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Low-sulphate water sample preparation for LSC detection of ^{35}S avoiding sulphate precipitation

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ABSTRACT: Information about groundwater residence times is essential for evaluating appropriate groundwater abstraction rates and aquifer vulnerabilities and hence for sustainable groundwater management in general. Naturally occurring radionuclides are suitable tools for related investigations. While the applicability of several long-lived radionuclides for the investigation of long-term processes has been demonstrated frequently, residence times of less than one year are only scarcely discussed in the literature. That is due to the rather small number of applicable radionuclides that show adequately short half-lives. A promising approach for investigating sub-yearly residence times applies radioactive sulphur. ^{35}S is continuously produced in the upper atmosphere from where it is transferred with the rain to the groundwater. As soon as the water enters the subsurface its ^{35}S activity concentration decreases with an 87.4 day half-life. This makes ^{35}S suitable for investigating sub-yearly groundwater residence times. However, the low ^{35}S activities in natural waters require sulphate pre-concentration for ^{35}S detection by means of liquid scintillation counting (LSC). That is usually done by sulphate extraction from large water samples with an anion-exchange resin (Amberlite IRA400, Cl-form), elution from the resin with NaCl, and precipitation as BaSO_4 . Our study aimed at optimizing the standard sample preparation procedure by avoiding the laborious precipitation step. We suggest (i) sulphate extraction using the exchange resin Amberlite IRA67 (OH-form), (ii) elution with ammonium hydroxide, (iii) evaporation of the eluate and (iv) dissolving the resulting dry precipitate in 2 ml H_2O . In contrast to the standard approach our method results in a final sample solution of low ionic strength, which allows applying the water miscible scintillation cocktail Hionic-Fluor[®]. Since Hionic-Fluor accepts only aqueous solutions of low ionic strength the approach is applicable for waters with high $^{35}\text{S}/^{32}\text{SO}_4^{2-}$ ratios, i.e., low total sulphate sample loads (e.g. rainwater).

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Keywords: ^{35}S ; liquid scintillation counting, method improvement; aqueous tracer; groundwater resources management; groundwater residence time

1 **1 Introduction**

2 The knowledge of groundwater residence times is mandatory for the sustainable management of
3 groundwater resources. The data can be used (i) for recommending groundwater abstraction rates that
4 ensure sustainable aquifer use, (ii) for assessing groundwater travel times and related matter
5 (and contaminant) transport, and (iii) for evaluating aquifer vulnerabilities regarding anthropogenic
6 contamination.

7 A suitable tool for investigating groundwater residence times is the application of environmental tracers, i.e.,
8 of naturally occurring substances that are generally suitable for studying water related physical and/or
9 chemical processes. Powerful in this regard are, besides stable isotopes, environmental radionuclides.
10 Ideally, their half-lives should be in the same time range as the investigated processes. Rather long-lived
11 radionuclides (such as ^3H , ^{14}C , ^{36}Cl , ^{39}Ar , ^{81}Kr , and ^{85}Kr) have proven suitable for studying long-term
12 processes. However, using radionuclides for covering shorter timespans, e.g. for the investigation of
13 groundwater residence times of less than one year, is only rarely discussed in the literature. This is mainly
14 due to the fact that only a rather small number of generally applicable natural radionuclides show adequately
15 short half-lives (such as the frequently applied ^{222}Rn (e.g., Treutler et al., 2007; Schmidt et al., 2010;
16 Petermann et al., 2018) or ^{224}Ra (e.g., Moore and Oliveira; 2008; Rocha et al., 2015)).

17 A promising novel approach for covering the sub-yearly timescale is based on the application of radioactive
18 sulphur (^{35}S). ^{35}S is continuously produced in the stratosphere by cosmic ray spallation of ^{40}Ar . After its
19 production ^{35}S rapidly oxidizes to sulphate, gets dissolved in the meteoric water and is finally transferred with
20 the rain to the groundwater (Tanaka and Turekian, 1991). $^{35}\text{SO}_4^{2-}$ activities in precipitation range generally
21 between ca. 5 and 100 mBq/l (Oh, et al. 2019; Urióstegui et al., 2015; Cho et al., 2011; Hong and Kim, 2005;
22 Osaki et al., 1999; own data). Since there is no natural ^{35}S source in the subsurface the ^{35}S activity
23 concentration in any freshly recharged groundwater starts to decrease by decay with an 87.4 day half-life as
24 soon as the rainwater enters the ground. This makes ^{35}S a potential residence time tracer suitable for
25 investigating groundwater ages between about three to nine months (i.e., between one and three ^{35}S half-
26 lives).

