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Analytical Method for Measuring Cosmogenic ^{35}S in Natural WatersStephanie H. Urióstegui,^{*,†} Richard K. Bibby,[‡] Bradley K. Esser,[‡] and Jordan F. Clark[†][†]Department of Earth Science, University of California, Santa Barbara, Santa Barbara, California 93106, United States[‡]Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, California 94551, United States

ABSTRACT: Cosmogenic sulfur-35 in water as dissolved sulfate ($^{35}\text{SO}_4$) has successfully been used as an intrinsic hydrologic tracer in low- SO_4 , high-elevation basins. Its application in environmental waters containing high SO_4 concentrations has been limited because only small amounts of SO_4 can be analyzed using current liquid scintillation counting (LSC) techniques. We present a new analytical method for analyzing large amounts of BaSO_4 for ^{35}S . We quantify efficiency gains when suspending BaSO_4 precipitate in Inta-Gel Plus cocktail, purify BaSO_4 precipitate to remove dissolved organic matter, mitigate interference of radium-226 and its daughter products by selection of high purity barium chloride, and optimize LSC counting parameters for ^{35}S determination in larger masses of BaSO_4 . Using this improved procedure, we achieved counting efficiencies that are comparable to published LSC techniques despite a 10-fold increase in the SO_4 sample load. $^{35}\text{SO}_4$ was successfully measured in high SO_4 surface waters and groundwaters containing low ratios of ^{35}S activity to SO_4 mass demonstrating that this new analytical method expands the analytical range of $^{35}\text{SO}_4$ and broadens the utility of $^{35}\text{SO}_4$ as an intrinsic tracer in hydrologic settings.

Hydrologic studies have demonstrated that naturally occurring sulfur-35 (^{35}S) in water as dissolved sulfate ($^{35}\text{SO}_4$) is a useful intrinsic tracer for both water and SO_4 .^{1–9} Cosmic ray spallation of atmospheric argon continually produces ^{35}S in the upper atmosphere,¹⁰ and $^{35}\text{SO}_4$ activities in precipitation range from 0 to 63 mBq/L.^{1–7,9} The 87.4 day half-life of ^{35}S makes it useful for investigating residence times of SO_4 and shallow groundwater on time scales of up to 1.5 years. To date, hydrologic studies using $^{35}\text{SO}_4$ as an intrinsic tracer have focused on low- SO_4 waters from alpine and subalpine basins.^{1–4,7–9,11} Hydrologic tracer applications using established techniques have been limited due to high minimal detectable activity (MDA) values and low SO_4 loading capabilities. In this study, we present a new analytical procedure to measure $^{35}\text{SO}_4$ activities in environmental waters containing a wide range of SO_4 concentrations.

Previous methods to measure $^{35}\text{SO}_4$ activities in environmental waters include preconcentration of approximately 100 mg of SO_4 followed by low-level liquid scintillation counting (LSC). On the basis of the 100 mg limit for SO_4 , low- SO_4 waters have typically been concentrated by passing 20 L of water through a column packed with an ion-exchange resin (Amberlite-400) using gravity filtration or a peristaltic pump.^{2,4,6–8,11} After eluting SO_4 off the resin, samples have been prepared for LSC by precipitating SO_4 as BaSO_4 collected onto glass fiber filters¹² or converting SO_4 to Na_2SO_4 crystals that are dissolved and the solution counted in a scintillation cocktail.¹³ While these methods have been successful for low- SO_4 waters (<5 mg/L), high- SO_4 waters (5–150 mg/L) contain low ^{35}S relative to the mass of SO_4 which necessitates analyzing a larger mass of BaSO_4 to achieve sensitive and

accurate measurements of $^{35}\text{SO}_4$. The LSC technique using glass fiber filters is inherently limited because of the difficulty in mounting SO_4 masses >100 mg onto the filters. A secondary technique of counting dissolved Na_2SO_4 is problematic because the charge and large size of the SO_4 anion impedes formation of a stable microemulsion in liquid scintillation cocktail and can cause phase instability.¹⁴ Concentrations as low as 0.1 M Na_2SO_4 (96 mg of SO_4 in 10 mL of water) are not recommended due to no or very little sample capacity for the common cocktails ULTIMA Gold AB, ULTIMA Gold LLT, and Insta-Gel Plus.¹⁴ To our knowledge, there are no cocktails available that could handle counting dissolved Na_2SO_4 for a sample load ≥ 1000 mg of SO_4 .

