Activity standardization of $^{32}$Si at PTB

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1. Introduction

The radioactive isotope $^{32}$Si, with a half-life ($T_{1/2}$) of about (153 ± 19) years (Ouellet and Singh, 2011) is a cosmogenic nuclide produced in the upper atmosphere by bombardment of $^{40}$Ar with cosmic rays. It is one of the few naturally occurring radionuclides that have the potential to bridge the dating gap between the relatively short-lived $^{14}$C ($T_{1/2} = 5730$ a) on the one hand, and the longer-lived $^{14}$C ($T_{1/2} = 7.15$ kyr) on the other hand. This would make it possible to better understand environmental processes such as glacier dynamics, ocean and atmospheric circulation, sedimentation in lakes and oceans or groundwater flows in the recent past (100–1000 years) (Veicht et al., 2021; and references therein). However, accurate dating requires precise knowledge of the radionuclides’ half-life. The so far inconsistent database on the nuclear properties of $^{32}$Si, as well as its extreme rarity, have hampered its application for environmental research studies using current technology. This unsatisfying situation is mainly due to the limited availability of the isotope and the high demands on the quality of the samples.

To overcome these obstacles, the SINCRON project was initiated by a consortium of several research groups from Paul Scherrer Institut (PSI), Eidgenössische Technische Hochschule Zürich (ETHZ), Institut de radiophysique (IRA), Labor Spiez, Physikalisch-Technische Bundesanstalt (PTB) and the Australian National University (ANU) with the goal of

1) producing sufficient $^{32}$Si material with the required high quality
2) developing reliable methods for activity determination and mass spectrometry to determine the half-life directly with high accuracy and low uncertainty and
3) developing stable source-detector systems for long-term measurements as an alternative way to determine the half-life.
The isotope $^{32}$Si was radiochemically separated and purified from vanadium discs which were irradiated in the target of the spallation neutron source SINQ at PSI with high-energy protons (Veicht et al., 2021). A total of about 20 MBq could be obtained and was partially provided for subsequent measurements, especially with LS counting and mass spectrometry. For these measurements, several conditions had to be met: liquid scintillation (LS) counting requires solutions in a suitable chemical form and with high radionuclide purity.

One of the most critical factors when measuring in liquid media is the chemical stability of the sample, especially when measurements have to be performed over long periods of time. Unfortunately, silicon tends to polymerize in basic or even neutral solutions, especially if its concentration is noticeably high. The result is the formation of insoluble compounds that form colloids, which are deposited on the vessel walls. This leads to uncontrollable changes in count rates and, thus, to unreliable results regarding long-term measurements for a half-life determination. Therefore, all samples were prepared in an acidic solution. In addition, potential radioactive contaminations may cause interferences and distort the results. A particular problem is that impurities of certain radionuclides, such as low-energy beta emitters, are difficult to detect and therefore cannot be corrected. As a result, significant efforts were made to purify the $^{32}$Si material and in particular to completely remove the $^3$H which was originally present in the samples. The extended descriptions of the radiochemical separation and the sample treatment were recently published (Veicht et al., 2021).

Numerous $^{32}$Si solutions were measured within the course of the SINCHR ON project, but there were some difficulties in the beginning, especially as the LS samples showed long-term instabilities. Moreover, discrepancies between the established LSC methods were found. In this paper, we report on the development and execution of the activity measurements using LS counting as carried out at PTB within the course of the SINCHR ON project. This includes numerous studies to understand the limited long-term stability of the LS samples and to arrive at samples that are stable over a long time.

2. Computation of LS counting efficiencies

The radionuclide $^{32}$Si decays via a beta minus transition to $^{32}$P which itself is a beta minus emitter. According to the Nuclear Data Sheets evaluation made by Ouellet and Singh (2011), the transition energy for the beta minus decay of $^{32}$Si is 227.2(3) keV which will also be used in this work. The more recent atomic mass evaluation AME2020 (Wang et al., 2021) states virtually the same value (227.19(30) keV). The maximum energy for the beta minus transition of $^{32}$P is 1710.66(4) keV and was taken from Wang et al. (2021). Both beta transitions are of an allowed nature. The beta spectra were computed with a special version of the BetaShape code provided by Prof. Mougeot (2015). This code allows for the atomic exchange effect which was found to be very important when comparing computed results with accurately measured beta spectra (see, e.g., Loidl et al., 2014) and when using beta spectra for LS counting methods such as CIEMAT/NIST efficiency tracing (CNET) and the triple-to-double coincidence ratio (TDCR) method (Kossert and Mougeot, 2015, 2021; Kossert et al., 2018). Fig. 1 shows computed beta spectra for $^{32}$Si in radioactive equilibrium with $^{32}$P. The Figure also shows the corresponding result when the atomic exchange effect is ignored. A rough estimation shows that the computed LS counting efficiencies decrease by about 0.3% when taking the atomic exchange effect into account. The effect is very similar for both methods (CNET and TDCR) that are used in this work.

Since $^{32}$Si and $^{32}$P are pure beta minus emitters, no further radio-nuclide data are required for the computation of the individual LS counting efficiencies. The situation is slightly different when considering a combined $^{32}$Si/$^{32}$P source. In this case, one has to account for the time-dependent activity ratio $A(32\text{P})/A(32\text{Si})$. In radioactive equilibrium this ratio is given by

$$
\frac{A(32\text{P})}{A(32\text{Si})} = \frac{T_{1/2}(32\text{Si})}{T_{1/2}(32\text{P})} = 1.000255675
$$

(1)

Even in this case, it depends on the half-life of $^{32}$Si and, thus, the computation of the overall counting efficiency also depends on the half-life. In the analysis reported on here, we have – as a starting point – assumed $T_{1/2}(^{32}\text{Si}) = 153(19)$ a and $T_{1/2}(^{32}\text{P}) = 14.268(5)$ d which were taken from Ouellet and Singh (2011). With these values we get $A(32\text{P})/A(32\text{Si}) = 1.000255389$. When substituting the $^{32}$P half-life with a somewhat older DDEP evaluation ($T_{1/2}(^{32}\text{P}) = 14.284(36)$ d, Bé et al., 2004) we get $A(32\text{P})/A(32\text{Si}) = 1.000255675$ which deviates by less than $3 \times 10^{-7}$ from the previous value. If we assume $T_{1/2}(^{32}\text{Si}) = 100$ a, which is a rather extreme change, we calculate $A(32\text{P})/A(32\text{Si}) = 1.000390798$ which deviates by about 0.014% from the initial value.

Fig. 2 shows the time-dependent activity ratio assuming two different values for the $^{32}$Si half-life.

The analyses which are presented in the following are made with the assumption that radioactive equilibrium has been reached (if not otherwise stated). We assume a conservative uncertainty of 0.1% for the equilibrium factor. This covers the rather small dependence on the half-

![Fig. 1. Computed combined beta spectrum for $^{32}$Si in equilibrium with $^{32}$P. The red dashed curve represents the outcome of a “classical” computation whereas the black curve takes the screening corrections and the atomic exchange effect into account. The atomic exchange effect leads to an elevation of the probabilities at very low energies (see, inner diagram). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
lives (in particular on the half-life of $^{32}$Si). In addition, this enables us to analyze all measurement data that were taken more than 140 days after the final chemical separation as if equilibrium had been reached.

