Optimization of BeO formation parameters for the measurement of ^{10}Be by AMS.

L. R. Romero[1], C. J. Ramírez-Martínez[1], C. G. Méndez-García[2], S. Padilla[3], C. Solís[4] and H. Huerta[4].

liviaromero@estudiantes.fisica.unam.mx

[1] Facultad de Ciencias, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico.
[2] INVESTIGADORA POR MÉXICO CONACyT - Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico.
[3] Facultad de Ciencias Experimentales, Universidad de Huelva, España.
[4] Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico.

Abstract. ^{10}Be has been widely studied over the last few years. The sensitivity offered by the Accelerator Mass Spectrometry technique (AMS) expands the efficient detection of ^{10}Be by 4-5 orders of magnitude. The chemical species most used in the measurement of ^{10}Be by AMS is beryllium oxide (BeO), which has been shown to offer the best conditions for measurements. In this work, several parameters in the BeO formation have been analyzed. The results show the efficiency of the protocol used but suggest that using Ag instead of Nb as a conductor could improve the measurement conditions.

1. Introduction

^{10}Be is a radioisotope usually produced by the interaction of cosmic rays with the components of the atmosphere, which are ^{14}N and ^{16}O. It is also produced, in smaller amounts, in the rocks by spallation reactions[1]. Meteoric ^{10}Be occurs mainly in the lower stratosphere and upper troposphere, with residence times of several years and about two weeks, respectively[2]. During these times, various atmospheric mixing occurs, such as stratosphere-troposphere exchange and atmospheric deposition transport that can influence surface ^{10}Be concentrations and deposition fluxes. ^{10}Be is attached to aerosols and is subsequently deposited on the earth's surface[1]. Once deposited on the surface, ^{10}Be adsorbs on particles with a pH greater than 6.

Meteoric ^{10}Be has been widely applied to different problems in recent decades. The study in rainwater[3-6], surface sediments[7-9], ice cores[10-11] and particulate matter[12-16] provides important information related to production and distribution in the atmosphere. It is also used to study atmospheric mixing, stratosphere-troposphere, as well as exchange and seasonal variations, which can provide the transport time from production to surface deposition of this radioisotope.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

The high sensitivity of AMS allows precise measurements of ^{10}Be concentrations in samples, in some cases, it is even the only possible way to quantify it. ^{10}Be half - life ($t_{1/2}$=1.36$\pm$0.07 Ma)[2] making it a perfect candidate for dating samples, landscape reconstruction, and the study of erosion surfaces. It is considered an environmental tracer[3]. The AMS facility at the National Laboratory of Accelerator Mass Spectrometry (LEMA), is based on a 1 MV High Voltage Europe Engineering isotope separator. Recently, new lines of research began to be opened for the analysis of ^{10}Be in environmental samples with different applications.

The ^{10}Be extraction protocols used at LEMA look for the best conditions for measuring efficiency and lowest background contributions given its low natural abundance. The optimization is essential since it maximizes current and stability, with which better statistics and higher precision in the ^{10}Be/^{9}Be ratio are obtained, resulting in more accurate ^{10}Be concentrations[1]. In this work, some parameters from the initial protocol were analyzed to have an optimized protocol. The optimal parameters were found in beam transmission, currents, and stability.

2. Methodology

The general protocol used for the extraction of ^{10}Be in natural samples is shown in Figure 1, its purpose is to extract Be from the samples and precipitate it as BeO, which can then be used as a target for the AMS measurement.

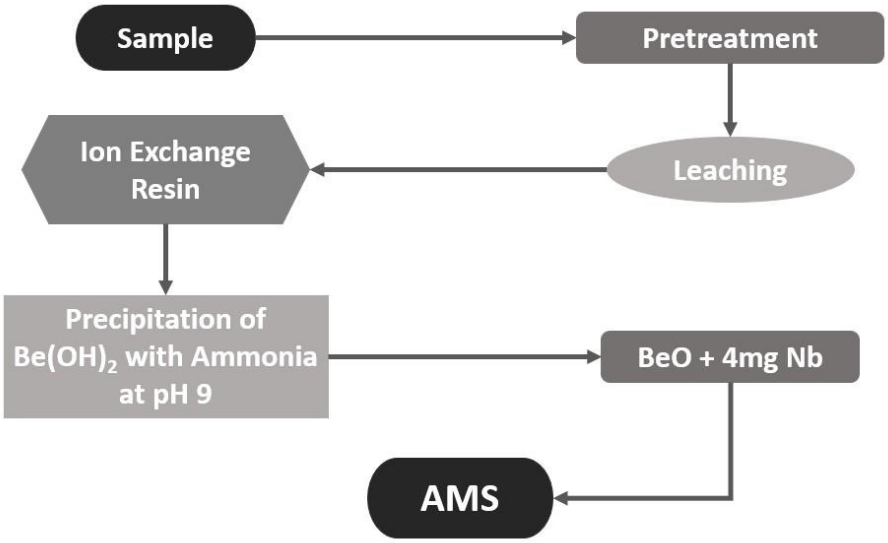

Figure 1. General diagram of measurement of ^{10}Be.