In order to expand the analytical range of $^{35}\text{SO}_4$ in high- SO_4 systems, we developed a new analytical method for $^{35}\text{SO}_4$ by improving preconcentration of the SO_4 , selecting high-purity BaCl_2 reagents to mitigate counting interferences, purifying the BaSO_4 precipitate, and optimizing LSC counting parameters.

EXPERIMENTAL SECTION

Preconcentration of Sulfate. Environmental waters contain a wide range of SO_4 concentrations; therefore, a batch method was used to preconcentrate $^{35}\text{SO}_4$ (Figure 1), with the goal of processing between 100 and 2000 mg of SO_4 per sample. The batch method was selected rather than the published column methods because samples collected in the

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Figure 1. Schematic diagram of $^{35}\text{SO}_4$ preconcentration, purification, and mounting for LSC.

field can be brought to the laboratory where multiple samples can be processed at the same time.

A laboratory sample matrix was created by dissolving anhydrous Na_2SO_4 containing no ^{35}S in 20 L of deionized water (DI) to obtain SO_4 concentrations of 5, 50, and 100 mg/L. The samples were transferred to buckets lined with plastic bags. During our method development work, we determined that anion exchange resin (Amberlite, IRA-400) efficiency was independent of pH for natural waters with neutral pH; however, we acidified samples to pH 3–4 with 5 M HCl prior to adding 20 g of resin to ensure that SO_4 is in solution. An industrial spinner was used to suspend the 20 g of resin in the sample for 2 h, binding the SO_4 to the resin. To establish the spin time for SO_4 sorption, sample aliquots were collected every 15 min for 2 h and the percent recovery was determined based on the SO_4 concentrations measured by ion chromatography (IC). After 2 h of resin suspension, laboratory samples with 5, 50, and 100 mg/L of SO_4 had SO_4 recoveries of 90%, 88%, and 70%, respectively (Figure 2). Using five industrial spinners and a 2 h-spin time per sample, our laboratory setup allows for the analysis of at least 10 samples in an average work day.

Figure 2. Percent recovery of SO_4 over 120 min for laboratory solutions containing 100, 1000, and 2000 mg of dissolved SO_4 .

The resin was then transferred to a column, and SO_4 was eluted off the resin with 250 mL of 5% NaCl solution. For 20 g of resin loaded with up to 1000 mg of SO_4 , greater than 96% recovery of SO_4 was achieved with 250 mL of 5% NaCl (aq). The samples were then acidified to pH 3–4 with 5 M HCl, heated, and Ba was added in excess (as dissolved $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) to form a BaSO_4 precipitate. The BaSO_4 precipitate was

allowed to settle overnight, then decanted and transferred to a 50 mL centrifuge tube. The BaSO_4 was triple rinsed with DI water.

Sample Mounting for LSC. Samples containing 100 mg or less of SO_4 were transferred to 20 mL plastic scintillation vials (PerkinElmer) using 5 mL of DI water. Since more than 5 mL of water is needed to transfer larger masses of SO_4 to scintillation vials, samples containing 100–2000 mg of SO_4 were transferred to glass scintillation vials, dried overnight in a 100 °F drying oven, and the dry weight of the BaSO_4 precipitate was recorded.

LSC Analysis. For this study, we analyzed ^{35}S as BaSO_4 in Insta-Gel Plus (PerkinElmer) scintillation cocktail. Insta-Gel forms a stable gel that suspends particulates for counting. The stability of the gel phase is dependent on temperatures being between 5 and 27 °C and the percentage sample load of water to cocktail being $\geq 20\%$.¹⁴ In this method, 5 mL of DI water was added to the dried BaSO_4 precipitate and the vial was shaken to completely suspend the precipitate in the DI water. To create a 28% sample load of water to gel in the vial, two 6.5 mL aliquots of Insta-Gel Plus were added and shaken after each addition to ensure even distribution of the precipitate. Samples were refrigerated for 30 min prior to loading onto a Quantulus 1220 Ultra-Low Level Liquid Scintillation Spectrometer (LSS) equipped with a chiller.