The LS counting efficiencies were calculated in a similar manner as described in previous articles (see, e.g., Nähle and Kossert, 2011; Kossert and Mougeot, 2021). The ionization quenching function was calculated by applying the methodology of the KB code (Los Arcos and Ortiz, 1997) taking the atomic composition of the samples into account. The $k_B$ parameter was selected to be 75 $\mu\text{m}$/MeV. When applying the CNET method, the same $k_B$ parameter was used when computing the $^3$H counting efficiency.

3. LS counters and analysis

For the LS measurements at PTB, two custom-built TDCR counters were used which are referred to as TDCR-M27 and TDCR-M29. In addition, a Wallac 1414 spectrometer and a TriCarb 2800 TR spectrometer were used to apply the CNET method. Details about these systems and further references can be found in a recent publication (Kossert et al., 2022).

The TDCR measurement data were corrected for accidental coincidences by applying a simple methodology proposed by Dutsov et al. (2020).

Since we assume that $^{32}$Si and $^{33}$P are in radioactive equilibrium, we can compute the combined beta spectrum (Fig. 1) and treat $^{32}$Si/$^{33}$P as one single pure beta-emitting radionuclide. As a consequence, one can easily apply correction algorithms to allow for potential PMT asymmetries in a TDCR system (Nähle and Kossert, 2011) and there is no need to apply more time-consuming algorithms which were proposed for complex decays (Kossert et al., 2020). In the case of the CNET method, no correction for potential PMT asymmetries was applied, but a corresponding uncertainty component was taken into account according to Kossert (2021).

A background correction was carried out for all measurements using experimental data from appropriate background samples.

As discussed by Kossert and Mougeot (2021), the determination of the quench-indicating parameter (QIP) can be biased when using commercial LS counters. The effect depends on the radionuclide under study, and it was clearly visible when measuring high-energy beta emitters. Moreover, the effect depends on the counting rates, and increases when higher sample activities are measured. The QIP bias can be quantified using the background sample as described by Kossert and Mougeot (2021). When studying $^{32}$Si/$^{33}$P, the effect was found to be negligible for almost all measurements carried out in the Wallac spectrometer. For the TriCarb spectrometer some measurements with low counting rates did not require any correction, but corrections had to be applied for higher counting rates (e.g., above 2000 s$^{-1}$). In a few cases, the counting rates were above 3300 s$^{-1}$. In these cases, the TriCarb data were not considered for the activity standardization as we identified problems in that range when studying other radionuclides.

Much of the initial work was spent on finding a suitable composition for the LS samples that should be as stable as possible. This required the production and measurement of a variety of sample compositions, e.g., with different aqueous content. Strictly speaking, the CNET method requires an identical composition for the corresponding tritium samples. In some cases, however, we have only used $^3$H samples with a similar content (e.g., 0.1 mL H$2$O while some $^{32}$Si samples contained only 0.05 mL H$2$O). In such cases, we have thus increased the corresponding uncertainty component for the tracer measurement (see below).

4. The $^{32}$Si solutions studied in this work

Table 1 gives an overview of the solutions that were studied in this work. Further details about the solutions, the measurements and analyses will be given in the following sections. In this paper, we use the solution identifiers and reference dates as defined at PTB (see Table 1).

The solutions were shipped from PSI to PTB in closed Eppendorf vials. When possible, the solutions were measured shortly after arrival at PTB in order to avoid long storage. This is particularly important for comparisons between project partners, and it will also be important when determining the half-life via a combination of activity and mass spectrometry measurements.

After sample preparation, leftovers of the solutions were placed in PTFE containers which were closed and then stored in a screwed glass container. As we shall see later, these measures are not always sufficient to ensure a constant activity concentration of the respective solutions over long periods.

Further samples were produced using specially designed cylindrical plastic scintillators as well as solid Cherenkov samples using custom-designed cylindrical glass materials. These sources were prepared for long-term measurements as an alternative way to obtain the $^{32}$Si half-life. Since these long-term measurements are not the subject of this article, a description of the sources and corresponding test measurements is omitted here.
Table 1
Overview of the $^{32}\text{Si}$ solutions investigated in this work. The materials were purified using ion-exchange chromatography and Si was present in the form of hexafluorosilicate ($\text{H}_2\text{SiF}_6$) (Veicht et al., 2021). The absence of photon-emitting impurities was confirmed by gamma-ray spectrometry measurements carried out at IRA (Nedjadi et al., 2020).

<table>
<thead>
<tr>
<th>Identifier (solution number) and reference date used at PTB</th>
<th>Origin and chemical composition</th>
<th>Arrival at PTB</th>
<th>LS samples prepared at PTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>2774, 1 January 2020, 0:00 CET</td>
<td>PSI (from single active V disc, 5 evaporations); separation: 9 March 2020; solution for ‘proof-of-concept’, 0.5 M $\text{HNO}_3$, $c^{(\text{nat})}\text{Si})=3\mu$g/g</td>
<td>14 May 2020</td>
<td>27 May 2020 (2 series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 series + 1 series with Cherenkov samples</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6 January 2021 (4 series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 November 2021 (1 series, unweighted sample for spectrum analysis)</td>
</tr>
<tr>
<td>2859, 20 July 2021, 12:00 CET</td>
<td>PSI (‘pre-master’, from 6 V discs) 10 evaporations, separation: 23 December 2020; aliquots also for ICP-MS and AMS (after reducing S and P content), 0.5 mol/L $\text{HCl}$, $c^{(\text{nat})}\text{Si})=18\mu$g/g</td>
<td>1 September 2021</td>
<td>8 September 2021 (1 sample series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 November 2021 (1 series, unweighted samples for spectrum analysis)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19 January 2022 (2 sample series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 August 2022 (1 sample series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11 January 2023 (1 sample series)</td>
</tr>
<tr>
<td>2874, 1 January 2022, 0:00 CET</td>
<td>PSI (from single active V disc; #1; 10 evaporations); separation: 14 July 2021, 0.5 M $\text{HCl}$, c $^{(\text{nat})}\text{Si})=3\mu$g/g</td>
<td>29 September 2021</td>
<td>2 February 2022 (2 series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 series</td>
</tr>
<tr>
<td>2875, 1 January 2022, 0:00 CET</td>
<td>PSI (from single active V disc; #2; 30 evaporations); separation: 14 July 2021, 0.5 mol/L $\text{HCl}$, c $^{(\text{nat})}\text{Si})=3\mu$g/g</td>
<td>29 September 2021</td>
<td>26 January 2022 (2 series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 series</td>
</tr>
<tr>
<td>2876, 1 January 2022, 0:00 CET</td>
<td>PSI (from single active V disc; #3; 50 evaporations); separation: 14 July 2021, 0.5 mol/L $\text{HCl}$, c $^{(\text{nat})}\text{Si})=3\mu$g/g</td>
<td>29 September 2021</td>
<td>1 November 2021 (2 series)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 series</td>
</tr>
</tbody>
</table>

5. First measurements with solution 2774

A first $^{32}\text{Si}$ solution was shipped from PSI to PTB in May 2020. The chemical separation was carried out on the 9th of March 2020 and details were described by Veicht et al. (2021). The corresponding chemical separation was meant to be a proof of principle, and afterwards, the methodology was improved for the preparation of further $^{32}\text{Si}$ solutions. The first LS samples were prepared at PTB on the 27th of May 2020, i.e., 79 days after the separation. Two LS sample series were prepared using 15 mL of Ultima Gold (UG) and 0.95 mL of water (1 mL for the background sample) in standard 20 mL glass vials from PerkinElmer. The weighed aliquots of the $^{32}\text{Si}$ solution were in the order of 50 mg.