The protocol begins by adding ^{9}Be in the samples because AMS requires high currents of the stable isotope, and the presence of ^{9}Be is null in natural samples. Then, the samples are then pre-treated (depending on their origin) and leached with different acids to make ^{10}Be available. After leaching, ^{10}Be is separated and purified using different ion exchange resins. Firstly, the samples are passed through an anion exchange resin Bio-Rad AG1-X8, to remove Fe and Mg, after ^{10}Be is separated using cation exchange resin AG50W-X8.

The result of the previous step is the purified Be fraction dissolved in a slightly acidic dilution. From this dilution, the Be is precipitated as $Be(OH)_2$ by the addition of ammonia to pH = 9. The $Be(OH)_2$ is freeze-dried for 24 h and subsequently calcined in a furnace at 1000°C for 1 h, whereupon BeO is obtained. This BeO is mixed with 4 mg which serves as a thermoelectric conductor to promote the formation of negative ions. Finally, the BeO + Nb mixture is pressed on aluminium cathodes and measured by AMS for 1h. Measured isotopic ratios $^{10}Be/^{9}Be$ were normalized to a standard sample with $^{10}Be/\ ^{9}Be = 2.709\times10^{-11}$ [18].

For the optimization of the BeO formation parameters, the intensity and stability of the beam currents were analyzed. In this case, ^{10}Be targets were prepared from 250 µL of the standard ^{9}Be dilution ($Be_4O(C_2H_3O_2)_6$ standard, 1000 mg/L for ICP-MS, Merck). Each variation in the different parameters was done in triplicate.

The first parameter analyzed was pH, the pH value established in the protocol is 9, in this study, the current variations were analyzed with BeO formed from $Be(OH)_2$ precipitated with ammonia at pH 7, 9, and 12. The second parameter was the calcination temperature; temperatures of 900°C, 1000°C, and 1100°C were examined. Lastly, the third and fourth parameters were the variations with different metallic matrices and their ratios.

The tuning was performed at +1 charge state both at the accelerator output and after the passive absorber (75 nm silicon nitride window)[19-20]. The behaviour and evolution of the beam currents of the different variations were measured in the high-energy zone every five minutes.

3. Results

The results of variation of pH, calcination temperature, and different carrier metals mixing are shown in Figures 2-6.

The pH variation to obtain $Be(OH)_2$ (Figure 2) shows that the best currents were obtained with a pH=9; at pH=7, the currents differ by 6.9% compared to pH=9, but these were more unstable. Whereas higher pH did not turn out to be optimal.

Figure 3 shows the calcination temperature variation. At 1000°C, the highest currents and beam stability are achieved; at higher temperatures, there is the best stability and produces 9.9% lower currents than 1000°C, but the smaller temperatures reduce 39.4% the currents compared to higher currents.

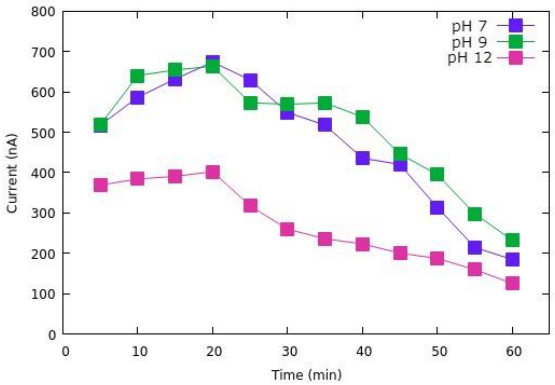

Figure 2. Results of pH Variation.

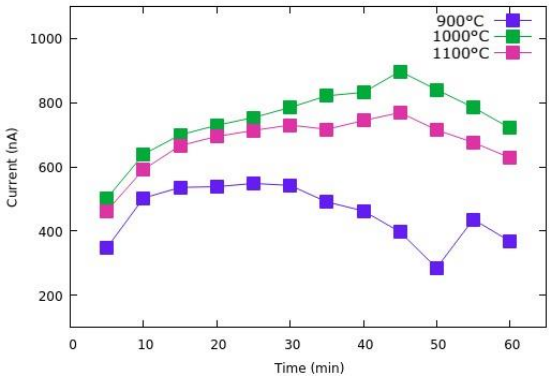

Figure 3. Results of Temperature Variation.