27 The idea of using ^{35}S as residence time tracer was first introduced nearly two decades ago (Michel et al.,
28 2000; Sueker et al., 1999). However, the published case studies were all limited to high geographical
29 elevations where snowmelt is the dominant hydrological recharge event, thus simplifying the annual ^{35}S input
30 function to the peak snowmelt. Since rainfall is likely to show a substantial variation in ^{35}S activity (e.g.,

31 Turekian and Tanaka, 1992; Plummer et al., 2001; own data) the experiences reported from these
32 alpine/subalpine watersheds are of only limited applicability in non-alpine climates.

33 The drivers of the variable ^{35}S activity in rain have not been systematically investigated yet and call for
34 further studies. Still, in any case the varying ^{35}S activities in rainfall require analysing a rather large number
35 of rain samples in order to set up reasonable ^{35}S input functions. That in turn makes a sample preparation
36 procedure desirable that is as straightforward as possible.

37 ^{35}S detection by liquid scintillation counting (LSC) requires pre-concentration of $^{35}\text{SO}_4^{2-}$ from large water
38 samples (generally up to 20 litres; an approach that requires smaller sample volumes (5 litres) that was
39 suggested by Oh et al. (2019) requires large-volume ultra-low-level LSC measurement). A related state-of-
40 the-art approach was suggested by Urióstegui et al. (2015) and improved by Schubert et al. (2019). It entails
41 (i) sulphate extraction from the water with an anion-exchange resin (Amberlite IRA400 / Cl-form), (ii) its
42 elution from the resin with a NaCl solution, and (iii) its precipitation from the eluate as fine-grained BaSO_4 by
43 addition of BaCl_2 . The precipitate is finally (iv) homogeneously suspended in the gel-forming Insta-Gel Plus®
44 scintillation cocktail and measured by LSC (Urióstegui et al., 2015; Schubert et al., 2019). The approach was
45 developed for water samples that contain sulphate with rather low $^{35}\text{S}/^{32}\text{SO}_4^{2-}$ ratios as they are typical for
46 groundwater. Although the approach allows measuring samples that contain sulphate loads of up to 1500 mg
47 it has four major disadvantages: (i) the BaSO_4 precipitation step is rather labour-intensive, (ii) the added
48 BaCl_2 may contain substantial amounts of ^{226}Ra thus increasing the LSC background, (iii) measuring gel
49 suspensions requires very careful sample preparation since very fine-grained precipitates are mandatory in
50 order to prevent inaccurate measurements due to self-absorption, and (iv) LSC measurement of
51 heterogeneous gel suspensions of low energy β -emitters (such as ^{35}S) always yields lower counting
52 efficiencies than counting of mono-phase emulsions. Therefore our study aimed at simplifying and improving
53 the sample preparation procedure by avoiding the BaSO_4 precipitation step and producing a mono-phase
54 emulsion of sample and LSC cocktail instead of a heterogeneous gel suspension. The improved approach is
55 applicable if waters with relatively high $^{35}\text{S}/^{32}\text{SO}_4^{2-}$ ratios (as they are typical for rainwater) are to be
56 measured.

57 A high $^{35}\text{S}/^{32}\text{SO}_4^{2-}$ ratio of the water (i.e., a higher relative ^{35}S activity) reduces the total SO_4^{2-} load of the
58 sample that is necessary for attaining a countable ^{35}S sample activity. Nevertheless, even low SO_4^{2-}
59 concentrations in aqueous samples complicate LSC measurement with most commercial LSC cocktails since
60 divalent anions (such as SO_4^{2-}) generally trigger phase separation in clear cocktail emulsions. Therefore, we
61 decided to use the LSC cocktail Hionic-Fluor® (PerkinElmer), which is reported to be specifically applicable

62 for aqueous samples with elevated ionic strengths. Still, the capacity of Hionic-Fluor[®] to hold elevated total
63 salt loads is also limited. In preliminary experiments we found that the cocktail (18 ml) is suitable for a total
64 sulphate load of the processed aqueous sample (2 ml) of up to 100 mg. Hence the cocktail accepts sulphate
65 loads of up to 20 litres rainwater (with an assumed SO₄²⁻ concentration of 5 mg/l).

66 Still, the ionic strength limitation requires a water sample preparation procedure that avoids the addition of
67 any ions that would increase the given sample intrinsic ion strength. Consequently, our study also aimed to
68 develop a sample preparation approach, in which the high salt concentration that is required for the elution of
69 sulphate from the ion exchange resin is achieved with ions that are volatile, thus allowing their easy removal
70 from the sample before LSC measurement.