Small amounts of nitromethane were added to some of the samples to vary the counting efficiency. The samples were measured in various LS counters to apply the CNET method and the TDCR method, and numerous repeat measurements were carried out. The measured LS spectra (Figures and details will be provided below in this section) clearly show the expected shape of $^{32}\text{Si}/^{32}\text{P}$. However, two major problems were identified when analyzing the data that were taken over several months:

1. The counting rates (after decay correction) revealed a decreasing trend of about 0.1% per week. When determining the activity concentration, a similar trend was seen. Interestingly this trend was a bit larger for the CNET method than for the TDCR method. An explanation for this observation will be given below.

2. The activity concentration determined from the first TDCR measurement (about 14.56 kBq/g) was found to be about 1.1% higher than that obtained from the first CNET measurement (about 14.4 kBq/g). An explanation for this phenomenon was found later and will also be discussed below in this paper.

Leftovers of the $^{32}\text{Si}$ solution were transferred to a PTFE container which was then closed and stored inside a glass container. In January 2021, three further series with LS samples were prepared aiming at an improved long-term stability. The first series was again prepared using 15 mL UG in glass vials. Here, however, the weighed portions were about 100 mg and no further water was added. The activity concentrations determined from the first measurements carried out within two days after sample preparation confirmed the previously determined activity concentrations, which indicated that the storage of the solution did not cause significant changes. However, it also confirmed the discrepancy between the two methods of about 1%. Repetition measurements in the TriCarb counter revealed an even worse long-term stability. Within one week, the counting rates were found to be lower by about 0.9%.

Another LS sample series was prepared with the same composition as described above but using high-density polyethylene (HDPE) vials (PerkinElmer). The deviation between the TDCR method and the CNET method was found to be about 1%, i.e., slightly lower than observed with the LS samples prepared in May 2020. The long-term stability was much better than for any sample series so far, with a decrease of about 0.36% in 11 months for TDCR and about 1.4% in 11 months for CNET. Since the stability of these samples is the best so far, the same composition was used for several measurements of the other solutions (see following sections). To simplify the spelling, we introduce the abbreviation "15UG.0.1W_HDPE", which is intended to represent this sample composition.

A third LS sample series was prepared using 15 mL UG AB with no additional water in glass vials. However, since the counting rates were found to be lower by a few percent only after a few days, this sample composition could be ruled out as being suitable for $^{32}\text{Si}$ solutions with this chemical composition ($\text{H}_2\text{SiF}_6$ in 0.5 M $\text{HNO}_3$). A fourth sample series was prepared using glass vials filled with 15 mL UG AB, 0.9 mL of water and a weighed portion of about 100 mg of the $^{32}\text{Si}$ solution. Here, the determined activity concentration derived from the first measurements, which were carried out directly after sample preparation, agreed with the above-stated values obtained with UG-based samples. After about three months, the counting rates were found to be lower by about 1%.

From the above-mentioned analysis we concluded that HDPE vials yield a better sample stability than glass vials. The stability was also found to be better when using UG rather than UG AB. However, the samples with UG in HDPE vials still showed a little trend. In the following we present the sample experiment that was useful to identify a possible cause for the sample instability.

Fig. 3 shows various LS spectra that were recorded in the Wallac 1414 spectrometer with its logarithmic amplification. In all cases, the data were normalized to the counting time (about 1800 s for each spectrum) and a background spectrum was subtracted. The first spectrum (A) was obtained from an LS sample that was prepared on 6th of January 2021 and measured about two days after sample preparation. The sample was prepared with 15 mL UG in a HDPE
vial and contained an aliquot (about 100 mg) of the $^{32}\text{Si}$ solution 2774. The spectrum shows the expected structure which corresponds to the sum of the spectra caused by the decays of $^{32}\text{Si}$ and $^{32}\text{P}$, respectively. The same sample was measured again on the 1\textsuperscript{st} of December 2021 and the corresponding spectrum (B) shows a significant deformation. The high-energy peak is much lower than before, the low-energy peak is much wider and in general the spectrum has more entries at lower channel numbers. It should be noted that such a spectrum deformation is unusual – in other cases, we observe only a little shift towards lower channel numbers and a slightly lower energy resolution. In December 2021, the content of the LS vial was transferred to another HDPE vial (D) and the original vial was rinsed twice with UG. The scintillator used for rinsing was transferred to other HDPE vials (spectra E and F). The original vial was filled with new UG and measured again (C). The corresponding spectrum is even more deformed and the peak that was initially seen at high channel numbers has become a shoulder of the very wide peak at low energies. It is important to note that spectrum C still contains more than 21% of the counts seen in spectrum B. This is remarkable because only a few very small droplets remained in the original vial when the scintillator was transferred, and two further rinsing processes were made. The deformed spectrum as well as the rather high counting rate could be the result of significant sorption effects, i.e., $^{32}\text{Si}$ and/or $^{32}\text{P}$ that attaches to the vial wall (including its bottom) or even diffusion into the vial wall. The corresponding spectra of the vials with the UG used for rinsing (D, E and F) have a similar shape as the initial spectrum recorded in January 2021 (A); spectrum D is just slightly shifted towards lower channel numbers and deformed which is related to a somewhat lower energy resolution. This can be explained by the aging of the scintillator and/or the absorption of oxygen that can reduce the scintillator’s performance.

The spectra A, E and F are shown again in Fig. 4 after a normalization. The spectra E and F have a similar shape as spectrum A. However, a surplus can be seen in the left ($^{32}\text{Si}$) peak. The pipette that was used for the transfer was cut into pieces. The pieces were placed in additional HDPE vials and filled with UG (spectra G, H and I in Fig. 3). Corresponding measurements of all samples thus
made it possible to draw up a balance sheet confirming that no activity was lost.

The spectrum C of the original vial that was rinsed a few times and then filled with UG is again shown in Fig. 5. After the measurements, the liquid scintillator was removed (apart from a few remaining droplets) and the spectrum of the empty vial was recorded (“C, empty”). Then, small amounts of UG were added, and after each addition a spectrum was measured. A few examples of these spectra for 1 mL UG and 16 mL UG are shown in Fig. 5.

Interestingly, the counting rate obtained when measuring the empty vial was quite high and increased only slightly when adding UG. The addition of UG, however, modifies the spectrum shape leading to more events at high channel numbers. Fig. 5 also shows a spectrum that was obtained with a Cherenkov sample, i.e., with an aqueous $^{32}$Si/$^{32}$P solution in a PE vial. This indicates that the shape of the spectrum “C, empty” cannot solely be explained by the Cherenkov effect.

