1 Introduction

Sustainable abstraction and supply of groundwater is a major socio-economic challenge of our modern society. Both globally growing population and more intensive agricultural activities make the management of groundwater resources a high priority issue. Related policy-based decisions require sufficient knowledge of mean groundwater residence times in exploited aquifers, i.e. mean "groundwater residence times". The information can be used for estimating the recharge rate of a groundwater resource (Cook and Solomon, 1997) and allows hence assessing (i) the volume of groundwater that can be sustainably abstracted, (ii) groundwater travel times and related matter (contaminant) transport, and (iii) the vulnerability of an aquifer to anthropogenic contamination or climate change. In some cases the assessment of timescales of water-rock interaction processes that might influence the groundwater quality can be of interest as well.

A powerful tool for investigating groundwater residence times (as well as groundwater flow and related solute transport processes) is the application of naturally occurring radioisotopes as environmental tracers. Cartwright et al. (2017) reviewed the possibilities and limitations of various radioisotopes (and other residence time tracers) for this purpose. The authors point out that since the groundwater residence time of a specific aquifer may range between a few months and > 1,000,000 years, the half-lives of the applied radioisotopes need to cover a comparable time range. They state that, while the radioisotopes ^{3}H, ^{14}C, and ^{36}Cl have already been commonly used in the past, general improvements in radio-analytical techniques brought about additional novel approaches that rely on application of the noble gas radioisotopes ^{39}Ar, ^{81}Kr, and ^{85}Kr. The six named radioisotopes cover half-lives between 10.76 years (^{85}Kr) and 301,000 years (^{36}Cl) permitting their use for determining groundwater residence times in comparable timescales. However, studies of radioisotopes as tracers that focus on residence times below one year are still scarcely discussed in the literature. In spite of its 12.3 a half-live ^{3}H might be applicable for detecting sub yearly residence times if the rainfall input function is very well constrained and the detection environment an ideal, i.e., far away from any nuclear source. However, the mandatory high quality data and ideal detection conditions are only rarely available.

Innovative approaches that focus on the sub yearly timescale include the application of the natural radioisotopes of radon (^{222}Rn) and beryllium (^{7}Be). ^{222}Rn starts to build up in any meteoric water (i.e. percolating rain or infiltrating surface water) as soon as it enters the subsurface due to the decay of ^{226}Ra that is omnipresent in any mineral matrix. However, with a half-live of only 3.8 days the ^{222}Rn activity in the infiltrating water reaches secular equilibrium with the ^{226}Ra in soil or aquifer after only

about three weeks, which makes ^{222}Rn only applicable for dating very young groundwater (Petermann et al., 2018; Treutler et al., 2007). In contrast, ^{7}Be with a half-life of 53.1 days allows investigating a much longer time span of up to eight months. It is produced through cosmic ray spallation of oxygen and nitrogen atoms within the upper atmosphere (Cooper et al., 1995). After its production it sticks to aerosols and gets washed out of the atmosphere mainly by precipitation (or settles by dry deposition). As soon as the rainwater seeps into the ground its exposure to cosmic rays stops and the ^{7}Be decay in the water is not supported by ^{7}Be production anymore making its decreasing activity concentration (in relation to its activity concentration in the fresh rainwater) an indicator of the groundwater residence time. However, ^{7}Be has a high tendency to sorb on organic phases, oxyhydrides and oxides; a substantial share of the dissolved beryllium is held back by soil particles and vegetation (Landis et al., 2014; Kaste et al., 2012), which limits its applicability as quantitative aqueous tracer.

A natural radionuclide that covers a comparable time range and could hence be alternatively applied as tracer is ^{35}S (Cooper et al., 1995). Just as ^{7}Be it is continually produced in the upper atmosphere (by cosmic ray spallation of atmospheric ^{40}Ar). After its production it rapidly oxidizes to $^{35}SO_4^{2-}$, gets dissolved in meteoric water and is finally transferred with the rain to the subsurface. ^{35}S activities in precipitation can be as high as ca. 65 mBq/l (Urióstegui et al., 2015). There are no significant natural sources of ^{35}S in the subsurface (Cooper et al., 1995). Hence its activity concentration in the meteoric water starts to decrease by decay as soon as the water seeps into the ground.

In contrast to beryllium SO_4^{2-} is highly mobile in groundwater and is hence not retarded by any mineral substrate. It displays very low reactivity and consequently a geochemical stability over a wide range of hydrochemical conditions. Under oxic and slightly reducing conditions sulfate is transported with the groundwater flow conservatively (Knöller et al., 2005). Under stronger reducing conditions, sulfate may be subject to bacterial reduction provided a bioavailable electron donor such as dissolved organic carbon is supplied (Knöller et al., 2008, Knöller and Schubert, 2010). If sulfate reducing conditions are prevailing, $^{35}SO_4^{2-}$ is likely to be affected by bacterial degradation in the same way as the stable isotope species of the sulfate molecule. If bacterial sulfate reduction is occurring, the application of the ^{35}S method is limited because of the fact that fractionation factors that might have to be used to correct the ^{35}S analytical results for potential degradation have not been investigated to date. However, bacterial sulfate reduction predominantly affects deep aquifer systems with high apparent groundwater residence times of several years to decades that can a priori not be investigated with the ^{35}S method, anyway.