71 **2 Material and methods**

72 A Quantulus GCT 6220 liquid scintillation counter was used for all ³⁵S activity measurements. The
73 measurements were done in the “Normal” counting mode with GCT correction either for 60 minutes or until
74 the previously set 2 Sigma threshold of statistical uncertainty (0.5 %) was reached (Tab. 1). The detection
75 background was counted and subtracted from the sample counts by measuring a ³⁵S-dead background vial,
76 which was treated in the same way as all ³⁵SO₄²⁻ containing lab-made “standards” and natural “samples” (for
77 details see sect. 3). With the aim to optimize the signal-to-noise-ratio of the measurement results the specific
78 LSC detection options were set as given in Tab. 1.

79 Tab. 1: Quantulus GCT 6220 settings for counting ³⁵S in aqueous solution with Hionic-Fluor[®] scintillation
80 cocktail

Parameter	Setting
Assay Type	DPM (single)
Quench Indicator	tSIE/AEC
2 Sigma Threshold	0.5 %
Counting Energy Window	3 – 167 keV
Coincidence Time	18 ns
Delay Before Burst	75 ns

81

82 **3 Experimental**

83 The following three sets of experiments, each aiming at an individual objective, were executed:

84 (i) The first set of experiments was carried out for developing and fine-tuning the Hionic-Fluor[®] based
85 sample preparation procedure. The experiments were carried out with five defined aqueous ³⁵SO₄²⁻
86 standard solutions with increasing total sulphate loads.

87 (ii) The second set of experiments was carried out for optimizing (i.e., minimizing) the load of anion-
88 exchange resin. Six experiments with identical $^{35}\text{SO}_4^{2-}$ spiked natural rain samples and increasing resin
89 loads were carried out.

90 (iii) The third set of experiments was carried out for confirming the practicability of the developed approach.
91 A set of seven natural rain samples taken during different rain events was prepared, measured and the
92 results evaluated.

93

94 3.1 Development of Hionic-Fluor[®] based sample preparation procedure

95 Each of the five $^{35}\text{SO}_4^{2-}$ standard solutions needed for the first set of experiments had a volume of 1 litre
96 (deionized water) and contained 10, 25, 50, 75 and 100 mg ^{35}S -dead sulphate, respectively. The five
97 solutions were filled in glass flasks and spiked with 150 Bq ^{35}S each (from a $\text{Na}_2^{35}\text{SO}_4$ stock solution;
98 Hartmann Analytic, Germany).

99 Experimental Step 1: Resin conditioning

100 As mentioned in sect. 1 measurement of ^{35}S activity concentrations in natural waters requires sulphate pre-
101 concentration. That is generally done by sulphate extraction from large water samples (generally 20 litres)
102 using a suitable anion-exchange resin. Since it was our aim to minimize the ion strength of the final
103 concentrated samples (in order to allow applying Hionic-Fluor as LSC cocktail) we decided against a
104 chloride-form resin (such as the usually applied Amberlite IRA400) and used the weak-base exchange resin
105 Amberlite IRA67 (OH-form) instead.

106 For each of the five experiments described in the following 2 g of the resin (*cf.* sect. 3.7) were put into a
107 50 ml plastic tube to which 25 ml deionized water were added. The tube was shaken and the water decanted
108 in order to remove all fine resin particles (“fines”) that might be present. Subsequently to this washing step
109 the resin was protonated (any OH-form resin needs to be protonated before its use), which was done with
110 pure acetic acid (CH_3COOH). 25 ml acetic acid were added to the resin and the tube was shaken in an
111 overhead shaker for 1 hour. After that the acid was decanted and the protonated resin washed twice with
112 deionized water in order to remove all excess acid.

113 Experimental Step 2: Sulphate extraction from the standard solutions

114 The total sulphate load (incl. the $^{35}\text{SO}_4$ spike) of the five 1 litre standard solutions (10, 25, 50, 75 and
115 100 mg, respectively) was extracted by adding the 2 g of protonated resin to each flask and shaking it in an
116 overhead shaker for 1 hour. Subsequently the solution was decanted and tested for any remaining sulphate
117 by means of ion chromatography (with overall negative results). Remaining droplets of solution were

118 removed from the sulphate-loaded resin by means of a vacuum pump and glass micro-fibre filters
119 (Schleicher & Schuell Grade GF 10). The five resulting sulphate-loaded resin samples were put into 50 ml
120 plastic tubes.