The experiments thus show that the sample instability is likely due to a kind of sorption phenomenon that is supposed to be a slow process. Indeed, the change in counting rates appears to be a rather steady and slow process, too. Thus, we conclude, that the LS measurements that are carried out within a few days after sample preparation can be used for an activity determination and an additional uncertainty component is added to allow for the sample instability. It might be that the scintillator (loaded with $^{32}$Si/$^{32}$P) penetrates the vial wall and/or that the HDPE material itself supports light emission. The experiment itself does not give a precise indication of where the activity is located. Experiments in which the vial was placed on an autoradiography film did not yield any useful new information, which is probably due to the complex geometry.

The phenomenon discussed above, in which the activity attaches itself to or penetrates into the vessel wall, seems to be linked to the fact that plastic vials were used. The rather small amount of water may also be a cause since it may influence the formation of inverse micelles. Fig. 6 shows two spectra of the same LS vial that was measured in May and November 2020, respectively. In this case, the 15 mL UG plus 1 mL water were placed in a glass vial. After about 6 months, the spectrum is shifted towards lower channel numbers, as it is often observed in LS counting, but the spectrum recorded in November 2021 is not as shifted towards lower channel numbers, as it is often observed in LS counting. Fig. 6 below.

In the next section we proceed with the analysis of the solution 2859. This will give us the activity concentration of that solution as well as further valuable information related to the long-term stability.

### 6. Solution 2859 (the “pre-master”)

The solution 2859 was prepared (finally separated) at PSI on 23rd of December 2020 and first measurements at PTB were carried out on 8th of September 2021, i.e., 259 days after the separation. This time difference justifies assuming radioactive equilibrium for the analysis. The sample series was prepared with 15 mL UG in HDPE vials. The weighed portion of the radioactive solution was about 20 mg per sample. Nitromethane was used to vary the counting efficiency. The first and the last LS sample of the sample series were produced with the same composition, i.e., no addition of nitromethane. The results of these two samples are very similar which supports the assumption of a homogeneous activity distribution within the $^{32}$Si solution. On the other hand, the dispersion of the data for this series of samples, as well as for some of the following series of samples, is partly in the range of about 2 per thousand. This is a bit larger than expected and will be taken into account when considering the uncertainty. The counting rates of the samples were higher than 5000 s$^{-1}$ and the TriCarb data were excluded from further analysis.

The activity concentrations derived from the measurements of the first days after sample preparation are very consistent. Fig. 7 shows the results of all individual samples as a function of the counting efficiency. In the case of the TDCR data, the counting efficiency corresponds to the efficiency to detect a coincidence in at least two PMTs, i.e., $\varepsilon = \varepsilon_D$. The results of the two TDCR counters TDCR-M27 and TDCR-M29 agree well and the CNET results from the Wallac counter are in excellent agreement with the TDCR result. Thus, the deviation of approximately 1% that was observed when studying solution 2774 is not seen with this solution. We thus concluded that the discrepancy seen with solution 2774 is neither due to a general problem of the LS measurements (e.g., sample preparation) nor due to the model. Instead, it is assumed that the first solution 2774 contains a radioactive impurity. We will come back to this question below.

The unweighted mean of the CNET results is $a_{\text{CNET}} = 108.86$ kBq/g and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 108.88$ kBq/g. The relative deviation between the two results is only about 0.02%. A summary of the activity concentrations with uncertainties will be given below.

While the analysis of the activity concentration described above included only the measurement data of the early measurements, it is worthwhile to look at further measurement data. These data are shown in Fig. 8. Each data point represents the weighted mean of the individual results of the four radioactive samples. The individual results of each...
sample are based on several repetition measurements ensuring low statistical uncertainties. As for solution 2774, the data show a clear decreasing trend that is more pronounced for the CNET method. The trend of the counting rates can be explained by the slow sorption-like process (see discussion above). For the CNET method, the counting efficiency is derived via the QIP, which is, however, not influenced by the sorption effect. Thus, the QIP values are rather stable and consequently the derived counting efficiency is almost constant, too. Hence, the decreasing trend in the counting rate is not compensated for. The situation is different when looking at the TDCR method. When the radionuclide attaches to the vial wall, the reduction of the triple coincidence counting rates will be higher than the reduction of the double coincidence counting rate. Thus, the TDCR parameter will decrease and, as a consequence, a lower detection efficiency is derived which leads at least to a partial compensation. Indeed, the measured SQP(E) and tSIE values were found to be quite stable with time, whereas the experimental TDCR parameter decreased with time.

6.1. Comparison of LS spectra for solution 2774 and 2859

Since the agreement between the two activity determination methods is much better for solution 2859 than for solution 2774, it was suspected that there might be a radioactive contamination in solution 2774. In this case, LS spectra are expected to yield further valuable information. However, an analysis of the spectra can be difficult due to the following considerations:

- LS spectra strongly depend on the LS sample composition, in particular on the quenching level.
- LS spectra were even found to depend on the counting rate, i.e., composition-matched samples may show a different shape if the activity is different.

![Fig. 6. Two LS spectra of the same LS sample that was measured in May 2020 and November 2020. The sample was prepared with 15 mL UG and 1 mL water in a glass vial.](image)

![Fig. 7. Activity concentration of the $^{32}$Si solution 2859 as obtained from the first sample series (8th of September 2021) for the CNET and the TDCR methods without discarded. The uncertainty bars represent only a statistical component which was calculated as a standard deviation of the mean of several repetition measurements.](image)
The sample and spectrometer characteristics may change with time.

To overcome these problems, a further experiment was designed. LS samples were prepared with aliquots of the solutions 2859 and 2774 using the composition 15UG_0.1W_HDPE. The samples were prepared in the same type of HDPE vials and using the same batch of UG. In addition, the samples were prepared in such a way that the counting rates were not too high and very similar (about 233 s⁻¹). As a consequence, the amounts of solution that could be added were very small (a few μL) and a precise gravimetric determination of the solution mass could not be carried out.

Fig. 9 (left) shows the corresponding spectra from the Wallac counter after background subtraction and normalization to the spectrum content above channel 300. The counting (live) time per 32Si LS sample was about 34600 s (real time: 36000 s). One can identify that the spectrum of solution 2774 contains a surplus of counts at low channel numbers. Fig. 9 also shows a 3H spectrum of a sample with a similar quenching level. The spectrum is very similar to the spectrum obtained by the difference between the two 32Si/32P spectra (see, Fig. 9 (right)).

In a further step of the analysis, the activity content of tritium can be determined. The activity \( A(3H) \) of the \(^3\)H sample used above at the time of the spectrum measurement can be calculated from the known activity concentration of the corresponding \(^3\)H solution, the solution mass and a decay correction. The above spectrum analysis made use of a scaling factor \( k_{\text{scale}} \) in order to match the \(^3\)H spectrum shape with the difference spectrum (Fig. 9, right) at low channel numbers. The \(^3\)H activity in the \(^32\)Si sample can thus be estimated applying \( A('3H') = A('3H') \cdot k_{\text{scale}} \). In addition, the \(^32\)Si activity \( A('32Si,'32P') \) can be determined by applying the efficiency tracing technique. Finally, an activity ratio \( A('3H')/A('32Si,'32P') = 2.9\% \) at the time of the spectrum measurement (22nd of November 2021) or \( A('3H')/A('32Si,'32P') = 3.14\% \) on the reference date (1st of May 2020) was determined. The identification of \(^3\)H and its quantification enable us to apply an impurity correction for the solution 2774 as it will be shown below. It should, however, be noted that the determination is based on the assumption that the solution 2859 is free of any radioactive impurity. In addition, we cannot exclude minimal amounts of further low-energetic impurities in solution 2774, such as \(^{41}\)Ca.