Optimization of Energy Window. The optimal counting region for LSC on a Quantulus 1220 was determined by counting a sample containing 100 mg of SO_4 precipitated as BaSO_4 that was spiked with a NIST-traceable ^{35}S standard. For both glass and plastic scintillation vials, the optimal window setting was determined by the figure of merit (FOM), a ratio of signal-to-noise that is the square of the counting efficiency divided by the background, E^2/B . Backgrounds and counting efficiencies were determined using various window settings and the high-energy beta Default settings on the Quantulus 1220. The theoretical maximum energy of ^{35}S is 167 keV with the average being 53 keV; however, the ^{35}S counting region for the Quantulus 1220 has a maximum energy of 39 keV.

On the basis of the FOM, the ideal counting region is window setting 148–415 (4–31 keV) for both the glass and plastic scintillation vials. Backgrounds in this narrower window setting are 0.83 and 1.33 counts per minute (CPM) for plastic and glass vials, respectively. Counting efficiencies for window 148–415 are $53.0 \pm 0.1\%$ for the plastic vial and $56.5 \pm 0.1\%$ for the glass vial, which are approximately double the detection efficiencies reported by Hong and Kim¹² (Table 1). To ensure the efficiency gain is due to the suspension of BaSO_4 in Insta-Gel Plus rather than differences between a Quantulus LSS and the more frequently used TriCarb LSS, 100 mg of SO_4 spiked with ^{35}S standard was counted on both instruments. For glass vials, the counting efficiencies for window setting 4–167 keV was 58.1% on the Quantulus 1220 and 60.3% on the TriCarb 3100 (Table 1), which suggests that the efficiency gain using this method is primarily due to the suspension of BaSO_4 in Insta-Gel Plus.

Reagent Purity. Expanding the analysis beyond the 100 mg of SO_4 established in previous studies necessitates counting a larger mass of SO_4 for environmental waters which contain high SO_4 concentrations (5–150 mg/L) with low ^{35}S activity. The additional BaCl_2 reagent ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) needed to precipitate SO_4 requires identifying reagent impurities that result in higher background count rates. Chemical separation of the SO_4 from other anions by precipitation in an acidic environment with Ba

Table 1. Summary of Counting Conditions for 100 mg of SO₄ in Plastic and Glass Scintillation Vials Using Various Window Settings

vial type	window setting (keV)	window setting (channel)	bkg (CPM)	efficiency (%) ^a	FOM (E ² /B) ^a
Quantulus 1220					
plastic	4–167	148–658	2.94	53.9 ± 0.1	989 ± 5
plastic	4–39	148–450	0.98	53.9 ± 0.1	2960 ± 14
plastic	4–31	148–415	0.83	53.0 ± 0.1	3379 ± 12
glass	4–167	148–658	4.71	58.1 ± 0.1	716 ± 4
glass	4–39	148–450	1.63	57.9 ± 0.1	2058 ± 10
glass	4–31	148–415	1.33	56.5 ± 0.1	2396 ± 10
TriCarb 3100					
plastic	4–167	148–658	1.65	57.0 ± 0.1	1969 ± 5
glass	4–167	148–658	1.62	60.3 ± 0.2	2245 ± 13
Hong and Kim ^b					
plastic	4–167	148–658	1.87	25.2 ± 1.2	340 ± 24
glass	4–167	148–658	2.18	21.9 ± 1.2	221 ± 17

^aUncertainties are standard deviations. ^bHong and Kim¹² backgrounds were prepared using GF/B filters and Ultima Gold LLT cocktail and counted on a Packard Tri-Carb 3170 TR/SL.

highly purifies the sample prior to counting. One concern is the isotope ¹³³Ba, a radionuclide that emits γ radiation with an energy that overlaps with the ³⁵S counting region. ¹³³Ba is a fission product with a 10.7 year half-life and is not found in nature so its presence should be low in the reagent; to verify this, we experimentally determined the amount of ¹³³Ba in various BaCl₂ lots obtained from different manufacturers. Approximately 20 g of BaCl₂·2H₂O from the five lots were counted by gamma spectroscopy. For each lot, the ¹³³Ba activity per gram of Ba was below the MDA (Table 2) indicating that ¹³³Ba is not present in amounts that would significantly contribute to background count rates in the ³⁵S region of interest.