^{35}S is a β-emitter (decaying to ^{35}Cl) and can be measured by liquid scintillation counting (LSC). Its half-life of 87.4 days makes it a potentially useful tracer for investigating groundwater residence times on timescales of up to 1.2 years. Studies on ^{35}S as an age tracer are scarce; those that exist are often limited to high geographical elevations where snowmelt is the dominant hydrological recharge event; thus simplifying the annual ^{35}S input function to the peak snowmelt (Shanley et al., 2005; Mitchel et al., 2000; Sueker et al. 1999; Cooper et al., 1995).

In contrast, ^{35}S concentrations in rainwater, i.e., in more moderate climate regions, may vary significantly even on short timescales of hours to days, resulting in a more involved ^{35}S input function. Furthermore the ^{35}S input function can be significantly affected by seasonal variations in rain intensity (and thus recharge). This constraint necessitates the recording of extended ^{35}S time series, both in rainwater and groundwater, for sound data interpretation in moderate climate zones. Furthermore, groundwater in moderate climate zones may show high SO_4^{2-} concentrations resulting in relatively low ^{35}S activities compared to the total SO_4^{2-} load of the sample in contrast to SO_4^{2-} loads in snowmelt. Analysing ^{35}S in waters with high SO_4^{2-} concentrations is generally challenging if a conventional LSC approach is applied (Urióstegui et al., 2015). The above named challenges limit the range of potential applications of ^{35}S as indicator for groundwater residence times in moderate climate zones (Clark et al., 2016).

Finally, it shall be pointed out that pre-concentration of ^{35}S is required for LSC counting since the low natural concentrations of ^{35}S in rain and groundwater necessitate large original water sample volumes. Urióstegui et al. (2015) suggested about 100 mg SO_4^{2-} as adequate load for sound ^{35}S detection by means of LSC and recommended accordingly a sample volume of 20 liters as appropriate for most meteoric waters. In practice, exchange resins are used to pre-concentrate SO_4^{2-} from the original water sample. The resin is subsequently eluted with aqueous NaCl solution and sulphate is precipitated by adding $BaCl_2$. This rather laborious sample preparation includes some steps that need to be improved.

The objective of this study was to develop, test and present an improved LSC based method that allows the detection of ^{35}S pre-concentrated from natural water samples that contain a wide range of SO_4^{2-} concentrations (up to 1500 mg) in a less labour-intensive way. The study aimed at the optimization of sample preparation, LSC setup and measurement protocol. All measurements were carried out with the liquid scintillation counter TriCarb 3170 Tr/SL.

2 Material and methods

After precipitation of ^{35}S containing SO_4^{2-} from aqueous solution as $BaSO_4$ a TriCarb 3170 Tr/SL liquid scintillation counter was used for the determination of the ^{35}S activity of the precipitate. The activity was measured after the homogeneous suspension of the ultra-fine-grained $BaSO_4$ particles in Insta-Gel Plus scintillation cocktail as described by Uriostegui et al. (2015).

With the aim to substantially improve the signal-to-noise-ratio of the measurement results, the optimization potential of three independent LSC detection options was investigated. Besides (i) optimization of the LSC counting window, two special features of the TriCarb 3170 Tr/SL, namely (ii) pulse decay discrimination and (iii) pulse index-based background reduction were examined for LSC performance improvement. The so called „figure of merit“ (FOM), i.e. the ratio of efficiency squared and background ($FOM = \varepsilon^2 / B$), was used to quantify the performance improvements. Furthermore, the quenching due to elevated $BaSO_4$ loads in the sample (and hence in the LSC vial) and the potential spill over of ^{226}Ra counts into the ^{35}S counting window were investigated and quantified.

For the execution of test measurements under varying conditions three sets of standards were produced (as described in detail in sect. 3). Each of the three sets contained seven individual standards with increasing SO_4^{2-} loads between 50 and 1500 mg (as described in detail in sect. 3). Standards with SO_4^{2-} loads higher than 1500 mg were not investigated because the corresponding volume of $BaSO_4$ was too large for the applied 20 ml LSC vials. Each of the seven standards of the first set was spiked with a ^{35}S activity of 290 Bq. The seven standards of the second set were all spiked with a ^{226}Ra activity of 1.1 Bq each. The seven standards of the third set were unspiked.

3 Experimental

3.1 Production of standards

Three sets of LSC standards were produced; set #1, set #2 and set #3. Each set contained seven individual standards with increasing loads of ^{35}S-dead SO_4^{2-} (as $BaSO_4$), namely 50mg, 100mg, 250mg, 500mg, 750mg, 1000mg and 1500mg SO_4^{2-}. Hence, 21 standards were produced in total. Each standard of set #1 was spiked with ^{35}S; each standard of set #2 was spiked with ^{226}Ra (for evaluating the spill over of ^{226}Ra counts into the ^{35}S counting window; see below for details). The standards of set #3 were not spiked at all but contained only ^{35}S-dead $BaSO_4$ in increasing concentration.

