

Long-term stability of carrier-added Ge-68 standardized solutions

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ABSTRACT

Tests for chemical stability were carried out on carrier-added ^{68}Ge solutions prepared and calibrated in 2007 and 2011 to evaluate the suitability of the specific composition as a potential Standard Reference Material. Massic count rates of the stored solutions were measured using a NaI(Tl) well counter before and after gravimetric transfers. The present activity concentration of the 2007 solution was also measured using live-timed anticoincidence counting (LTAC) and compared to the 2007 calibrated value. The well counter data indicated no change in massic count rate to within uncertainties for either solution. The LTAC measurements gave a difference of -0.49 % in the activity concentration 2007 solution over 7 years. However, the uncertainty in the decay correction over that time, due to the uncertainty in the ^{68}Ge half-life, accounted for the majority (0.67 % out of 0.83 %) of the standard uncertainty on the activity concentration. The results indicate that these carrier-added solutions are stable with regard to potential activity losses over several half-lives of ^{68}Ge .

Keywords: Germanium-68, solution stability, reference materials

1. Introduction

Over the past several years, there has been increasing interest in the development of radioactivity standards for ^{68}Ge in equilibrium with its ^{68}Ga daughter. This is due to its applicability in a variety of research areas, including in particle physics for neutrino detector calibration (Piepke and Cook, 1997); in nuclear medicine as a long-lived calibration surrogate for short-lived positron emitters, such as ^{18}F (Doot, *et al.* 2014; Zimmerman and Cessna 2010); and in the development of the $^{68}\text{Ge}/^{68}\text{Ga}$ generator for a variety of radiopharmaceutical applications (Rösch 2013).

Because of its relatively long half-life ($t_{1/2} = 270.95(26)$ d) (DDEP 2015), ^{68}Ge is particularly suited for preparation as a radioactivity solution reference material. Under certain chemical conditions, however, it can become unstable, resulting in losses of activity due to volatility, precipitation, or adsorption (Marinsky 1961, Mirzadeh and Lambrecht 1996). Undissolved tetrahalide Ge compounds are known to be volatile (Marinsky 1961), meaning that potential activity losses can occur from dried droplets of solution in storage vessels. Moreover, the solubility of GeCl_4 in concentrated HCl is low and its solutions are unstable at HCl concentrations above $6 \text{ mol}\cdot\text{L}^{-1}$ (Mirzadeh and Lambrecht 1996; Meinken, *et al.* 2005), suggesting that droplets of a solution of GeCl_4 in even moderately dilute HCl can be made to form precipitates or volatilize during evaporation (which effectively increases the HCl concentration).

Nearly all of the literature that exists on the radiochemistry of Ge deals with carrier-free solutions, since most applications require as high specific activity as possible. However, it is normal practice in national metrology institutes (NMIs) to include carrier ions when the intent is to provide a solution that will be stable for extended periods of time. This is done primarily to minimize adsorption losses of the radioactive ions on the surface of the storage container since, by doing this, the fraction of radioactive ions relative to the total number of ions available for adsorption is small.

So far, a small number of NMIs have reported on the standardization of $^{68}\text{Ge}/^{68}\text{Ga}$, each using a different carrier solution composition. Schönfeld, *et al.* (1994) reported using a master solution containing $0.5 \text{ mol}\cdot\text{L}^{-1}$ HCl with $20 \mu\text{g}$ each of GaCl_3 and GeO_2 per mL of solution. Grigorescu, *et al.* (2004) did not specify the composition of the solution used in their standardization, but it could be assumed that it was carrier-free, since they observed losses of 20 % to 26 % for their dried point sources, despite having precipitated the ^{68}Ge as the much less soluble and less volatile $^{68}\text{GeS}_4$.

In 2008, we reported on the first standardization of $^{68}\text{Ge}/^{68}\text{Ga}$ at the National Institute of Standards and Technology (NIST) (Zimmerman, *et al.* 2008). The solution used at that time consisted of 45 μg each of Ge^{+4} and Ga^{+3} per gram of solution prepared with $0.5 \text{ mol}\cdot\text{L}^{-1}$ HCl, which is about six times the Ga^{+3} concentration and 3 times the Ge^{+4} concentration used by Schönfeld *et al.* (1994). There was no expectation from the literature that the chemistry of the ^{68}Ga would be likely to cause any of the same chemical problems as anticipated for ^{68}Ge (Lewis 1961) when maintained in solution, although Velikyan, *et al.* (2004) noted that volatility losses may still occur for dried samples. For the preparation of the carrier in preparing the original NIST standard in 2008, the addition of Ga^{+3} ions was made out of an abundance of caution and to minimize adsorption.