During our method development work, however, we found ²²⁶Ra in every BaCl₂ lot. ²²⁶Ra is a long-lived radionuclide (1600 year half-life) in the ²³⁸U decay series and is the predominant species of the radium isotope. The daughter products of ²²⁶Ra include short-lived alpha-emitting (²²²Rn, ²¹⁸Po, ²¹⁴Po, ²¹⁰Po) and beta-emitting (²¹⁴Pb, ²¹⁰Pb, ²¹⁴Bi, ²¹⁰Bi) radionuclides, most of which have half-lives on the order of minutes to days. Because of the very similar chemistry between barium and radium, separation of the two elements is difficult and, given the amount of barium needed per sample to form the BaSO₄ precipitation, it was not feasible to perform large scale separation chemistry in our laboratory.

²²⁶Ra activity in the BaCl₂ lots was experimentally determined by dissolving 3.8 g of BaCl₂·2H₂O from each lot in 10 mL of DI water in glass scintillation vials, and 10 mL of High Efficiency Mineral Oil (PerkinElmer) was added to each vial. The samples were sealed and stored for 19 days prior to analysis on the Quantulus 1220 LSS to allow for ²²⁶Ra and its daughter products to reach equilibrium. The ²²⁶Ra activity varied between 21 and 1145 mBq per sample with the lowest activity observed for the high-purity $\geq 99.999\%$ trace metal basis reagent. The ²²⁶Ra activity per gram of Ba ranged from 9.85 to 533.28 mBq/g (Table 2).

Of secondary concern would be the presence of ²²⁸Ra (5.75 year half-life), which could also contribute to higher background count rates. The maximum beta emission for ²²⁸Ra is below the counting region for ³⁵S; however, its daughter product ²²⁸Ac (6.15 h half-life) does emit a gamma ray energy which could affect the ³⁵S counting region. Since ²²⁸Ac also emits a gamma ray at 911.1 keV, gamma spectroscopy was used to determine the amount of ²²⁸Ra in 20 g of BaCl₂·2H₂O from the five BaCl₂ lots. Similar to the results for ¹³³Ba, ²²⁸Ra was below the MDA (Table 2) indicating that very little ²²⁸Ra is present in the BaCl₂ lots.

Background Reduction from Optimization of Instrument Parameters. Unless the Quantulus 1220 is calibrated correctly, ²²⁶Ra and its daughter products lead to higher backgrounds in the ³⁵S counting region. Specifically, alpha emissions of ²²⁶Ra, ²²²Rn, ²¹⁸Po, ²¹⁴Po, ²¹⁰Po can be interpreted as beta events, particularly for reagent lots containing higher amounts of ²²⁶Ra. Additionally, the background contribution would increase over time as the ²²⁶Ra daughter products reach equilibrium. Finally, larger masses of BaSO₄ have higher quench resulting in a shift of alpha emissions into the ³⁵S counting region that can also lead to higher backgrounds.

To mitigate the increased background count rate from the ingrowth of ²²⁶Ra, we optimized two software selectable parameters on the Quantulus 1220 LSS: the Pulse Shape Analyzer (PSA) and the Pulse Amplitude Comparator (PAC). The PSA discriminator setting provides a means to separate pure beta emissions from pure alpha emissions. Unless the PSA setting is on, alpha events will be interpreted as beta events.

We set the optimal PSA setting using a NIST-traceable ²⁴¹Am standard, which is a pure alpha emitter. The solution was prepared with PerkinElmer Ultima Gold LLT cocktail and counted under various PSA setting ranging from 40 to 65. PSA 40 was the optimum setting because it was the lowest PSA that achieved 100% alpha counting efficiency in the alpha counting region (channel 500–900), minimizing spillover of alpha counts into the ³⁵S beta counting region (channel 148–415) and thus reducing the background count rate in the ³⁵S region.