Highly water soluble Na_2SO_4 was used to prepare the standards. It was measured by both gamma spectrometry and LSC for any containing radioactivity prior to sample preparation and only Na_2SO_4 was used that was free of any ^{35}S. $BaCl_2$ was used for the preparation of the standards to precipitate SO_4^{2-} as $BaSO_4$. It was also tested for radioactivity and the tests revealed low but detectable amounts of ^{226}Ra, which was accounted for in the setup of the experiments and in the assessment of the experimental results (see sect. 3.3).

Three sets of Na_2SO_4 standard solutions were made by pipetting from a saturated Na_2SO_4 stock solution (i.e. 170 g/L at 20 °C) into 50 mL centrifuge vials. Each of the three sets comprised seven individual standards with increasing Na_2SO_4 loads that matched the range of SO_4^{2-} loads given above. The standards of set #1 and set #2 were subsequently spiked with 10 µL of a $^{35}SO_4^{2-}$ stock solution ($Na^{35}SO_4$; carrier free) and 2 mL of an aqueous ^{226}Ra stock solution, respectively. That resulted in activity concentrations of about 290 Bq ^{35}S in each vial of set #1 and about 1.1 Bq ^{226}Ra in each vial of set #2. (The aqueous standard $Na^{35}SO_4$ and ^{226}Ra stock solutions were obtained from the PTB - National Metrology Institute, Germany and Hartmann Analytic, Germany, respectively.) The seven standards of set #3 were not spiked at all but served as background standards representative for the increasing SO_4^{2-} loads.

Subsequently distilled water was added to each of the 21 centrifuge vials in order to equalize the individual volumes to 15 ml for each of the standards. All solutions were acidified with five drops of 6M HCl to a pH of 2.5. In order to quantitatively precipitate the dissolved SO_4^{2-} as $BaSO_4$ the vials were placed in water filled beakers and heated in the water bath to nearly 100°C before adding a volume of 35 mL 0.5M aqueous $BaCl_2$ solution to each of the vials. After allowing about 12 hours for the $BaSO_4$ to precipitate quantitative precipitation was checked by visual examination of the supernatant solution after adding a few more drops of 0.5M $BaCl_2$ solution. Since no additional sulphate precipitation was observed in any of the vials quantitative precipitation was assumed.

The vials were centrifuged for 10 min at 4000 rpm, the supernatant water was removed with a pipette and the precipitate was washed with distilled water. This washing process was repeated once more. Then the vials were centrifuged again, the supernatant water was tested for neutrality and removed with a pipette. Then the precipitate was dried within the vials at about 100°C to complete dryness (for at least two hours). The resulting dry clumps of $BaSO_4$ precipitate were next quantitatively transferred into 20 mL LSC vials and weighted for recovery and potential loss of SO_4^{2-} during standard preparation. We used plastic vials instead of glass vials because they display a lower background than

glass vials due to their lower intrinsic radioactivity (no traces of ^{40}K). Plastic also has a lower density resulting in a lower probability of particle/photon interactions with the vial wall. Finally, a glass rod was used to pulverize the precipitate directly in the LSC vials.

Insta-Gel Plus (PerkinElmer) was chosen as the scintillation cocktail that is most suitable for the purpose. Due to its typical gel formation it allows the homogeneous distribution of suspended solids (such as $BaSO_4$ powder) within the counting. Therefore, it is ideal for counting the $Ba^{35}SO_4$ precipitate.

The $BaSO_4$ powder was suspended in 5 mL distilled water by shaking the vials for homogenization. Subsequently 6.5 mL Insta-Gel Plus were added to each vial and the vials were shaken again. Finally, another 6.5 mL Insta-Gel Plus were added, and the vials were shaken homogenization and gelation were complete. A total volume of 13 ml of Insta-Gel Plus are needed of 5 ml water aqueous suspensions are to be measured because gel formation is dependent on a proper water/cocktail ratio. Prior to the actual LSC measurement the vials were refrigerated for about 30 min in order to reduce the counting background (pers. comm. Richard K. Bibby, Lawrence Livermore National Laboratory, Livermore, USA). Measurement of refrigerated samples results in a reduction of the counting background because it reduces chemoluminescence. Furthermore gel formation of the sample/cocktail mixture is temperature-dependent. Since a refrigerated LSC counter is used, it is recommended that the stability of the gel is tested by cooling the sample prior to counting.

3.2 Optimization of the counting window

For optimization of the counting window LSC measurements were carried out with the standard sets #1 and #3 (i.e. ^{35}S and background). After measuring the actual standards with a certain energy window, the "Replay“ option of the TriCarb was used for iterative optimization of the window (the "Replay“ option allows re-evaluation of the raw count data based on different evaluation settings without any additional measurement of an individual sample). The variable window settings that were iteratively tested covered the complete range from 0 keV up to the theoretical endpoint of the ^{35}S-β-spectrum at 167keV.