Since the original standardization in 2007, a few ^{68}Ge calibrations have been performed in our laboratory for outside entities and a large number of in-house measurements have been made, but only recently have we begun considering preparing a set of standardized solution ampoules for distribution as ^{68}Ge reference standards.

One primary concern in the preparation of a solution standard that will be held in inventory for an extended period of time is the chemical and physical stability of the artifact solution. There is, therefore, a desire to have specific information regarding the long-term stability of carrier-added solutions.

In addition to the concern regarding the stability of a potential reference solution, NIST is responsible for preparing the solutions that will be used in an upcoming ^{68}Ge measurement comparison being organized under the aegis of the Consultative Committee for Ionizing Radiation, Section II (Measurement of Activity) of the Bureau International des Poids et Mesures. For the comparison, a solution composition nearly identical to the one used in our original standardization (and in the present

work) is to be used. Thus there is a need to ensure the stability of the solution over the course of the exercise, which could be up to a year.

This study was undertaken to investigate the long-term stability of the carrier-added ^{68}Ge solution used in the NIST ^{68}Ge standard to evaluate its suitability as a standard reference material and to provide assurance of the stability of the solution used in the ^{68}Ge international comparison.

2. Materials and Methods

Two different solutions of ^{68}Ge , each having the composition noted above, were used in these studies. The first, denoted E1A1R2, was prepared in April 2007 as part of the primary standardization studies reported in Zimmerman, *et al.* (2008). The activity concentration at the reference time of those experiments (12:00 EST on 1 May 2007) as measured by live-timed anticoincidence counting (LTAC) (Bobin 2007) was $3.104(18) \times 10^6 \text{ Bq}\cdot\text{g}^{-1}$. The ampoule containing the solution was opened one day after preparation to perform a dilution and the remainder was transferred using a polyethylene pycnometer to another NIST 5 mL ampoule, which was then flame sealed. The ampoule was opened in September, 2013 for another experiment and the remaining solution was again transferred via pycnometer to a NIST 5 mL ampoule, which was then flame-sealed.

The second solution, denoted PE1D, was prepared in October 2011 from a new stock solution of ^{68}Ge and dispensed into several NIST 5 mL ampoules, which were then flame-sealed. Three of the ampoules from that series, PE1DA1, PE1DA2 and PE1DA3, were used in the present study. The ^{68}Ge activity concentration of the master solution had been calibrated several months before using NIST “ 4π ” γ ionization chamber “A” (IC “A”) and the calibration factor determined during the 2007 primary

standardization (Zimmerman *et al.* 2008). Applying the appropriate dilution factors to the solution in the ampoules, the ^{68}Ge activity concentration was $2.24(1) \times 10^4 \text{ Bq}\cdot\text{g}^{-1}$ at the reference time of 12:00 EST, 2 February 2011. The ampoules from this series were used in several counting experiments since the time of preparation, but remained sealed the entire time.

The experiments described in this paper were conducted in July and November of 2014, thus the “ages” of E1A1R2 and PE1D, in terms of time elapsed after preparation of the original solution, were nominally 87 months to 91 months and between 34 and 38 months, respectively.

Each of the ampoules, as well as blank sample holders (including specially constructed plastic ampoule adapters), was counted 4 times for 3 minutes live time per counting cycle in a Wallac Wizard 2480 (PerkinElmer, Waltham, MA)¹ gamma well counter (γwc). The total number of counts in the spectra ranged from 1.1×10^6 to 1.6×10^6 . Each ampoule was opened and the contents were gravimetrically transferred to a new ampoule via polyethylene pycnometer. Each of the new filled ampoules was then flame sealed. Four days later, the ampoules were counted in the γwc for 7 cycles of 3 minutes each.

Since the activity concentration of solution E1A1R2 was low enough to be measured by LTAC, 2 hemisphere sources and a single blank were prepared about one month after the well counter measurements by adding nominally 31 mg of solution E1A1R2 to each hemisphere, which contained 3 mL of HiSafe III (PerkinElmer, Waltham, MA) scintillant. The LTAC measurements were then performed in the same manner as those performed during the original standardization (Zimmerman, *et al.* 2008).

¹ Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

3. Results and Discussion

The massic count rates from the γ wc measurements were calculated based on the observed counting rates in the entire spectrum and the masses recorded during their respective preparations. For the massic count rates measured after the transfers, the new measured masses were used; for the pre-transfer measurements, the masses recorded during the most recent preparation of each respective ampoule were used.