Optimization of the PAC further reduced the background. The PAC rejects optical cross talk between photomultiplier

Table 2. Summary of ²²⁶Ra, ²²⁸Ra, and ¹³³Ba Activity for BaCl₂ Lots Obtained from Different Manufacturers

batch ID	vendor	grade	lot no.	²²⁶ Ra/BaCl ₂ ·2H ₂ O (mBq/g)	²²⁶ Ra/Ba (mBq/g)	²²⁸ Ra/Ba (mBq/g)	¹³³ Ba/Ba (mBq/g)
Batch 1	BDH	ACS	129517	80.40	143.01	<15.11	<3.67
Batch 2	BDH	ACS	3174C512	27.44	48.81	<15.93	<4.38
Batch 3	BDH	ACS	3174C512	26.38	46.93	<16.57	<5.32
Batch 4	Aldrich	$\geq 99.999\%$ trace metal basis	MKBK5701 V	5.54	9.85	<11.84	<3.26
Batch 5	Aldrich	NA ^a	05519PF	299.81	533.28	<17.23	<8.29

^aNA = Not available.

tubes (PMTs) by comparing the amplitude of the pulses from each PMT and determining the amount of pulse amplitude variation that may be tolerated. Because higher PAC settings lower both background count rates and counting efficiency, the optimum PAC setting was determined by the FOM so as to lower the background without significantly reducing counting efficiency. We counted 1000 mg of SO_4 as BaSO_4 suspended in Insta-Gel Plus under the following PAC settings: 1 (Default), 50, 100, 150, 175, 200, and 225. The largest FOM occurred at PAC 150 followed by PAC 100 (Table 3), indicating that a

Table 3. Background Count Rates and Counting Efficiencies for 1000 mg of SO_4 under Various Pulse Amplitude Comparator Settings

PAC setting	bkg (CPM)	efficiency (%)	FOM
1	1.50	66	1901
50	1.47	67	2481
100	1.42	63	2781
150	1.28	61	2907
175	1.29	59	2709
200	1.33	54	2432
225	1.21	49	2389

PAC setting between 100 and 150 is the optimal setting for measuring low-level beta emission from ^{35}S . For sample analyses in this study, we used a PAC setting of 120.

After both the PAC and PSA settings were optimized, background count rates were quantified by precipitating 1500 mg of SO_4 with each of the five BaCl_2 lots. Samples were counted after 7 days under PAC 1 and PSA OFF (Default); PAC 1 and PAC 40; and PAC 120 and PAC 40 settings. As expected, the highest background was observed for samples precipitated with the Batch 5 reagent which contained the highest amount of ^{226}Ra activity (Table 4). Using the optimized PAC 120 and PSA 40 settings reduced the background count rate by at least 30% for all five BaCl_2 lots.

Table 4. Background Count Rates for 1500 mg of SO_4 Precipitated with Different BaCl_2 Lots under Various PAC and PSA Settings

batch ID	bkg (CPM)		
	Default	PAC 1, PSA 40	PAC 120, PSA 40
Batch 1	7.54	5.80	3.69
Batch 2	3.12	2.63	1.85
Batch 3	3.25	2.53	1.75
Batch 4	1.72	1.38	0.98
Batch 5	32.30	26.05	18.22

Optimization of PSA and PAC settings and use of higher-purity BaCl_2 reagent significantly reduces but does not eliminate background count rates in the ^{35}S region of interest. Background count rates are positively correlated with the amount of precipitated BaSO_4 ; however, the optimal PAC 120 and PSA 40 settings lowers the slope of background relative to Default settings (Figure 3).

Ingrowth of ^{226}Ra daughter products results in a time dependent background, particularly under the Default settings where alpha emissions are interpreted as ^{35}S beta events. Once Insta-Gel Plus is added and the sample vials are sealed, ^{226}Ra decays to the short-lived radionuclide ^{222}Rn (half-life 3.8 days), which is a gas that becomes trapped in the cocktail and

Figure 3. Background count rate for varying masses of SO_4 precipitated with Batch 2 BaCl_2 reagent containing 48.81 mBq of ^{226}Ra per gram of Ba under the following settings: PAC 1 and PSA OFF (Default); PAC 1 and PSA 40; PAC 120 and PSA 40. Count rate generally increases with increasing mass of SO_4 for all settings; however, PAC 120 and PSA 40 setting resulted in lower background count rates, particularly for SO_4 masses ≥ 1000 mg.

potentially in the vial headspace. Over the course of several weeks, ingrowth of ^{222}Rn and its daughters occurs until ^{226}Ra reaches secular equilibrium with its daughters. For illustration, 1500 mg of SO_4 was precipitated with the low purity Batch 5 BaCl_2 reagent (533.28 mBq of ^{226}Ra per gram of Ba) and counted repeatedly over an 8-day period. The background count rate at approximately 1 week (170 h) after vials were sealed was 37.38 cpm under the Default settings, which was reduced to 25.10 cpm under the optimized PAC 120 and PSA settings (see Figure 4). The lower rate of increase under the optimized setting indicates that potential ingrowth of ^{226}Ra daughter products into the ^{35}S counting region was mitigated.