3.3 Pulse decay discrimination (PDD)

A general increase in radiation background with increasing $BaSO_4$ load was observed for all three sets of standards. That suggested the $BaCl_2$, added for the sake of $BaSO_4$ precipitation from the aqueous

solutions, as potential background radiation source. Barium and radium are both members of the alkaline-earth metal group and thus chemically similar, so that substitution of barium by radium is possible. Adding $BaCl_2$ for preparation of the standards may hence result in a contamination of the standards with radium. That assumption is backed by Urióstegui et al. (2015) who found substantial amounts of radium in several investigated $BaCl_2$ batches. Not only the counts of the ^{226}Ra itself but also the counts of its short-lived progeny may spill over into the ^{35}S counting region resulting in higher backgrounds there. In particular the alpha emissions of ^{222}Rn, ^{218}Po, ^{214}Po, ^{210}Po can be misinterpreted as ^{35}S decay events (Urióstegui et al., 2015).

A gamma spectrometry analysis of the used $BaCl_2$ batch confirmed the presence of ^{226}Ra and thus also its short-lived progeny. The measurement was carried out by low-level gamma-spectrometry based on the distinct ^{226}Ra gamma emission energy of 186.1 keV. (Due to the purity of the $BaCl_2$ a contribution of ^{235}U - 185.7 keV - to the peak area could be ruled out.) For the measurements a coaxial Low-Energy HPGe detector, n-type (ORTEC) with an active volume of 39 cm^3 and a 0.5 mm Be window was applied. Detector and measuring geometry were calibrated using the certified reference material IAEA-RGU1. Two samples of the used $BaCl_2$ batch were measured for about 24 h in 150 cm^3 cylindrical capsules. Spectra analysis was performed with the software Gamma-W®.

Since the ^{226}Ra radiation background of the ^{35}S-dead $BaSO_4$ precipitate could not be avoided due to its origin, pulse decay discrimination (PDD) was used to reduce contribution of this background to the overall counts of the measurements. PDD is based on the length of the pulse that is recorded in the electronic circuits of the liquid scintillation counter. Pulses induced by an alpha decay have a longer tailing than those from a beta decay (Buchtela et al., 1974; Thorngate et al., 1974). PDD classifies all detected counts as either alpha or beta events based on the respective pulse length.

The homogeneously suspended $BaSO_4$ particles result in a strong influence of self-absorption. Hence, the use of classical spill-over plots, as they are routinely applied for samples that are homogenously dissolved in a cocktail, appeared not appropriate for optimization of the PDD discriminator setting. We therefore followed a strategy that considers the spill-over of alpha-decays derived from ^{226}Ra and its short lived progeny as „additional background“ and applied the FOM to determine the optimum PDD setting. For calculation of the sulphate-load specific FOM values, the standards of set #1 (^{35}S spiked) were applied to determine the individual counting efficiencies (ε), while the standards of set #3 were measured for quantification of the associated ^{35}S-dead backgrounds (B).

3.4 Pulse index discrimination

A very effective method to reduce the overall background in TriCarb instruments is pulse index discrimination, which reduces photomultiplier crosstalk. Photomultiplier crosstalk may occur if natural radioactivity (^{40}K) or cosmic radiation induces the release of photons by the Cerenkov Effect in one of the two photomultipliers (PMT). These photons might also arrive at the second PMT thereby fulfilling the coincidence counting condition. Consequently these events are recorded by the instrument as real counts. However, detailed analysis of the pulses (pulse index discrimination) allows distinguishing Cerenkov events from liquid scintillation events thereby enabling correction for these background signals (Passo and Kessler, 1992). In combination with the BGO guard used in low level counters as the TriCarb 3170 Tr/SL it also targets background scintillation counts caused by external radiation (e.g. cosmic radiation) (Noakes and Valenta, 1996).

Since high energetic beta events in the cocktail may induce pulse indices that resemble background counts, the possibility to attenuate the pulse index correction for measuring high-energetic nuclides by increasing the so called „delay-bevor-burst“ (DBB) time was introduced. However, since ^{35}S is relatively low-energetic and, as in our case, by self-absorption quenched to even lower energies, an improvement of the counting sensitivity by fine-tuning the DBB time appeared unlikely. Still, another study suggested a significant improvement by increasing the DBB time for measuring $BaSO_4$ precipitates (Hong and Kim, 2005). We therefore also tested the effects of longer DBB times.

4 Results

4.1 Production of standards

The SO_4^{2-} recovery check by weight confirmed the quantitative recovery of the sulphate that was added to the individual standard solutions as dissolved Na_2SO_4. In particular, the transfer of the $BaSO_4$ precipitate from the centrifuge vial into the LSC vial as dry clump simplified the handling of the material considerably. In the LSC vials the $BaSO_4$ clumps could be easily and completely pulverized with a glass rod allowing a homogeneous distribution of the powder within the scintillation gel.