121 Experimental Step 3: Sulphate elution from the resin

122 The sulphate was subsequently eluted off the resin with ammonium hydroxide (25 %) (NH_4OH). 50 ml
123 ammonium hydroxide were added to each of the five plastic tubes and the tubes were shaken in an
124 overhead shaker for 1 hour. After elution the ammonium hydroxide solution was decanted and the resin was
125 washed twice with 40 ml deionized water in order to capture all eluted sulphate. The aqueous washing
126 solution was added to the decanted ammonium hydroxide. Since it is mandatory to desorb the sulphate
127 quantitatively from the resin each resin sample was eluted and washed as described three times. The
128 resulting eluent solution (in total 150 ml NH_4OH and ca. 240 ml H_2O) contained, besides the extracted SO_4^{2-} ,
129 high concentrations of NH_4^+ and CH_3COO^- , thus resulting in an ionic strength that is too high for the Hionic-
130 Fluor cocktail.

131 (Besides: KOH cannot be used for sulphate elution from the resin because (i) of the unavoidable ^{40}K content
132 in the eluate and because (ii) of the fact that potassium would add unwanted ionic strength to the eluate,
133 which cannot be removed by evaporation.)

134 Experimental step 4: Eluate evaporation

135 The high ionic strength of the eluate could be substantially reduced because both NH_3 and CH_3COOH can
136 easily be evaporated from the eluate. In order to do this as gently as possible the five eluates were heated in
137 glass beakers to about 100 °C on a hotplate under a fume-hood until about 75% of the solutions were
138 evaporated. The remaining solutions did not contain any notable (smell) amounts of ammonium hydroxide
139 anymore (the boiling point of a 25% NH_4OH solution is 37.7 °C) and could thus be evaporated to dryness in
140 a laboratory sand-bath at about 70°C outside the fume-hood. In order to minimize any sulphate losses during
141 this processing step the last ca. 10 ml of each of the five concentrated eluates were transferred into 20 ml
142 LSC vials (glass) and evaporated to dryness directly in there. This resulted in dry water soluble ammonium
143 sulphate precipitate ($[\text{NH}_4]_2\text{SO}_4$) sitting in the five LSC vials that were later on used for the LSC
144 measurements.

145 Experimental Step 5: Cocktail production

146 Subsequently 2 ml deionized H_2O were added to each of the LSC vials containing the precipitate and the
147 precipitates were dissolved resulting in five aqueous pH neutral solutions of an ionic strength that is suitable
148 for the Hionic-Fluor cocktail. 10 ml of Hionic-Fluor were added to each of the solutions. Subsequently the

149 vials were shortly shaken by hand until the mixture turned from milky to translucent. A milky cocktail mixture
150 indicates that the ionic strength is too high for the cocktail. In this case up to eight more millilitres of Hionic-
151 Fluor can be added to the applied 20 ml vial.

152

153 3.2 Optimization of the resin load

154 As mentioned above 2 g of resin were used in each of the sample preparation procedure experiments for
155 sulphate extraction (sect. 3.1; Experimental Step 2). Choosing this resin load resulted from a set of seven
156 experiments that aimed at optimizing the resin load. For execution of the experiments seven litres of natural
157 rainwater were enriched with ^{35}S -dead sulphate to reach a sulphate concentration of 100 mg/l (i.e., the
158 maximum sulphate load used for the experiments described in sect 3.1). The seven litres were filled in seven
159 1 litre flasks. Each of the solutions was spiked with 165 Bq ^{35}S . The seven solutions were treated and
160 checked for ^{35}S recovery as described in sect 3.1 with the only difference that not the described standard
161 load of resin (i.e., 2 g) was added (Experimental Step 2) but 0.1, 0.25, 0.5, 1, 2, 3, and 4 g, respectively.
162 Sulphate recovery measurements were done both by LSC (100% sulphate recovery = 165 Bq ^{35}S in vial after
163 Experimental Step 5) and by ion chromatography (100% sulphate recovery = SO_4^{2-} -free solution after
164 Experimental Step 2).

165

166 3.3 Preparation of natural rain samples

167 The developed sample preparation approach was finally tested with a set of seven natural rain samples. The
168 samples were taken during consecutive rain events (Aug. 11th, 16th, 19th, 21st, 30th and Sept. 9th, 16th 2019)
169 by rain collection from a 30 m² laminated metal roof, which was kept clean before and during the period of
170 sampling. Immediately after each rain event the water was collected from a closed plastic barrel attached to
171 a rainwater downpipe. From each rain event 20 litres of water were sampled in a suitable jerry can. In the
172 laboratory the rain samples were filtered through glass micro-fibre filters (Schleicher & Schuell Grade GF 10)
173 in order to get rid of suspended fine particles. Then the samples were transferred into open canisters, 2 g of
174 conditioned resin was added (*cf.* sect. 3.2) and the water was stirred with a magnetic stirrer overnight.
175 Subsequently the water was decanted and the resin samples treated as described sect. 3.1 (Experimental
176 Steps 2 - 5).