The average pre- and post-transfer massic count rates for the 4 ampoules, along with the percent differences, obtained from the γ wc measurements are given in Table 1. The uncertainties on each of the average count rates are the standard deviations on 4 or 7 measurements on each source. Routine quality control measurements with an ^{129}I check source indicate that the measurement reproducibility is on the order of about 0.2 % and this component was added in quadrature along with the standard deviations of the pre- and post-transfer massic counting rates to form the uncertainty on the percent difference. The maximum difference for the four samples was 0.25 % and not surprisingly, this was for the oldest of the solutions. Solution E1A1R2 was also the only solution to exhibit a difference in measured massic count rate that was larger than the respective pre- and post-transfer uncertainties. In every case, however, the percent difference in massic count rate is consistent to within uncertainties with zero change.

For the sake of comparing the new LTAC activity for solution E1A1R2 to the original calibrated value, the nuclear data used to analyze the LTAC data in this study were the same as used in Zimmerman *et al.* (2008), although the recommended values for the positron emission probabilities in the ^{68}Ga daughter

have since been updated. The currently recommended value is $P_{\beta^+} = 0.8888(41)$ (DDEP 2015), compared to the value of $P_{\beta^+} = 0.8914(15)$ that was used in 2007.

The LTAC activity concentration for E1A1R2, when decay-corrected to the original calibration reference time, was measured to be $3.089(26) \times 10^6 \text{ Bq}\cdot\text{g}^{-1}$. The relative combined standard uncertainty is 0.83 %, with the largest component (0.67 %) due to the uncertainty in the ^{68}Ge half-life and the decay correction over 7 years. Comparing the old and new activity concentration values, the new LTAC measurement gives an activity concentration that is 0.49 % lower than the original calibrated value, which is well within the uncertainties from both the original standardization and the present measurements.

The measurements in this study clearly indicate that the composition used in our original 2007 standardization of ^{68}Ge gives a solution whose activity concentration is stable with respect to adsorption, volatility, precipitation, and other activity losses over about 7 years. The γ_{wc} data suggest that no change in activity concentration could be seen for the solution that had been stored for 3 years. For the 7 year old solution that had undergone several manipulations prior to this study, the γ_{wc} data indicated a magnitude of 0.25 % for possible effects to be seen, although this is still within the normal measurement variability for that instrument.

The LTAC data provided additional evidence of the stability of the solution by recovering the activity concentration of the 7 year old solution that had undergone several manipulations to within experimental uncertainties. Even without the large uncertainty component due to the 7-year decay correction, the activity concentration obtained in the present work is in agreement with the previously calibrated value.

For most applications, one would expect that a calibrated ^{68}Ge solution could have a useful shelf life of about 3 half-lives (2.22 years), by which time the activity concentration would have decreased by an order of magnitude. These studies demonstrate that a solution containing a small amount of Ga^{+3} and Ge^{+4} ions in $0.5 \text{ mol}\cdot\text{L}^{-1}$ HCl (45 μg each of Ge^{+4} and Ga^{+3} per gram of solution) is stable against activity losses during transfers within this time period. Concerns about the possibility of losses in similar solutions distributed as part of an ongoing international comparison of ^{68}Ge can also be assuaged as a result of these studies.

4. Conclusion

By applying two different methods to study potential losses in two carrier-added (45 μg each of Ge^{+4} and Ga^{+3} per gram of solution in $0.5 \text{ mol}\cdot\text{L}^{-1}$ HCl) solutions of $^{68}\text{Ge}/^{68}\text{Ga}$, we have established that these types of solutions are stable over a period of at least 7 years. No losses of activity were observed when transferring solutions from one glass ampoule into another, even after having been stored for up to 3 years. The activity concentration of a solution that was standardized in 2007 was recovered within measurement uncertainties 7 years later when using primary standardization methods.

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Table 1. Massic count rates for ^{68}Ge solution ampoules before ($R_{m,\text{Pre}}$) and after ($R_{m,\text{Post}}$) transferring into new ampoules, as measured in the gamma well counter (γwc). The quoted uncertainties are the standard deviations on either 4 (for $R_{m,\text{Pre}}$) or 7 (for $R_{m,\text{Post}}$) measurements of the massic count rate for each ampoule. The difference (in percent) between the count rates is given in the final column. The uncertainty on the percent difference includes an additional component of 0.2 % corresponding to measurement reproducibility.

Ampoule	$R_{m,\text{Pre}} \text{ (s}^{-1}\cdot\text{g}^{-1}\text{)}$	$R_{m,\text{Post}} \text{ (s}^{-1}\cdot\text{g}^{-1}\text{)}$	$\Delta, \%$
E1A1R2	2651.2(14)	2657.7(36)	+0.25(25)
PE1DA1	1266.2(20)	1266.7(16)	+0.04(29)
PE1DA2	1265.7(15)	1267.1(14)	+0.11(26)
PE1DA3	1265.4(12)	1266.1(14)	+0.06(24)