precipitate BaSO_4 . BaSO_4 precipitate is separated from solution by filtration. This procedure is repeated until no white precipitate forms when $\text{Ba}(\text{NO}_3)_2$ solution is added. HNO_3 and AgNO_3 solutions are then added to the filtrate to precipitate AgCl again. The AgCl precipitation is washed with de-ionized water and dried before analysis by AMS.

There are a number of problems with this method. First, during precipitation of BaSO_4 colloids or suspended particles of BaSO_4 can form and these are difficult to separate from solution by normal filtration with 0.2- or 0.45- μm filters. If solution contains these particles, AgCl precipitate made from this solution may be contaminated by S in particles. Ultra-filtration could be used to remove colloids and particles, but this work would be the detriment of total operation time for the procedure. Second, to achieve very

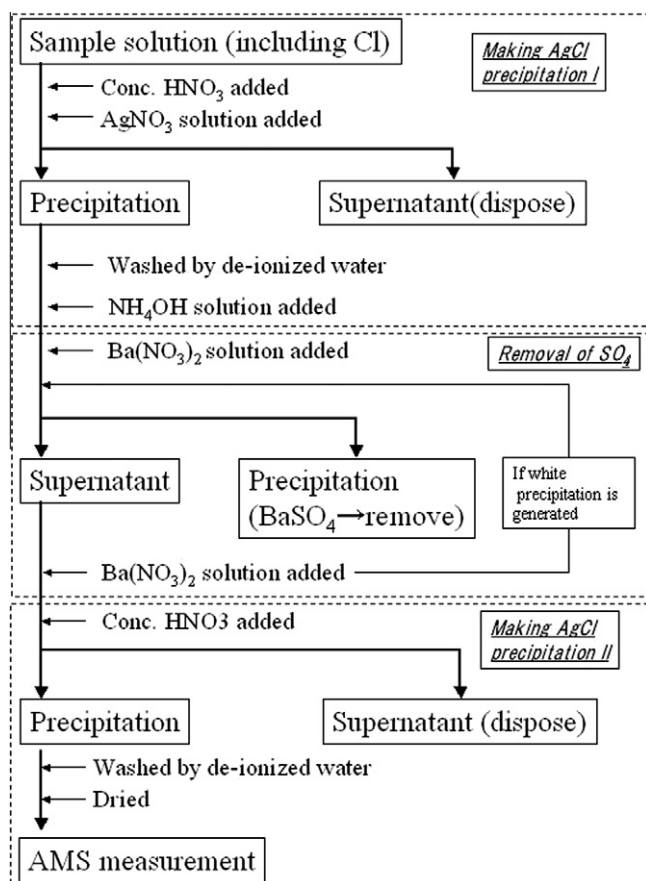


Fig. 1. Scheme of preparation procedure for AgCl precipitation by BaSO₄ method.

low S concentration, the BaSO₄ precipitation has to be repeated, particularly for samples with low ³⁶Cl/Cl (10⁻¹⁴). The number of iterations determined by subjective judgment of the operator from change in the solution as Ba(NO₃)₂ solution is added. Furthermore, it takes approximately 1 week or more to complete the entire process because of the time required for BaSO₄ precipitate to grow enough for easy removal from the liquid phase. The recovery of chlorine with the BaSO₄ method is typically lower than 70–80% [14,15]. Incomplete recovery may cause isotopic fractionation and alter the ³⁶Cl/Cl value for the sample. For dilute samples, concentration of Cl⁻ has to be performed in advance using heating [14] or resin [13]. The disadvantages of the BaSO₄ method can be summarized as follows: it may be difficult to separate Cl⁻ and SO₄²⁻ ions precisely and stably, the separation procedure is time consuming, the recovery is not high, and a separate system for concentration of Cl⁻ is required for groundwater samples with low Cl⁻ concentrations.