It shall also be pointed out that homogeneous distribution of the pulverized $BaSO_4$ precipitate in the gel filled vials leads to a significantly better counting efficiency than collecting the precipitate on a translucent filter and counting the included ^{35}S on this filter applying a liquid LSC cocktail (e.g. Ultima Gold LLT) without chemical dissolution of the filter (as suggested by Hong and Kim, 2005). Furthermore it shall be mentioned that it is important to add the aqueous spike solutions (^{35}S

and ^{226}Ra) not to the LSC vials at the end of the standard preparation process (e.g. with the 5 mL distilled water that are added prior to the Insta-Gel Plus) but rather to the aqueous solutions prior to the $BaSO_4$ precipitation. Both ^{35}S and ^{226}Ra need to be amalgamated within the particles of the $BaSO_4$ precipitate for sound determination of the individual quench.

4.2 Optimization of the counting window

A representative example of the results of the measurements and the subsequent replay runs that were carried out with sets #1 (^{35}S) and #3 (background) aiming at the optimization of the counting window is displayed in Fig. 1. For the four standards with sulphate loads between 50 and 250 mg highest FOMs were found in energy windows with a lower window limit ranging between 2.5 and 3.5 keV and an upper limit ranging between 42 and 43 keV. For the three standards with sulphate loads between 500 and 1500 mg the highest FOMs were found with a lower window limit between 0.0 and 0.5 keV and an upper window limit between 35 and 39 keV.

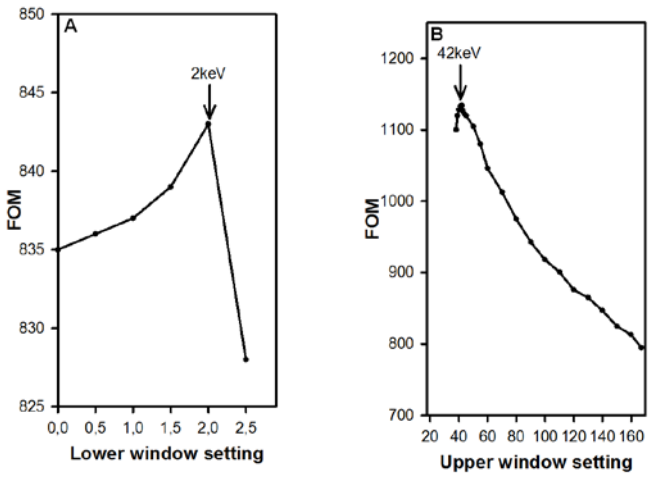

Fig. 1: Optimizing the energy window setting; ^{35}S-dead standards containing increasing loads of $BaSO_4$ (set #3) were used as background standards, while standards spiked with ^{35}S (set #1) were applied to determine counting efficiencies, both at different window settings. As an example window optimization is displayed for the standards with a SO_4^{2-} load of 250mg. (A) Lower window limit was increased stepwise and ε^2/B (FOM) was calculated. (B) Upper channel setting was lowered stepwise with optimized lower channel until a maximum for the FOM was reached.

The counting windows that yielded the highest FOMs at the individual sulphate loads are compiled in Tab. 1. While generally the background increases with the sulphate load (as expected), the application of the optimized window settings resulted in a substantial background reduction for all individual

standards of the ^{35}S-dead set #3 (Fig. 2A). Although narrowing the counting window causes generally a slight decrease in counting efficiency (Fig. 2B) as determined with standard set #1, a distinct increase of the FOM could be achieved for all sulphate loads due to the more decisive background reduction (Fig. 2C).

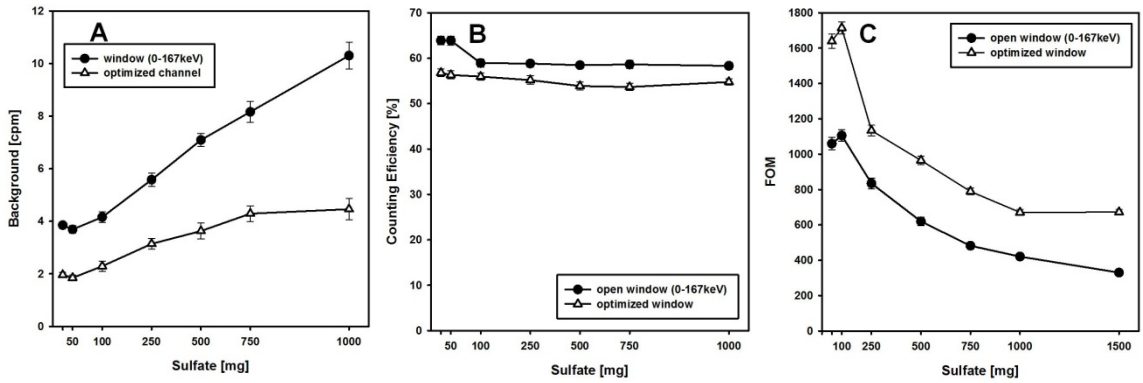

Figure 2: Effect of window optimization on counting performance at different SO_4^{2-} loads; (A) Background with open window (i.e. 0 - 167 keV) vs. optimized channel as given in Tab. 1. (B) Counting efficiency with open window vs. optimized channel. (C) FOM with open window vs. optimized channel.