The LS samples that were used for the above analysis and for the
spectra shown in Fig. 9, were also measured in the TriCarb counter. The corresponding spectra are shown in Fig. 10 and support the assumption that solution 2774 contains an \( ^3 \)H impurity.

6.2. Further measurement of solution 2859

Two further sets of samples from solution 2859 were prepared in January 2022. Again, the sample composition 15UG_0.1W_HDPE was used. One idea of these additional measurements was to check the consistency of the TDCR and CNET measurements using two sample series with the same compositions. One of the series should be measured first with the CNET method while the other should be measured at the same time with TDCR. After these initial measurements, the samples were measured using the other method. In this way, we can ensure that slight differences in the results are not due to the remaining small sample instability. The results of both sample series were in excellent agreement and can thus be combined. The results of the individual samples are shown in Fig. 11. The unweighted mean of the CNET results is \( a_{\text{CNET}} = 109.08 \) kBq/g and the unweighted mean of the TDCR results is \( a_{\text{TDCR}} = 109.20 \) kBq/g. The relative deviation between the two results is about 0.22% which is a bit higher than the relative deviation obtained with the first sample series. Moreover, the activity concentration determined from the new measurements is about 0.3% higher than that from the first sample series. This indicates that the storage of the solution is imperfect and could lead to an increasing activity concentration with time (e.g., due to a loss of solvent).

In August 2022, a further sample series with solution 2859 was prepared. This time, the sample composition corresponds to 15 mL UG plus 1 mL HCl (0.5 mol/L) in HDPE vials. The corresponding data are shown in Fig. 12. A number of measurements were carried out in TDCR-M29 and no significant trend can be identified within the first 143 days. Also, the CNET measurements were repeated a few times. After 66 days, the result was found to be 0.155% lower than that obtained from the first measurement. The unweighted mean of the initial CNET results is \( a_{\text{CNET}} = 109.79 \) kBq/g and the unweighted mean of the TDCR results is \( a_{\text{TDCR}} = 109.90 \) kBq/g. The relative deviation between the two results is about 0.1%. The activity concentration is about 0.9% higher than that derived from the measurements of the first sample series. The latter deviation (increase) could again be due to imperfect storage. However, the deviation might also be a consequence of the fact that LS samples were prepared with a different recipe. Thus, a further set of LS samples was prepared in January 2023, as explained in the following.

In January 2023, further samples with solution 2859 were prepared. This time, two samples were prepared with the same recipe as in August 2022, i.e., with 1 mL HCl (0.5 mol/L). Two additional samples were prepared without adding HCl. All samples were prepared using 15 mL of UG in HDPE vials. The samples were measured in the Wallac counter (11 Jan.), TDCR-M29 (12 Jan.) and in the TriCarb (13 Jan.). Measurements were repeated in the Wallac counter (20 Jan.) and in TDCR-M29 (23 Jan.). The results of TDCR-M29 and the Wallac counter are illustrated in Figs. 13 and 14, respectively. The analysis reveals that:

i) The results obtained from the first measurements of the samples without HCl are about 0.2% lower than those obtained from the first measurements of the samples with HCl.

ii) The results of the repetition measurements agree well with the initial results when samples with HCl are considered (relative deviation \( \ll 0.1 \)%).

iii) The results of the repetition measurements are considerably lower (about 0.3% for TDCR; about 0.6% for CNET) when samples contain no HCl.

Fig. 10. Spectra of two composition-matched \( ^{32} \)Si/\( ^{32} \)P LS samples as measured with the TriCarb spectrometer with linear (top left) and logarithmic (top right) scale of the abscissa. The samples were prepared with the solutions 2859 and 2774, respectively. A \( ^3 \)H spectrum is also shown. Its content corresponds to the difference between the two other spectra (see bottom plot).
This experiment confirms that the addition of HCl is important for long-term stability. For future measurements only samples with HCl are considered as being suitable. Moreover, we can conclude that samples without HCl (as used for some of the solutions discussed in this article) can be used for an activity determination only if results of fresh samples are used. In these cases, we apply a correction factor of 1.002 and add an extra uncertainty component of 0.2%. However, this correction is only applied at the end of the analysis (Section 11).

From the LS samples prepared in January 2023 only those with HCl are used to determine the activity concentration. The unweighted mean of the initial CNET results is \( a_{\text{CNET}} = 109.97 \) kBq/g and the unweighted mean of the TDCR results is \( a_{\text{TDCR}} = 110.22 \) kBq/g. The relative deviation between the two results is about 0.23%. The mean activity concentration (110.09 kBq/g) is about 0.2% higher than that derived from the measurements of the August 2022 sample series. Now, this deviation is assigned to imperfect storage.

Fig. 11. Activity concentration of the \( ^{32}\text{Si} \) solution 2859 as obtained from two further sample series (19th of January 2022) for the CNET and the TDCR methods. The uncertainty bars represent only a statistical component which was calculated as a standard deviation of the mean of several repetition measurements.

7. Solution 2874

The above analyses of solutions 2774 and 2859 indicate that solution 2774 contains an \( ^{3}\text{H} \) impurity, but a minor impurity in solution 2859 cannot be completely ruled out. The small deviations between the results from the CNET method and the TDCR method might be due to an unidentified impurity.

Thus, PSI prepared three further \( ^{32}\text{Si} \) solutions that were shipped to PTB. The solutions were prepared from different single proton-irradiated vanadium discs. The solutions were also subjected to a further process which we refer to hereafter as “evaporation”. In this process the aqueous amount was significantly reduced, but complete dryness was avoided to prevent larger losses of \( ^{32}\text{Si} \). The aqueous fraction (solvent) was then replaced, and further similar evaporation steps were carried out. Ten evaporations were carried out for solution 2874, 30 for solution 2875 and 50 for solution 2876.

Fig. 12. Activity concentration of the \( ^{32}\text{Si} \) solution 2859 as obtained from one further sample series (31st of August 2022) for the CNET and the TDCR methods. The uncertainty bars represent only a statistical component which was calculated as a standard deviation of the mean of several repetition measurements.
It should be noted that similar (but fewer) evaporations were also carried out when preparing solutions 2774 and 2859. Two sets of samples with the solution 2874 were prepared in February 2022. Again, the sample composition 15UG_0.1W_HDPE was used. Also, here, one of the sample series was first measured with the CNET method while the other was measured in a TDCR counter simultaneously. After these initial measurements, the samples were measured using the other method. The results of both sample series were in excellent agreement and can thus be combined. The results of the individual samples are shown in Fig. 15. The unweighted mean of the CNET results is $a_{\text{CNET}} = 17.55$ kBq/g and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 17.60$ kBq/g. The relative deviation between the two results is about 0.28% which is a bit higher than the relative deviations obtained when studying solution 2859.