177 During the experiments with the natural rainwater samples it was found that problems might occur if the
178 sample is not clean. Particulate matter can be washed out of the atmosphere by the falling rain or it can be
179 washed off (e.g.) a roof that is used for rain collection. Particulate organic matter may develop with time due

180 to algae growth in any unprocessed sample. During sulphate extraction (Experimental Step 2) the resin
181 scavenges not only the sulphate from the water sample but also particulate matter and turns (more or less)
182 yellow or brown during the extraction step. Thus, the resulting eluate (Experimental Step 3) is of brownish
183 colour, too. Consequently the final sample/cocktail mix might show strong colour quench. As a consequence
184 of the experiments with natural samples one more step was added to the sample processing protocol: “wet
185 ashing” of the particles in the (about 25) last millilitres of eluate at the end of the evaporation step
186 (Experimental Step 4) by adding about the same volume of hydrogen peroxide (30%). The wet ashing
187 resulted in a clear colourless eluate and subsequently a pure white $(\text{NH}_4)_2\text{SO}_4$ precipitate.

188

189 **4 Results and discussion**

190 4.1 Optimization of the resin load

191 Aim of the experiments described in sect. 3.2 was to find the optimum load of Amberlite IRA67 (OH-form) for
192 extracting 100 mg sulphate from an aqueous solution (rainwater). As mentioned above, the sulphate
193 recovery was detected in two ways, by LSC (^{35}S) and by ion chromatography (sulphate). The results of the
194 LSC measurements are displayed in Tab. 2.

195

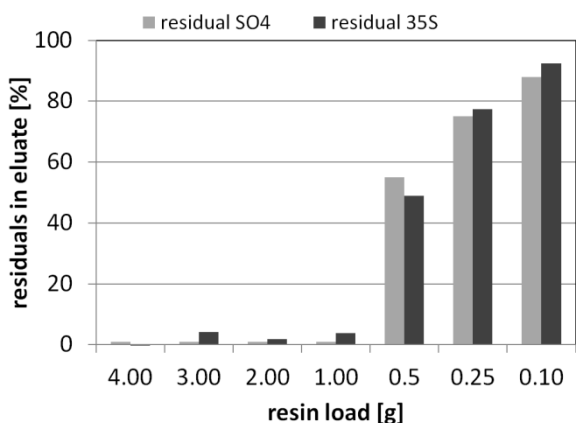
196 Tab. 2: Sulphate (^{35}S) recovery quantification by LSC with the aim to optimize the resin load (Amberlite
197 IRA67) for extracting 100 mg sulphate (spiked with 165 Bq ^{35}S) from 1 litre aqueous solution (rainwater)

Resin Load [g]	Recovery ^{35}S [Bq]	Recovery ^{35}S [%]
4.00	165	100.0 ± 0.5
3.00	158	95.6 ± 0.5
2.00	162	98.0 ± 0.5
1.00	159	95.9 ± 0.5
0.50	84	51.0 ± 0.3
0.25	37	22.5 ± 0.2
0.01	12	07.5 ± 0.1

198

199 Fig. 1 compares the ^{35}S activities that remained in the solutions (calculated from the detected ^{35}S recoveries
200 shown in Tab. 2) with the sulphate concentrations that remained in the solution after extraction as analysed
201 by ion chromatography.

202



203

204 Fig. 1: ^{35}S activities and SO_4^{2-} concentrations that remained in the solutions after extraction applying different
 205 loads of Amberlite IRA67 resin

206

207 The well matching results displayed in Fig. 1 indicate that 1 g is the minimum resin load (Amberlite IRA67)
 208 for extracting 100 mg sulphate from an aqueous solution. Lower resin loads resulted in an incomplete
 209 sulphate recovery. Higher loads on the other hand are generally not recommendable because of the
 210 increasing difficulty in sample handling (in particular the decanting in Experimental Steps 1, 2 and 3) and
 211 because of the unnecessarily generated additional costs. However, in order to guarantee complete sulphate
 212 extraction also for slightly higher ionic strengths of the water samples we suggest using 2 g Amberlite as
 213 optimum resin load. That amount was used through all further experiments.