Table 1: Effect of window optimization on Figure of Merit (FOM)

Sulphate [mg]	FOM open window	FOM optimized *(channel setting)*
50	1060	1645 *(3-43keV)*
100	1106	1714 *(3-42keV)*
250	835	1134 *(3-42keV)*
500	620	969 *(0-39keV)*
750	482	799 *(0-37keV)*
1000	421	671 *(0-35keV)*
1500	330	672 *(0-35keV)*

Based on this data set we suggest an optimum window setting of 3 - 42 keV for samples containing up to 500 mg sulphate („low sulphate“) and a window setting of 0 - 37 keV for samples with sulphate loads above 500 mg („high sulphate“) as a compromise for routine measurements. These settings

were retained for all subsequent measurements. As mentioned above, sulphate loads higher than 1500 mg are not feasible due to practical considerations.

4.3 Pulse decay discrimination (PDD)

The gamma spectrometry measurement revealed a ^{226}Ra activity of the used $BaCl_2$ of 5 ± 0.4 Bq/kg. Even though this activity concentration is comparably low for commercially available $BaCl_2$ batches (Uriostegui et al., 2015), the ^{226}Ra-derived counts (i.e. the counts from ^{226}Ra and its short-lived progeny, namely the alpha emitters ^{222}Rn, ^{218}Po, ^{214}Po and the beta emitters ^{214}Pb and ^{214}Bi) are the major cause of the increasing background that was observed for higher $BaSO_4$ loads.

FOM measurements at different PDD discriminator settings were executed with the standard sets #1 and #3. Based on the results optimal PDD settings (as indicated by the highest FOM) were determined for “low” (<500 mg) and “high” (>500 mg) sulphate loads (*cf.* sect. 4.2). They were found to be PDD 100 and 90, respectively (Fig. 3). Applying these settings on the ^{226}Ra spiked standards of set #2 resulted in a reduction of about 50% of the ^{226}Ra-derived counts in the optimized ^{35}S energy window (*cf.* sect. 4.2) as compared to measurements without PDD (Supplementary figure S1)) in the open window.

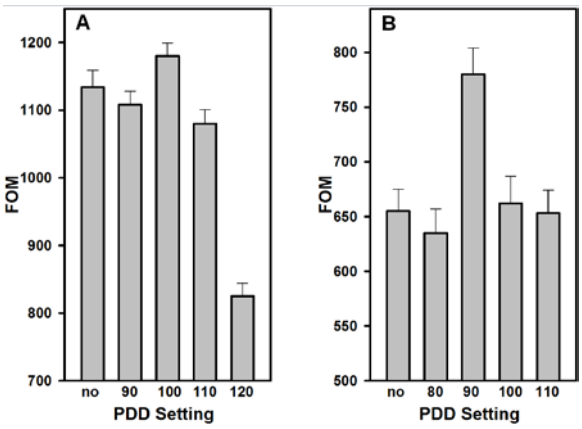

Figure 3: Effect of Pulse Decay Discrimination (PDD) on FOM; exemplary results for (A) a low (250mg) and (B) a high sulphate load (1500mg) at the respective optimized channel settings

4.4 Pulse index discrimination

Hong and Kim (2005) suggested a DBB value of 200 ns to maximize the FOM for ^{35}S measurements in aqueous samples in 10ml/10ml proportions with Ultima Gold LLT as scintillation cocktail. Still, the application of Insta-Gel Plus for ^{35}S determination in $BaSO_4$ as discussed here may necessitate a

different setting. In our measurements the shortest possible DBB time of 75ns, which is the default setting of the TriCarb recommended for measuring low energetic nuclides such as ^{3}H or also ^{14}C (whose E_{max} is very close to ^{35}S), was found to give the best results (Fig. 4).

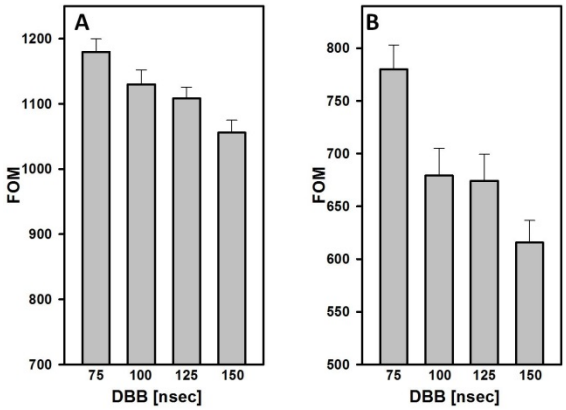

Figure 4: Effect of different Delay Before Burst (DBB) times exemplary results for (A) a low (250mg) and (B) a high sulphate load (1500mg) at the respective optimized channel settings

5 Discussion

5.1 Recommendation of a detection setup

Based on the achieved data, we recommend settings as given in Tab. 2 for counting ^{35}S-containing $BaSO_4$ precipitates in the gel-forming Insta-Gel Plus cocktail the. Results for different amounts of sulphate measured under these conditions are given in Tab. 3.