In this study, we tried a ion-exchange column chromatography (column method) to separate Cl⁻ and SO₄²⁻ ions in water samples for later ³⁶Cl/Cl measurement by AMS. With this method we aimed to eliminate the disadvantages of the BaSO₄ method. Our method provided complete and simple separation of Cl⁻ and SO₄²⁻.

2. Materials and methods

2.1. Materials

2.1.1. Resin

Dowex 1X8 (200–400 mesh size) is a commonly used anion-exchange resin with homogenous particle size, which is a key factor in obtaining good chromatograms. It was adopted as the stationary

Table 1
Anion composition of simulated groundwater (SG) samples.

Groundwater sample	Concentration of anion (mg/L)			
	F ⁻	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
SG-1	5.39	0.81	4.42	80.67
SG-2	5.27	0.82	4.48	N.D.
SG-3	N.D.	0.82	4.47	80.67

N.D.: not detected.

phase in the column method for these reasons. The purchased Dowex 1X8 was washed with de-ionized water and then all Cl on the resin was replaced with NO₃. This step was performed to avoid contamination of sample by Cl on resin and a change in the majority type of resin in the column as the eluent (Section 2.1.2) passed through the column. In some cases, a change in the majority type of resin may cause a large change in resin volume and breaking of the column. The resin was conditioned with NO₃ using the following procedure. Wet resin (50 mL) was placed in a column with 25-mm I.D. The following solutions were run sequentially through the column: 1000 mL of 1.25 × 10⁵ mg/L HNO₃, 500 mL of 1.0 mol/L NaNO₃, and 1000 mL of 1.25 × 10⁵ mg/L HNO₃. The resin was then removed from column and suspended in 1.25 × 10⁵ mg/L HNO₃ for 3 d. The supernatant was removed and replaced with fresh 1.25 × 10⁵ mg/L HNO₃ solution every day. This procedure ensured that all Cl on the resin was completely replaced by NO₃, and no Cl⁻ was detected in the final supernatant. The washed resin was suspended in 1.25 × 10⁵ mg/L HNO₃ solution until use.

2.1.2. Eluent

The following characteristics are beneficial for an eluent in the column method: has little influence on AgCl precipitation (after the column separation) as the target of AMS measurement, promotes column separation of Cl⁻ and SO₄²⁻, and causes little change in the volume of the resin. Solutions containing I⁻, Br⁻ and NO₃⁻ should promote Cl and S separation because the affinity of ions to ion-exchange resin is as follows: SO₄²⁻ > I⁻ > NO₃⁻ > Br⁻ > Cl⁻ > OH⁻. Among these ions, NO₃⁻ would have the smallest influence on AgCl formation because AgNO₃ is reasonably soluble in water. In contrast, the low solubilities of AgI and AgBr mean these compounds would co-precipitate in large amounts with AgCl if I⁻ or Br⁻ solutions were used as eluent. Consequently, we selected HNO₃ as the eluent in this study. The column was pre-conditioned with NO₃⁻ (Section 2.1.1) to avoid changes in the resin volume with this eluent.

2.1.3. Solutions

A first series of experiments were conducted with a model solution (model solution-1) that contained 100 mg/L Cl⁻ and SO₄²⁻. Model solution-1 was prepared by dissolving NaCl and Na₂SO₄ into de-ionized water. A further model solution (model solution-2) containing 1 mg/L Cl⁻ and SO₄²⁻ was prepared from NaCl and Na₂SO₄. Model solution-2 was used to investigate the application of the column method to dilute solutions.

For a second series of experiments, NaF, NaHCO₃, NaCl and Na₂SO₄ were dissolved into de-ionized water to prepare a simulated groundwater sample that had contact with granite rock and low Cl concentration. Three types of simulated groundwater were prepared to investigate the effect of coexisting anions (Table 1).

Extracted and modified pore water and diluted seawater were used in a third series of experiments. The ionic compositions of these waters are summarized in Table 2. A drilled core was suspended in de-ionized water for 4 days to extract the components of the pore water. The supernatant from the soaked core was retained. After filtration (filter pore size 0.2 mm), the filtrate was

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