214

215 4.2 Measurement of standard solutions

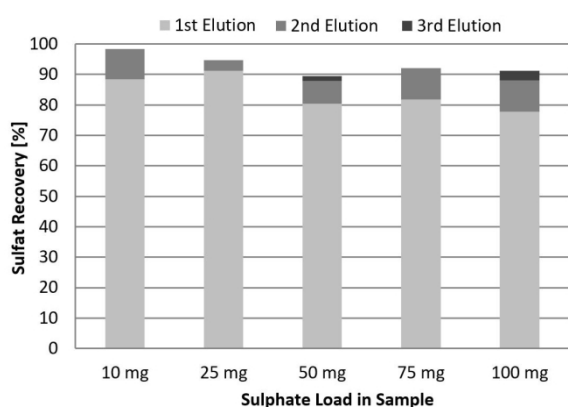
216 The performance of the developed approach was evaluated based on the reproducibility of the defined pre-
 217 set $^{35}\text{SO}_4^{2-}$ activity concentration of five standard solutions (i.e., 150 Bq). Since no remaining sulphate was
 218 detected in any of the solutions after sulphate extraction (Experimental Step 2) the most critical step of the
 219 approach turned out to be the quantitative desorption of the sulphate from the resin (Experimental Step 3).
 220 The detection results in Tab. 3 show that sulphate recovery after only one elution/washing cycle was only
 221 between about 78 and 92 %, which is not satisfying. After a second elution/washing cycle the recovery rates
 222 increased to between 88 and 98 %. For the two standard solutions that still showed recoveries below 90 % a
 223 third elution/washing cycle was executed resulting in overall recoveries for all standards between 91 and
 224 98 %. The recovery rate seems to depend to a certain degree on the total sulphate load of the sample. The
 225 higher the sulphate load the more elution/washing cycles are needed to achieve a satisfying $^{35}\text{SO}_4^{2-}$ recovery
 226 (Tab. 3, Fig. 2).

227

228 Tab. 3: Sulphate recovery (measured as $^{35}\text{SO}_4^{2-}$ by LSC) after elution from the resin in three consecutive
 229 elution/washing cycles

Sulphate Load [mg]	Cycle 1 [%]	Cycle 2 [%]	Cycle 3 [%]	Recovery Σ [%]
10 mg	88.4	10.0	/	98.4
25 mg	91.2	3.5	/	94.7
50 mg	80.4	7.4	1.6	89.4
75 mg	81.8	10.3	/	92.1
100 mg	77.8	10.4	3.0	91.1

230



231

232 Fig. 2: Sulphate recovery (measured as $^{35}\text{SO}_4^{2-}$ by LSC) after elution from the resin in three consecutive
 233 elution/washing cycles

234

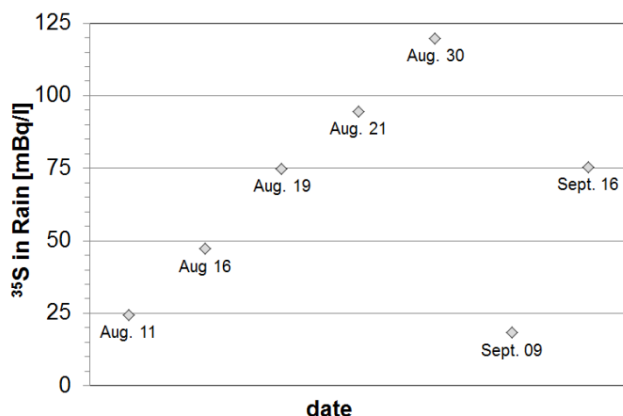
235 Another potential source of error is the loss of very fine sulphate loaded resin particles during the decanting
 236 process in step 2. To avoid this error the resin should be washed thoroughly in the beginning in order to get
 237 rid of the fines (Experimental Step 1). Furthermore the evaporation should be done as gentle as possible (in
 238 particular at the end of the process) in order to avoid losing sulphate due to sputtering of the remaining
 239 solution in the glass beaker.

240 4.2 Measurement of natural rain samples

241 Seven 20 litre rain samples were taken during seven rain events. Aim of the experiments was to prove (or
 242 disprove) that the approach developed under lab conditions (i.e., with pure chemicals) is also applicable for
 243 natural samples.

244 The seven rain samples that were collected, processed and measured as described above showed ^{35}S
 245 activity concentrations between 18 and 120 mBq/l with a mean value of 65 mBq/l. These values show that
 246 the ^{35}S activity concentration of rainwater might vary substantially. Comparable data was published by Visser

247 et al. (2019). The authors reported ^{35}S activities in precipitation recorded over a two years period varying
248 between $3.0\pm 0.4\text{ m Bq/l}$ (in January 2015) and $103\pm 1\text{ mBq/l}$ (in May 2015).