Table 2: Recommended instrument settings for counting ^{35}S-containing $BaSO_4$ suspensions in Insta-Gel Plus

	Sulphate load 0-499 mg	Sulphate load 500-1500 mg
Counting mode	Low level	Low level
Counting window	3 - 42 keV	0 - 37 keV
Pulse decay discriminator	100	90
Delay before burst	75 nsec	75 nsec

Table 3: Counting performance at optimized settings according to Table 2

Counting conditions	Sulphate load [mg SO_4^{2-}]	Background [cpm]	Efficiency [%]
	50	2.15	56.7
„Low sulphate“	100	2.20	56.2
	250	2.35	56.2
	500	2.86	52.9
„High sulphate“	750	3.22	52.6
	1000	3.26	53.3
	1500	3.69	53.6

With optimized settings the counting efficiencies were in the range of 50 - 60 % indicating that quench correction is necessary for dpm or Bq reporting. External standardization with a γ-emitting ^{133}Ba source (tSIE or SIS value), as conventional method, appears not suitable for $BaSO_4$ precipitates, since it records chemical and colour quenching but cannot quantify the amount of self-absorption in the particles, resulting in so called „physical quench“ (*cf.* sect. 5.2). We therefore recommend quench correction where the (known) amount of $BaSO_4$ in the sample is correlated to the counting efficiency as determined with a comparable standard spiked with $Ba^{35}SO_4$. The efficiencies shown in Tab. 3 indicate that the quench level remains close to constant for a rather large range of SO_4 loads. Thus, in practice, it might be sufficient to determine the counting efficiency for “low” and “high sulphate” samples only once and proceed from the assumption that the quench level is practically constant over either of the two sample ranges. In the case of our detection setup one could assume a counting efficiency of about 56% for “low” and 53% for “high sulphate” concentrations.

5.2 Background information related to quench correction

The use of ^{35}S as a tracer in groundwater studies requires extremely sensitive procedures that allow detecting the low ^{35}S levels present in the samples. The processing of large water sample volumes includes the removal of other naturally occurring radioisotopes from the samples by ion-exchange chromatography and the pre-concentration of the ^{35}S by $Ba^{35}SO_4$ precipitation as an absolute prerequisite (e.g. Urióstegui et al., 2015).

Liquid scintillation counting is the method of choice to measure ^{35}S activities. However, LSC measurement of low energetic β-emitters like ^{35}S customarily requires samples in a solution that is homogenously miscible with the scintillation cocktail. Measuring solid samples is generally hampered by self-absorption. An approach to circumvent the latter limitation is the use of gel-forming scintillation cocktails that allow the measurement of small particles as microsuspension in a stable gel. Carbonate precipitation has been used for a long time to measure ^{14}C as $Ba^{14}CO_3$ (Larson, 1973). Likewise, sulphate precipitation with $BaCl_2$ can be applied to concentrate ^{35}S-sulphate from high water volumes for measurement in a liquid scintillation counter that can accommodate a maximum sample/cocktail mixture of 20 ml. However, with this approach a considerable influence of self-absorption in the suspended particles ("physical quenching") has to be taken into account. The major contribution to the loss of counting efficiency ("total quenching") will be caused by self-absorption rather than by chemical and colour quenching as known from homogenous liquid sample/cocktail mixtures.

The by far most commonly applied method to measure and correct for the influence of the latter is standardization with an external γ-source (L`Annunziata, 2012). In the case of TriCarb counters the shift of a Compton spectrum generated by a ^{133}Ba source is applied to quantify chemical and colour quench of a sample and expressed as the so called "tSIE-value" (Kessler, 1991). However, since the generation of Compton-electrons mainly occurs in the liquid cocktail phase of a microemulsion and only to a negligible part inside the particles, the tSIE does not reliably measure physical quench by self-absorption in the particles. We therefore do not recommend the tSIE value for quench correction of $BaSO_4$ precipitates.

In principle, the "Spectral Index of the Sample" (SIS), which detects quench by recording the shift of the sample spectrum towards lower energies would be applicable for recording physical quench, provided the quench curve is set up with ^{35}S-containing $BaSO_4$ suspensions in Insta-Gel Plus. However, for low level measurements statistical accuracy of this quench indicator is too low.

Best results were achieved when counting efficiencies were determined with standards mimicking the sample composition, i.e. the $BaSO_4$ load.

5.3 Impact of the $BaSO_4$ particle size on the counting efficiency

We found higher counting efficiencies compared to reports from other groups (Hong and Kim, 2005; Urióstegui et al., 2015), in particular for higher $BaSO_4$ loads. As mentioned above, the major cause of loss of counting efficiency is self-absorption in the $BaSO_4$-particles. Since self-absorption is highly

dependent on the particle size, we took special care during preparation of our standards to produce particles for the final measurement that were as small as possible. Therefore, this seems to be the most plausible explanation for our higher counting efficiencies. Likewise, we did not see a striking decrease of counting efficiency with increasing $BaSO_4$ loads. For chemical quenching a reduction of counting efficiency would be expected for higher loads of the quenching agent. However, no compounds that could cause chemical quenching are present in our standards. The $BaSO_4$ present in particles does not contribute to chemical quenching and the amount of water is constant for all $BaSO_4$ loads. The decreasing counting efficiencies at higher $BaSO_4$ loads observed in the former reports might hence rather be due to an increasing size of the $BaSO_4$ particles with higher $BaSO_4$ loads resulting in stronger physical quench. If the particle size remains unchanged with an increasing $BaSO_4$ load the influence of physical quenching should remain close to constant, as observed in our study.