8. Solution 2875

The methodology used for solution 2874 was also applied to solution 2875 and the two sets of samples with the composition 15UG_0.1W_HDPE were prepared in January 2022. The results of both sample series were in excellent agreement and can thus be combined. The results of the individual samples are shown in Fig. 16. The unweighted mean of the CNET results is $a_{\text{CNET}} = 26.97$ kBq/g and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 27.04$ kBq/g. The relative deviation between the two results is about 0.28% which corresponds to the findings for solution 2874.

9. Solution 2876

For solution 2876 two sets of samples with the composition 15UG_0.1W_HDPE were already prepared in September 2021, i.e., before radioactive equilibrium had been reached. Thus, the ingrowth of $^{32}$P was taken into account assuming that there was no $^{32}$P at time 0 (14th of July 2021). The results of both sample series were in excellent agreement and can thus be combined. The results of the individual samples are shown in Fig. 17. The unweighted mean of the CNET results is $a_{\text{CNET}} = 36.09$ kBq/g and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 36.18$ kBq/g. The relative deviation between the two results is
about 0.26% which is similar to the findings for solutions 2874 and 2875.

After a few measurements that were used to determine the activity concentration, further measurements were carried out to study again the long-term stability. As in previous studies with solution 2774, the derived activity concentration decreases with time. This effect is larger for the CNET method as it can be seen in Fig. 18.

Fig. 19 shows the corresponding counting efficiency as a function of time. As explained above, the quench indicating parameters SQP(E) and tSIE are quite stable and, as a consequence, the derived efficiency is almost constant when applying the CNET method. The situation is different for the TDCR method. Here, the TDCR parameter decreases with time which causes a decrease in the determined counting efficiency. This leads to a partial compensation of the sample instability.

Two additional sets of samples with the composition 15UG_0.1W_HDPE were prepared in January 2022. Here, radioactive equilibrium can be assumed. The results of both sample series were in excellent agreement and can thus be combined. The results of the individual samples are shown in Fig. 20. The unweighted mean of the CNET results is $a_{\text{CNET}} = 36.16 \text{ kBq/g}$ and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 36.22 \text{ kBq/g}$. The relative deviation between the two results is about 0.17%. The activity concentration is in agreement with that obtained from the first two sample series (relative deviation 0.14%).

The analyses of solutions 2874, 2875 and 2876 yield similar deviations between the results of the CNET method and the TDCR method. Thus, we could not identify a significant effect when carrying out more than 10 evaporations.

10. Solution 2774 with impurity correction

In January 2021, one new set of samples with 15 ml UG and 0.1 ml.
H₂O in glass vials was prepared using solution 2774. Here, radioactive equilibrium has been reached. The data were first analyzed as before, i.e., no impurity correction was applied. As a consequence, the derived activity concentration shows a trend when varying the counting efficiency (Fig. 21) and the relative deviation between the results from the CNET method and the TDCR method was found to be about 0.8%. Then, the data were analyzed allowing for an impurity correction assuming $k_{\text{imp}} = A(^3\text{H})/A(^{32}\text{Si}/^{32}\text{P}) = 3.03\%$ at the time of measurements. This activity ratio is taken from the above analysis by applying a decay correction. The consideration of impurities for the CNET method is well-established (Kossert et al., 2015). Here, it is even easier since the $^3\text{H}$ counting efficiency is directly obtained from the tracer measurement.

The experimental TDCR value corresponds to $\text{TDCR}_{\text{Mix}}$ and can thus directly be used to obtain $\epsilon_D(Mix, \lambda)$. The total net counting rate for double coincidences can be expressed by

$$R_{\text{total, net, D}} = A(^{32}\text{Si}/^{32}\text{P}) \left[ \epsilon_D(^{32}\text{Si}/^{32}\text{P}, \lambda) + k_{\text{imp}} \cdot \epsilon_D(^3\text{H}, \lambda) \right]$$

Thus, the $^{32}\text{Si}$ activity is then given by

$$A(^{32}\text{Si}/^{32}\text{P}) = R_{\text{total, net, D}} / \epsilon_D(Mix, \lambda)$$

From the known TDCR_{Mix} one can easily determine the corresponding free parameter $\lambda$, and thus gets also access to $\epsilon_D(^{32}\text{Si}/^{32}\text{P})$. It is

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**Fig. 17.** Activity concentration of the $^{32}\text{Si}$ solution 2876 as obtained from the first two sample series (14th of November 2021) for the CNET and the TDCR methods. The uncertainty bars represent only a statistical component which was calculated as a standard deviation of the mean of several repetition measurements.

**Fig. 18.** Determined activity concentration for solution 2876 as a function of time. All results refer to the same reference date (1 January 2022, 0:00 CET).
important to note that $TDCR_{\text{Mix}} < TDCR = \epsilon_{T}(^{32}\text{Si}/^{32}\text{P})/\epsilon_{D}(^{32}\text{Si}/^{32}\text{P})$. Ignoring the $^3\text{H}$ would therefore lead to an underestimation of the counting efficiency for $^{32}\text{Si}/^{32}\text{P}$. This explains why a tritium impurity has a stronger effect on the TDCR method than on the CNET method.

Fig. 21 also contains the results that were obtained after impurity corrections. The previously observed trends were significantly reduced and the agreement between the CNET method and the TDCR method improved as well. The unweighted mean of the CNET results is $a_{\text{CNET}} = 14.30$ kBq/g and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 14.31$ kBq/g. The relative deviation between the two results is about 0.04%.

A second sample series was prepared on the same day (6th of January 2021) but using the composition 15UG_0.1W_HDPE. The corresponding results are shown in Fig. 22 with and without impurity correction. Again, the results become much more consistent when the impurity correction is taken into account. The unweighted mean of the CNET results is $a_{\text{CNET}} = 14.34$ kBq/g and the unweighted mean of the TDCR results is $a_{\text{TDCR}} = 14.37$ kBq/g. The relative deviation between the two results is about 0.22%.

These results underline the importance of the impurity correction and strongly support the hypothesis of an $^3\text{H}$ impurity.

Two further sample series were prepared using UG AB. The corresponding results of the first measurements are in agreement with the above-stated results. However, since the stability of the samples with UG AB was not satisfactory, we omit a detailed description of the analysis and the results. If the impurity correction is applied to the data that were obtained from the early measurements in 2020, we also get consistent results for the activity concentration.

11. Compilation of all activity results with uncertainties and some conclusions

The aim of this section is to summarize all results in order to determine a final result for the activity concentration of each $^{32}\text{Si}$ solution. It
is helpful to consider all solutions together, as this provides valuable information for the assessment of uncertainties.

Table 2 contains the activity concentrations that were obtained from the measurements described above. Results from early tests or samples with very low stability were omitted.