249
250 Fig. 3: ^{35}S activities in seven natural rain samples; the respective error bars (on average 0.6 mBq/l) are
251 smaller than the symbols and hence not visible

252

253 5 Conclusion

254 The introduced approach is recommended as alternative to the established method for ^{35}S detection in
255 natural water samples which necessitates BaSO_4 precipitation. The major advantages of avoiding the
256 sulphate precipitation step are (i) that the sample processing is less labour intensive, (ii) that it prevents
257 potential addition of ^{226}Ra to the sample with the BaCl_2 that is added for the sake of BaSO_4 precipitation
258 (Urióstegui et al. 2015), (iii) that it minimizes self-absorption by the suspended precipitate and (iii) that
259 counting in a mono-phase emulsion is generally more accurate and reproducible and yields higher counting
260 efficiencies. The introduced approach is applicable if high $^{35}\text{S}/^{32}\text{SO}_4^{2-}$ ratios, i.e., low sulphate sample loads
261 can be expected, e.g. in rainwater.

262 Due to the generally low ^{35}S activity concentration in any natural water samples the quantitative sulphate
263 recovery is of highest priority for each of the described steps of the procedure, particularly for Experimental
264 Steps 3 and 5.

265 The detected variability of the ^{35}S activity concentration in rainwater is of major relevance for setting up a ^{35}S
266 input function that would be needed for using ^{35}S as groundwater residence time tracer. The occurrence of
267 cyclical and/or non-cyclical changes of the ^{35}S activity in rain needs to be understood (Oh, et al. 2019; Lin et
268 al. 2016; Cho et al., 2011). Related research that necessitates extended ^{35}S time series and that is focussing
269 on parameters and processes that might influence the ^{35}S activity concentration (season, rain intensity,
270 frequency of isolated showers, erratically occurring stratospheric intrusions into the lower atmosphere) is
271 ongoing.