Figure 4. Background count rates for 1500 mg of SO_4 precipitated with Batch 5 BaCl_2 reagent containing 533.28 mBq of ^{226}Ra per gram of Ba. After the vial was sealed, the sample was counted under various PAC and PSA settings over approximately 170 h.

On the basis of the time-dependent ingrowth of ^{226}Ra daughter products, our preference was to count the samples as quickly as possible to minimize the background count rate in our ^{35}S region of interest. Waiting 20 days to count the sample allows for full ingrowth of ^{226}Ra daughters; however, the background count rate will necessarily be higher due to ^{226}Ra spilling into the ^{35}S counting region. Additionally, there will be significant decay of ^{35}S over the 20-day period ($\sim 14\%$) due to its 87.4 day half-life. This limits the effectiveness of the decay

analysis and, it should be noted, ^{226}Ra ingrowth would affect any procedure that counts BaSO_4 directly.

Counting Configurations for Sample Analysis. Given that ^{226}Ra impurities exist in all BaCl_2 lots, which affect the background count rates in the ^{35}S counting region, care should be taken with respect to the activity of ^{226}Ra , mass of SO_4 counted as BaSO_4 , and time that elapses between when sample vials are sealed and counted. For this study, we limited the BaCl_2 reagent used to those lots containing ^{226}Ra concentrations of <50 mBq per mg of BaSO_4 . Samples were counted within 36 h of being sealed to minimize the increased background count rate due to ingrowth of ^{226}Ra in the ^{35}S region of interest and to minimize the decay of ^{35}S . Using high purity BaCl_2 reagent and counting samples within 36 h of being sealed, the optimized PAC and PSA instrument parameters reduced the background from 1.65 to 1.04 cpm for 1000 mg of SO_4 (Figure 5).

Figure 5. $^{35}\text{SO}_4$ energy spectra and background count rate for 1000 mg of ^{35}S -free SO_4 precipitated as BaSO_4 . The SO_4 was precipitated using Batch 2 BaCl_2 reagent containing 48.81 mBq of ^{226}Ra per gram of Ba. Relative to the Default settings background count rate of 1.65 cpm, the optimized PAC 120 and PSA 40 settings reduced the background to 1.04 cpm.

For environmental samples, we created a BaSO_4 mass-dependent background subtraction based on the generally observed linear relationship between increasing SO_4 mass and increasing background count rate (Figure 3) and used this subtraction to calculate net count rate and sample activity. Using ^{35}S -dead BaSO_4 in the same matrix as the sample itself (e.g., same BaSO_4 mass, same cocktail, same vial type, and same count time) for the mass-dependent background subtraction accounts for any potential counting interferences due to radionuclides such as ^{133}Ba or Ra isotopes from the BaCl_2 reagent or ^{40}K that may be present in the glass vial.

Using optimized instrument settings, the effect of BaSO_4 mass on counting efficiency was determined. A series of ^{35}S standards were prepared in glass scintillation vials by spiking varying masses of SO_4 with a NIST-traceable ^{35}S standard prior to precipitation with Ba. An attenuation curve of the counting efficiency versus the mass of SO_4 demonstrates that counting efficiency decreases linearly as SO_4 mass increases (Figure 6). For 1000 mg of SO_4 , the $19.0 \pm 0.1\%$ counting efficiency is similar to the $21.4 \pm 1.2\%$ efficiency for 100 mg of SO_4 reported by Hong and Kim¹² despite an order of magnitude increase in the mass of SO_4 .

With the correct ratio of water to Insta-Gel Plus cocktail and maintaining the samples at the recommended Insta-Gel

Figure 6. Counting efficiency for various masses of SO_4 precipitated as BaSO_4 . Efficiency decreased as the SO_4 mass increased.

temperature range ($5\text{--}27^\circ\text{C}$),¹⁴ counting efficiency is expected to remain stable due to minimal gravimetric settling of BaSO_4 in the vial. Gravimetric settling of BaSO_4 would lead to a decrease in counting efficiency over time. To examine how efficiency changed over time, 1000 mg of SO_4 was spiked with ^{35}S standard, suspended in Insta-Gel Plus, and counted at day 1 and again 12 days later. The counting efficiency at day 1 was $19.0 \pm 0.1\%$ and at day 12 was $19.5 \pm 0.1\%$, indicating that gravimetric settling of BaSO_4 is minimal due to a uniform and stable mixture of sample and Insta-Gel Plus.