A first conclusion is that in all cases, the result from the TDCR method is slightly higher than that obtained from the CNET method. The mean value of all relative deviations is about 0.20%. One may now wonder what the cause of this small discrepancy might be. There are minor uncertainties due to the model (e.g., beta spectrum shape and ionization quenching) and, of course, the measurements are prone to systematic effects. However, due to the excellent agreement that was found for $^{90}$Sr/$^{90}$Y (Kossert and Mougeot, 2021), we expect a better agreement for $^{32}$Si/$^{32}$P. As explained above, we quantified the $^3$H impurity with the assumption that solution 2859 is free of any radioactive contaminant, but we cannot exclude the presence of further low-energetic impurities. If we assume – as a thought experiment – that a $^{32}$Si/$^{32}$P solution contains (further) 0.75% $^3$H, the corresponding impurity corrections would cause a reduction of the TDCR results (about −0.3%) and of the CNET results (about −0.11%) and the deviation (mean of all deviations) would vanish. In the following we estimate corresponding uncertainty components for the TDCR method (0.3%) and for the CNET method (0.11%) for all solutions. We emphasize that we have no real evidence for further $^3$H. The analyses of the three solutions with various numbers of evaporation procedures actually suggest the opposite. The estimation for these additional uncertainty components can thus be regarded as a safety measure. The estimated uncertainty would also cover other scenarios, such as the potential presence of $^{41}$Ca as a radioactive impurity.

The analyses in this work also revealed that the spread of individual

Fig. 21. Activity concentration of the $^{32}$Si solution 2774 as obtained from an additional sample series in glass vials (6th of January 2021) for the CNET and the TDCR methods with and without impurity correction. The uncertainty bars represent only a statistical component which was calculated as a standard deviation of the mean of several repetition measurements.

Fig. 22. Activity concentration of the $^{32}$Si solution 2774 as obtained from an additional sample series in HDPE vials (6th of January 2021) for the CNET and the TDCR methods with and without impurity correction. The uncertainty bars represent only a statistical component which was calculated as a standard deviation of the mean of several repetition measurements.
data is a bit larger than expected (e.g., compare with $^{90}$Sr/$^{90}$Y; Kossert and Mougeot, 2021). In a few cases, the results of single samples deviate from other samples by about 0.2%. These deviations are neither caused by the model (in several cases all results agree well) nor by the measurements (samples with deviation for CNET have similar deviation for TDCR). We, therefore, conclude that the occasional fluctuations are due to a slight inhomogeneity of the solutions. This is accounted for by an extra uncertainty component.

A further important observation concerns the reproducibility of results after storage of the solution. Results of samples obtained after a few months of storage were in some cases several per thousand higher than the original results. This is of particular importance for the half-life determination since it must be ensured that the results from activity determination and mass spectrometry are closely linked. For the determination of the final value, we have thus selected the results of the first measurements (excluding stability checks). (Note: the fact that results of new sample series are higher could not be eliminated by changing the $^{32}$Si half-life).

As shown in this paper, the limited long-term stability was more relevant for the CNET method than for the TDCR method. This is also taken into account when estimating the corresponding uncertainty contributions.

Complete uncertainty budgets are shown in Table 3. Some of the components were already discussed, and others were determined following established procedures (Kossert et al., 2015). The uncertainty for the decay corrections was conservatively estimated and can be adopted for all solutions except for solution 2774. The results and uncertainty would be valid even if the half-life of $^{32}$Si was 120 a.

For solution 2774 this particular uncertainty component needs to be increased to 0.13%, since the elapsed time between measurement and reference date is considerably longer than for the other solutions. The uncertainty for the decay correction may be revisited after completing the new half-life determination.

### Table 2
Activity concentrations obtained from the measurements as described in this paper. The table includes only results from measurements using HDPE vials for the LS sources. It should be noted that results that were obtained from LS samples without 1 mL HCl (0.5 mol/L) were corrected (multiplication with 1.002(2)).

<table>
<thead>
<tr>
<th>Solution</th>
<th>Reference date</th>
<th>Month of sample prep.</th>
<th>$a$ in kBq/g from CNET</th>
<th>$a$ in kBq/g from TDCR</th>
<th>Rel. dev. between TDCR &amp; CNET</th>
<th>Combined result: $a$ in kBq/g</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>2774</td>
<td>01/01/2020, 0:00 CET</td>
<td>Jan-21</td>
<td>14.37</td>
<td>14.40</td>
<td>0.22%</td>
<td>14.38</td>
<td>Impurity correction applied</td>
</tr>
<tr>
<td>2859</td>
<td>01/01/2022, 0:00 CET</td>
<td>Feb-22</td>
<td>17.59</td>
<td>17.64</td>
<td>0.28%</td>
<td>17.61</td>
<td>Result from two sample series</td>
</tr>
<tr>
<td>2859</td>
<td>01/01/2022, 0:00 CET</td>
<td>Jan-22</td>
<td>27.02</td>
<td>27.09</td>
<td>0.28%</td>
<td>27.06</td>
<td>Result from two sample series</td>
</tr>
<tr>
<td>2875</td>
<td>01/01/2022, 0:00 CET</td>
<td>Nov-21</td>
<td>36.16</td>
<td>36.25</td>
<td>0.26%</td>
<td>36.21</td>
<td>Radioactive non-equilibrium taken into account.</td>
</tr>
<tr>
<td>2876</td>
<td>01/01/2022, 0:00 CET</td>
<td>Jan-21</td>
<td>36.23</td>
<td>36.29</td>
<td>0.17%</td>
<td>36.26</td>
<td>The result is about 0.14% higher than that from the previous measurement. The difference is assigned to imperfect storage of the solution.</td>
</tr>
</tbody>
</table>

### Table 3
Standard uncertainty components assigned to the activity concentration $a$ of the $^{32}$Si solution 2859 measured by LS counting when using LS samples with 15 mL Ultima Gold and 1 mL of HCl (0.5 mol/L). For samples without additional HCl a further uncertainty component (0.2%) must be added. Very similar uncertainty budgets also hold for solutions 2874, 2875 and 2876. Slightly higher uncertainties are obtained for solution 2774 due to a larger uncertainty assigned to the decay correction (see text).

<table>
<thead>
<tr>
<th>Uncertainty component</th>
<th>TDCR $u(a)/a$ in %</th>
<th>CNET $u(a)/a$ in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counting statistics</td>
<td>0.034</td>
<td>0.071</td>
</tr>
<tr>
<td>Weighing</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Dead time</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Background</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Adsorption</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>TDCR value</td>
<td>0.098</td>
<td>n.a.</td>
</tr>
<tr>
<td>H calibration (uncertainty of $^3$H activity and fact that $^3$H samples sometimes had a slightly different composition)</td>
<td>n.a.</td>
<td>0.11</td>
</tr>
<tr>
<td>Potential low-energetic impurity</td>
<td>0.3</td>
<td>0.11</td>
</tr>
<tr>
<td>Ionization quenching</td>
<td>0.055</td>
<td>0.01</td>
</tr>
<tr>
<td>Sample (in)stability</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>Inhomogeneity</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Model and other decay data</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>PMT asymmetry</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Decay correction</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Combined uncertainty</td>
<td>0.40</td>
<td>0.31</td>
</tr>
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</table>

### 12. Validation and bilateral comparison between PTB and IRA
In this section we describe a few measures to verify some of the results. The determined activity concentrations depend directly on the computed counting efficiencies. In order to validate these calculations, we have also computed the efficiency curves with a stochastic model using a modified version of the MICELLE code (Grau Carles, 2007; Kossert and Grau Carles, 2010; Kossert et al., 2014). The most important modification concerns the beta spectrum calculation. The original calculation was replaced, and the spectrum was read from a file.
generated with BetaShape to ensure that the required effects (atomic exchange effect and screening corrections) were taken into account. The efficiency curves are shown in Fig. 23. The curves are very similar despite the fact the models for the ionization quenching function were slightly different.