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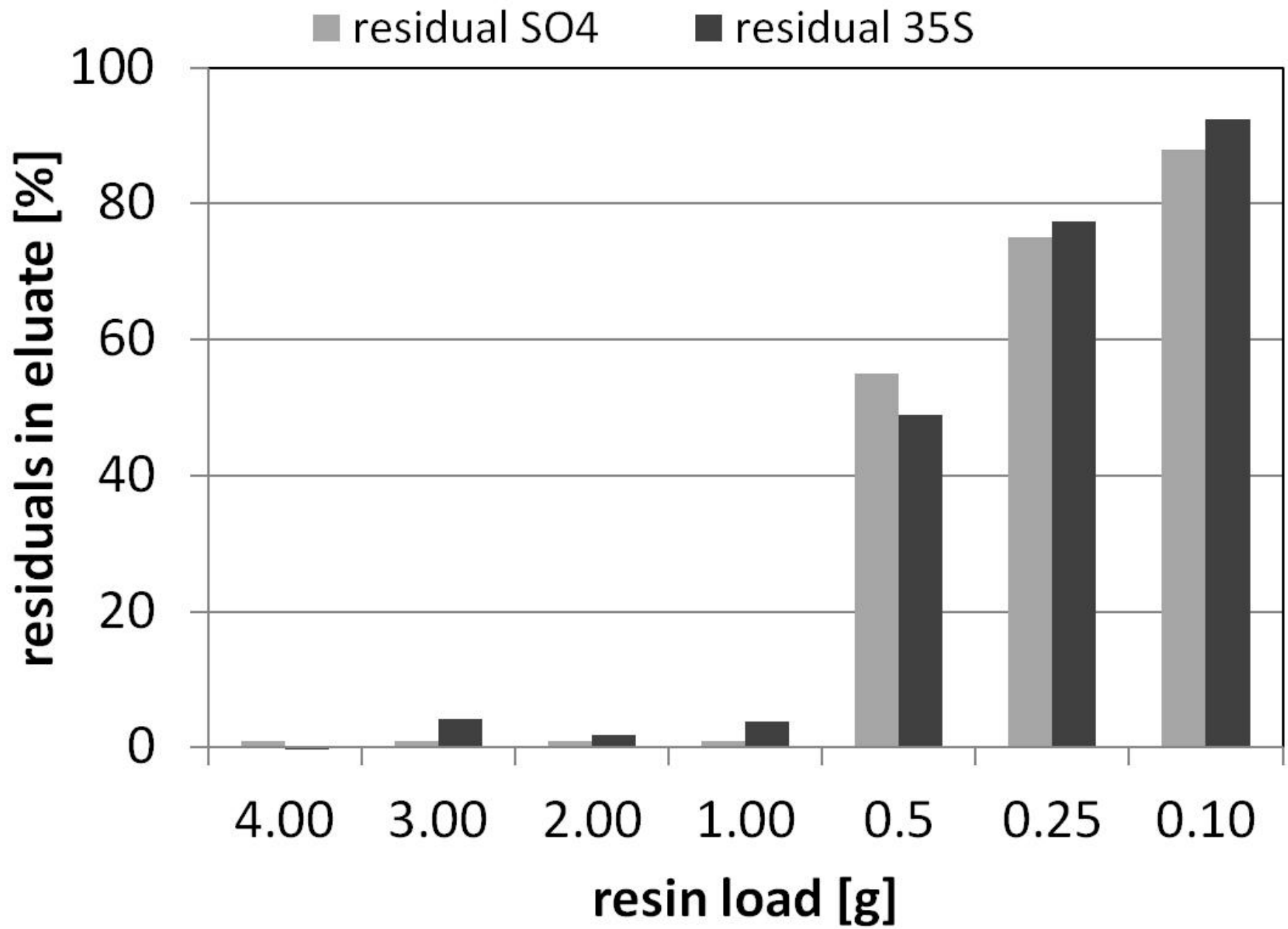
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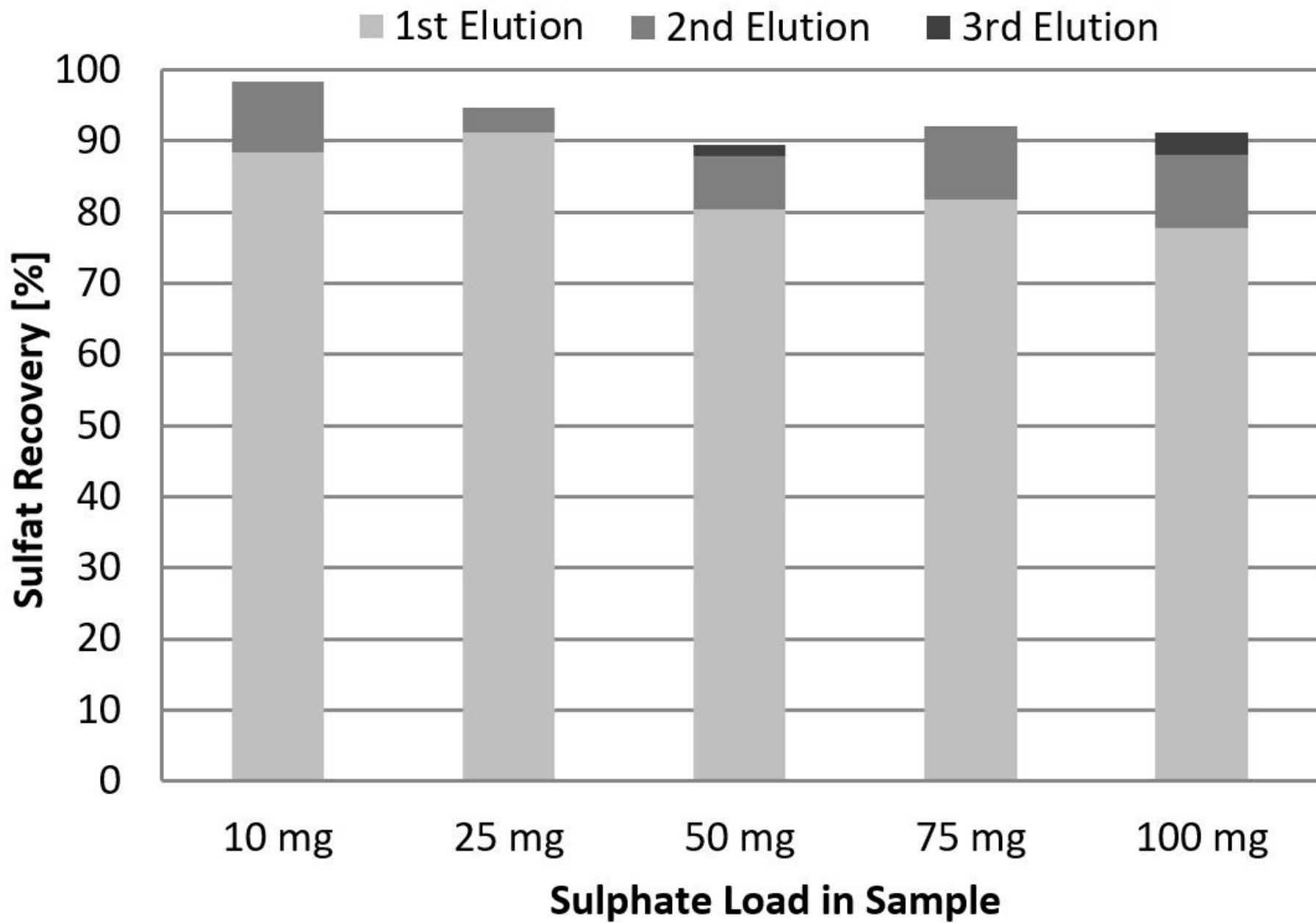
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