RESULTS AND DISCUSSION

We evaluated this method on environmental waters by collecting and processing surface waters and groundwater from Orange County, California. These waters ranged in SO_4 concentration from 0.8 to 215 mg/L. Samples were collected by filtering up to 20 L of water through a $0.45\ \mu\text{m}$ high-capacity filter into polypropylene containers. All samples were processed and analyzed following the method outlined in this study.

Sample Purification. In analysis of natural waters, dissolved organic materials resulted in impurities that lead to color quenching and higher background count rates. Two techniques were tested to remove organics and mitigate sample quenching: an activated carbon treatment before BaSO_4 precipitation and a wet ashing treatment after BaSO_4 precipitation. For the activated carbon treatment, after eluting the resin with NaCl, samples were passed through a column containing 4.0 g of 20–40 mesh activated carbon. The samples were then acidified to pH 3–4 with 5 M HCl, heated, and precipitated as BaSO_4 . For the wet ashing treatment, the BaSO_4 is transferred to a centrifuge tube with 25 mL of DI water, heated in a hot water bath, and treated with concentrated HCl and H_2O_2 .

To evaluate the effectiveness of activated carbon and wet ashing at mitigating color quenching, surface waters were collected from Del Valle Reservoir in Alameda County, CA. The surface waters contained 6.1 mg/L of dissolved organic carbon. Samples (5 L) of Del Valle water were filtered through a $0.45\ \mu\text{m}$ high-capacity filter, acidified to pH 3–4 with 5 M HCl, then gravity fed through 20 g of anion exchange resin. After elution of the sample with 250 mL of 5% NaCl (aq), samples were either passed through a column containing 2.0 g of activated carbon, wet ashed following BaSO_4 precipitation, or treated with both activated carbon and wet ashed. Table 5 summarizes the experimental conditions for the Del Valle waters.

The Quantulus 1220 used in this study has a standard quench parameter (SQP) that quantifies quenching of a sample by subtracting the spectrum of the sample alone from that of an

Table 5. Summary of Standard Quench Parameters (SQP) for Del Valle Water Treated with Activated Carbon and/or Wet Ashing

treatment	SQP
background ^a	726.98
no treatment	701.27
activated carbon treatment	717.39
wet ashing	717.40
activated carbon and wet ashing	722.81

^aBackground contained 120 mg of ³⁵S-dead SO₄, which is a similar to the mass recovered for Del Valle samples.

external standard with the sample in the counting chamber. The SQP value is analogous to the transform Spectral Index of the External Standard (tSIE) parameter on the Tri-Carb LSS. SQP values decrease depending on the amount of quenching; higher quenching correlates with lower SQP values. Compared to laboratory background, progressive cleaning of the Del Valle sample resulted in a SQP closer to the background reference value of 726.98 (Table 5). On the basis of this finding, all environmental samples are treated uniformly with activated carbon in the new method. If any color is present after the activated carbon treatment, wet ashing is performed.

Sample Analysis and Measurement Precision. Activities and one sigma counting errors for Orange County surface waters and groundwater are provided in Table 6. In the case of field duplicates, samples were not homogenized prior to sample processing. The results were yield-corrected by determining the total amount of SO₄ in the samples (concentration determined by IC multiplied by the volume of water analyzed) relative to

the gravimetric recovery of SO₄ as BaSO₄ prior to the addition of Insta-Gel Plus. Samples were decay-corrected to the collection date. Total recovery of SO₄ typically ranged between 30 and 98%, with samples containing SO₄ concentrations of >100 mg/L resulting in SO₄ recovery of <40%. Reproducibility of the measurements was evaluated through comparison of field duplicates using the relative error ratio (RER):

$$\text{RER} = \left| \frac{S - D}{\sqrt{\sigma_S^2 + \sigma_D^2}} \right| \quad (1)$$

where *S* is the sample ³⁵SO₄ activity (mBq/L); *D* is the field duplicate ³⁵SO₄ activity (mBq/L); and σ_S^2 and σ_D^2 are one sigma counting errors for the sample and field duplicate (mBq/L), respectively.