A further and more important validation was made by means of a bilateral comparison between IRA and PTB. To this end, PTB provided the raw data from one TDCR measurement of three LS samples and one background sample in TDCR-M29 to IRA. The data were then analyzed in both laboratories and the final results are shown in Table 5. The participants agreed to use the same reference date (27\textsuperscript{th} of January 2022) corresponding to the date when the measurement was carried out.

IRA used its own code to calculate the efficiencies and activities, considering the PMTs asymmetry and the micelle effect (Nedjadi et al., 2017). It uses the full beta spectra of \( ^{32}\text{Si} \) and \( ^{32}\text{P} \), including the screening, atomic exchange, finite size, recoil and radiative corrections. Two ionization quenching functions were used for this comparison. One is based on the electron stopping power from the ESTAR database (ESTAR, 2022) and the corresponding result is denoted with the subscript \( \text{ESTAR} \). The other function is based on the stopping power modelled by Tan and Xia (2012) and the corresponding result is denoted with the subscript \( \text{TX} \).

The results shown in Table 5, for a \( k_B \) value of 75 \( \mu \text{m/MeV} \), can be considered as being in good agreement with relative deviations in the order of 0.1%.

Table 4

<table>
<thead>
<tr>
<th>Solution</th>
<th>Reference date</th>
<th>( a ) in kBq/g from CET</th>
<th>( u(a) ) in kBq/g from CET</th>
<th>( a ) in kBq/g from TDCR</th>
<th>( u(a) ) in kBq/g from TDCR</th>
<th>Final result: ( a ) in kBq/g</th>
<th>Final result: ( u(a) ) in kBq/g</th>
</tr>
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<tr>
<td>2774</td>
<td>01/01/2020, 00:00 CET</td>
<td>14.37</td>
<td>0.06</td>
<td>14.40</td>
<td>0.07</td>
<td>14.38</td>
<td>0.06</td>
</tr>
<tr>
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<td>20/07/2021, 12:00 CET</td>
<td>109.08</td>
<td>0.41</td>
<td>109.10</td>
<td>0.49</td>
<td>109.09</td>
<td>0.41</td>
</tr>
<tr>
<td>2874</td>
<td>01/01/2022, 00:00 CET</td>
<td>17.59</td>
<td>0.07</td>
<td>17.64</td>
<td>0.08</td>
<td>17.61</td>
<td>0.07</td>
</tr>
<tr>
<td>2875</td>
<td>01/01/2022, 00:00 CET</td>
<td>27.02</td>
<td>0.1</td>
<td>27.09</td>
<td>0.12</td>
<td>27.06</td>
<td>0.1</td>
</tr>
<tr>
<td>2876</td>
<td>01/01/2022, 00:00 CET</td>
<td>36.16</td>
<td>0.14</td>
<td>36.25</td>
<td>0.16</td>
<td>36.21</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Table 5

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( a ) in kBq/g, PTB</th>
<th>( a ) in kBq/g, ( \text{IRA}_{\text{ESTAR}} )</th>
<th>relative deviation between PTB and ( \text{IRA}_{\text{ESTAR}} )</th>
<th>( a ) in kBq/g, ( \text{IRA}_{\text{TX}} )</th>
<th>relative deviation between PTB and ( \text{IRA}_{\text{TX}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27.040</td>
<td>27.052</td>
<td>0.04%</td>
<td>27.023</td>
<td>–0.06%</td>
</tr>
<tr>
<td>3</td>
<td>27.053</td>
<td>27.082</td>
<td>0.11%</td>
<td>27.050</td>
<td>–0.01%</td>
</tr>
<tr>
<td>4</td>
<td>27.009</td>
<td>27.055</td>
<td>0.17%</td>
<td>27.024</td>
<td>0.06%</td>
</tr>
<tr>
<td>Mean</td>
<td>27.034</td>
<td>27.063</td>
<td>0.11%</td>
<td>27.032</td>
<td>–0.01%</td>
</tr>
</tbody>
</table>

were carried out at different times and thus parts of the deviations could result from different storage times. It is also noteworthy that both institutions estimated very similar uncertainties, as shown in Table 6.

13. Final conclusions and outlook

In this article, we have reported on a systematic development of analysis methods and LS sample preparations, ultimately leading to a successful activity standardization of \( ^{32}\text{Si} \) with low uncertainty. This is an important step towards a new determination of the \( ^{32}\text{Si} \) half-life for which the number of \( ^{32}\text{Si} \) nuclei has yet to be determined. Several groups of the SINCHRON consortium are working intensively to adapt corresponding mass spectrometry methods but this proves to be very demanding in the case of \( ^{32}\text{Si} \).

Initial discrepancies between the two LS methods can be attributed to a low-energy impurity which was only present in a first \( ^{32}\text{Si} \) solution. It was possible to identify and quantify \( ^{3}\text{H} \) as contaminant and to apply corresponding impurity corrections.

Experimenting with different recipes for LS sample preparation has finally led to samples that are stable over a long period of time. The addition of hydrochloric acid proved to be key, but it must be stressed...
Table 6  
Comparison of final results for the activity concentrations a of various solutions as determined at PTB and IRA. A decay correction was applied to the results from IRA to obtain data for the same reference dates defined at PTB (see, e.g., Table 4). For the decay correction T_{1/2}^{32}Si = 153(19) a was assumed. For solution 2774 (M32Si1) both institutes applied an impurity correction to allow for the $^3$H content.

<table>
<thead>
<tr>
<th>Solution Identifier</th>
<th>PTB a in kBq/g</th>
<th>IRA a in kBq/g</th>
<th>$\sigma(a)$ in kBq/g</th>
<th>relative deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2774 M32Si1</td>
<td>14.38</td>
<td>14.32</td>
<td>0.07</td>
<td>-0.44%</td>
</tr>
<tr>
<td>2874 M32Si1</td>
<td>27.06</td>
<td>26.89</td>
<td>0.09</td>
<td>-0.62%</td>
</tr>
<tr>
<td>2876 M32Si1</td>
<td>36.21</td>
<td>36.17</td>
<td>0.12</td>
<td>-0.11%</td>
</tr>
</tbody>
</table>

that the precise role of the concentration of the stable silicon $c(^{32}\text{Si})$ has yet to be investigated. Stable LS samples are not only relevant when aiming at low uncertainties; some of the samples will continue to be measured and corresponding data may be used for an independent half-life determination in the future.

CRedT authorship contribution statement

Karsten Kossert: Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Mario Veicht: Writing – review & editing, Investigation. Ionut Mihalcea: Investigation. Youcef Nedjadi: Writing – original draft, Methodology, Investigation, Formal analysis. Dorothea Schumann: Writing – original draft, Supervision, Project administration, Investigation, Funding acquisition. Dmytro Symochko: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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