Furthermore it shall be pointed out that very high $BaSO_4$ loads might lead to light scattering at the particles which could reduce the amount of photons that reach the photomultipliers of the LSC instrument. We observed an influence of this effect with sulphate loads above 1500 mg and therefore recommend not exceeding this limit (besides the fact that the corresponding volume of $BaSO_4$ is inappropriate for the applied 20 ml LSC vials). Altogether careful preparation the standards resulted in close to constant counting efficiencies over broad ranges of sulphate load, thereby enabling simple standardization for dpm/Bq reporting.

5.4 Minimizing of spill-over from α-emitters

The optimization of the window setting had a major impact on the signal-to-noise ratio, as quantified by the increase of the FOM. Optimal window settings not only reduce that natural background, but also help to prevent spill-over of counts, in particular from ^{226}Ra and its progeny, into the ^{35}S window. The lower energy regions of the β-emitters ^{214}Pb and ^{214}Bi will always overlap with any setting of the ^{35}S window. Consequently, setting the window as narrow as possible will help to reduce background originating from these ^{226}Ra daughter nuclides. If unquenched, the α-emitting daughters should appear above the maximum energy of ^{35}S. However, α-particles are much more affected by self-absorption as β-electrons. Since quenching of a α-emitter results in a shift of the α-peak to lower energies, self-absorption is likely to cause a spill in to the ^{35}S window. Therefore, especially lowering the upper limit of the ^{35}S-window helps to reduce α-derived background.

In addition, the PDD-based α/β-option helps to reduce remaining α-spill. The improvement of the signal-to-noise ratio by applying this option clearly indicates that α-spill can contribute to the background counts, even in the optimized window.

5.5 Background information related to the delay-before-burst setting

All measurements in our study were conducted in the low-level count mode of an instrument that is equipped with a BGO guard. This count mode provides efficient background reduction by applying pulse-index-discrimination to reduce background originating from events outside the cocktail, mainly caused by Cerenkov-effects in the detection chamber, e.g. by the interaction of cosmic radiation with components of the detection chamber or by ^{40}K contaminations (Roessler et al., 1991). The method is based on the observation that each β-event that is registered by the photomultipliers is followed by a number of after-pulses. The pulse-index is defined by the number of after-pulses that are registered in the photomultiplier. Since most of the background events that occur outside the cocktail produce more after-pulses than the β-events in the cocktail, the pulse-index can be applied to reduce this kind of background. The low-level count mode applies most stringent pulse-index discrimination, and is therefore the method of choice for low-level measurements. However, the delay after a β-event that is defined in order to distinguish between true β-events within the cocktail and external events, depends on the counting conditions, in particular on the energy of the β-particles and the used cocktail. Therefore this “delay-before-burst” (DBB) can be adjusted (Passo and Kessler, 1993).

Prolongation of the DBB time becomes e.g. necessary when using long fluorescence lifetime (“slow”) scintillation cocktails that produce a significantly delayed signal, i.e. cocktails that contain di-isopropylnaphthalene (e.g. Ultima Gold LLT) in combination with higher energy β-emitters (Salonen et al., 2012). Insta-Gel Plus does not belong to the “slow” cocktails since it is based on 1,2,4-trimethylbenzol. In contrast to Hong and Kim (2005) who used Ultima Gold LLT in their study, the shortest possible DBB time was found to be the best setting for measuring strongly quenched ^{35}S in the Insta-Gel Plus cocktail.

6 Conclusion

A powerful tool for investigating groundwater residence times is the application of naturally occurring radioisotopes as environmental tracers. Commonly applied radioisotopes (^{3}H, ^{14}C, ^{36}Cl, ^{39}Ar, ^{81}Kr, ^{85}Kr) are suitable for covering water residence times ranging between a few years and over one million

years. The omnipresent natural radionuclide ^{35}S adds perfectly to this set of tracers since it is applicable for investigating groundwater residence times of up to 1.2 years. However, the very low activity concentration of ^{35}S in groundwater is challenging. In addition, its concentration in rainwater (^{35}S input function) may vary substantially even on short timescales. These challenges can be met by optimizing both sample preparation procedure and LSC measurement protocol. Improved sample preparation focusses on the homogeneous suspensions of fine-grained ^{35}S-containing $BaSO_4$ in the Insta-Gel Plus scintillation cocktail. The improvements in instrument setting include the LSC counting window, the pulse decay discriminator setting and the delay before burst setting. Numerous experiments resulted in related recommendations. The recommended settings allow the measurement of low activity concentrations of ^{35}S, which was previously pre-concentrated from natural water samples, containing SO_4^{2-} loads of up to 1500 mg with a reasonably high statistical reliability.

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