Field replicates with RER ratios at or below 3.0 are considered reproducible. All but two of the 19 total RER ratios were below 3.0, with the two outliers having RER ratios of 3.5 and 5.4. For duplicates with RER ratios below 3.0, the mean RER value was 1.33, indicating that good precision was achieved for the majority of the environmental samples.

CONCLUSIONS

We have developed a robust analytical technique for measuring ³⁵SO₄ in environmental waters that contain a wide range of SO₄ concentrations. Compared to previous published methods,^{12,13} the advances include (1) significant improvements to loading large masses of BaSO₄ precipitate in Insta-Gel Plus cocktail for counting while maintaining high counting efficiency comparable to published techniques despite a 10-fold increase in the SO₄ sample load; (2) purification of BaSO₄ by the removal of

Table 6. ³⁵SO₄ Activities and One Sigma Counting Errors for Orange County Groundwater and Surface Water Samples

site ID	collection date	SO ₄ (mg/L)	³⁵ SO ₄ ± 1σ (mBq/L)	field duplicate ³⁵ SO ₄ ± 1σ (mBq/L)	RER
Surface water					
SAR	February 5, 2013	137	8.3 ± 1.9	19.0 ± 2.4	3.5
SAR	April 2, 2013	133	16.2 ± 1.7	NA ^a	
WB	February 4, 2013	110	14.9 ± 1.7	20.6 ± 2.0	2.2
WB	April 1, 2013	125	22.0 ± 1.8	NA ^a	
LJ	February 4, 2013	117	13.6 ± 1.7	16.0 ± 2.0	0.9
LJ	April 1, 2013	215	16.0 ± 2.3	15.0 ± 2.3	0.3
AL	February 5, 2013	119	8.6 ± 1.6	18.5 ± 2.1	2.7
MB	April 2, 2013	0.8	1.5 ± 0.2	1.2 ± 0.2	0.9
KB	February 5, 2013	109	17.1 ± 1.7	19.4 ± 1.9	0.9
KB	April 1, 2013	188	28.4 ± 2.5	11.1 ± 2.0	5.4
Groundwater					
KBS 3.1	February 5, 2013	112	15.9 ± 1.8	11.3 ± 1.8	1.8
KBS 3.1	April 2, 2013	177	5.4 ± 1.8	NA ^a	
AM07	February 5, 2013	17.3	4.5 ± 0.4	3.4 ± 0.5	1.7
AM07	April 16, 2013	46.3	3.1 ± 0.4	2.4 ± 0.5	0.6
AM08	February 5, 2013	15.7	3.0 ± 0.4	2.8 ± 0.3	0.5
AM08	April 16, 2013	20.7	2.4 ± 0.3	2.1 ± 0.3	0.9
AM48	February 5, 2013	25.2	3.9 ± 0.5	4.2 ± 0.6	0.2
AM48	April 4, 2013	44.3	2.7 ± 0.4	4.3 ± 0.6	2.3
AMD12.1	February 5, 2013	17.9	2.9 ± 0.3	3.8 ± 0.5	1.5
AMD12.1	April 16, 2013	9.1	1.7 ± 0.2	2.6 ± 0.3	2.8
AMD12.2	February 5, 2013	136	4.8 ± 1.6	10.3 ± 1.8	2.3
AMD12.2	April 16, 2013	142	0.8 ± 1.2	NA ^a	
PW1	February 5, 2013	27.8	4.3 ± 0.5	4.4 ± 0.6	0.1

^aNA= Field duplicate was not available.

dissolved organic matter which eliminates color quenching in liquid scintillation counting; (3) identification of ^{226}Ra impurity in BaCl_2 reagents which affect ^{35}S determination; (4) mitigation of the ingrowth from ^{226}Ra daughter products by optimization of instrument parameters; (5) utilizing a batch method to decrease sample analysis time and increase throughput. Implementing our improvements allowed us to successfully analyze high- SO_4 surface waters and groundwater, which has not been previously attempted. Additionally, compared to published techniques, these advancements significantly improve ^{35}S determination in low- SO_4 waters as well.

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Notes

The authors declare no competing financial interest.

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