For different carrier metals (Figure 4), with iron (Fe), the lowest currents are obtained, and copper (Cu) increases them by 21.9%, both are unstable. On the contrary, niobium (Nb) and silver (Ag) generate the highest currents having an improvement of 53.8% and 57.6%, respectively, compared to Fe, and present good stabilities.

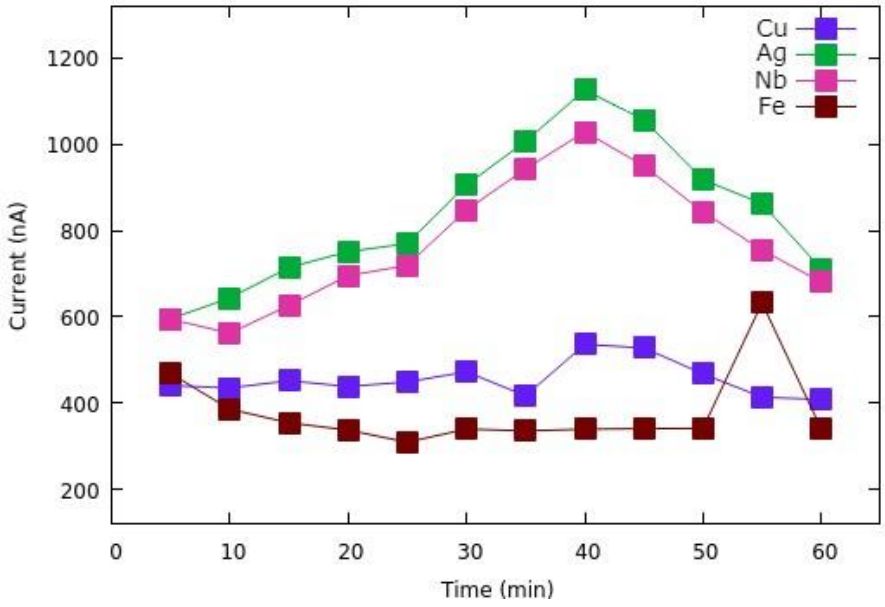

Figure 4. Results of Carrier Metal Variation.

By analyzing different proportions of the carrier metal used in the protocol and exchanging it for silver, the following results are obtained. For Nb (Figure 5), 1:1 and 1:2 ratios give lower currents; 1:3 ratio showed an increase in current of 92.2% compared to 1:1 ratio; higher ratios (1:4 and 1:5) duplicate the currents of 1:3 ratio; in the stability for ratios 1:4 and 1:5, no defined stability plateau is observed, however, the variations between currents are slight up to minute 40, which allows measuring ^{10}Be in natural samples. For Ag (Figure 6), with 1:3 ratio, the currents are small and have a difference of 4.7% with 1:4 ratio; but the best currents are achieved with 1:5 and 1:6 ratios, with a little difference between them (1.9%); all ratios present similar stability.

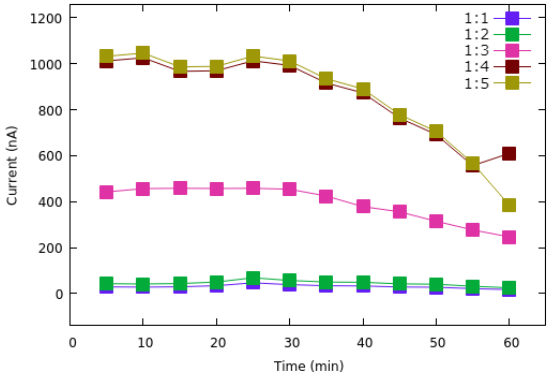

Figure 5. Results of the Niobium Proportions.

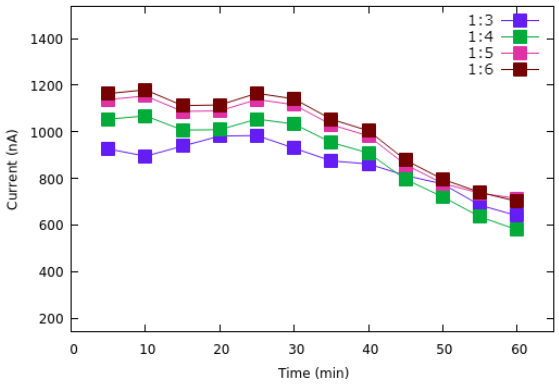

Figure 6. Results of the Silver Proportions.

Finally, the initial and optimized protocol was applied to real samples, the figure 7 the results with Ag show improvement in the currents and stability with a percentual difference of 25.6% compared to the initial protocol. The concentrations of ^{10}Be in the samples that were applied to the optimized protocol showed a lower uncertainty with respect to the initial protocol, 4 and 7%, respectively.

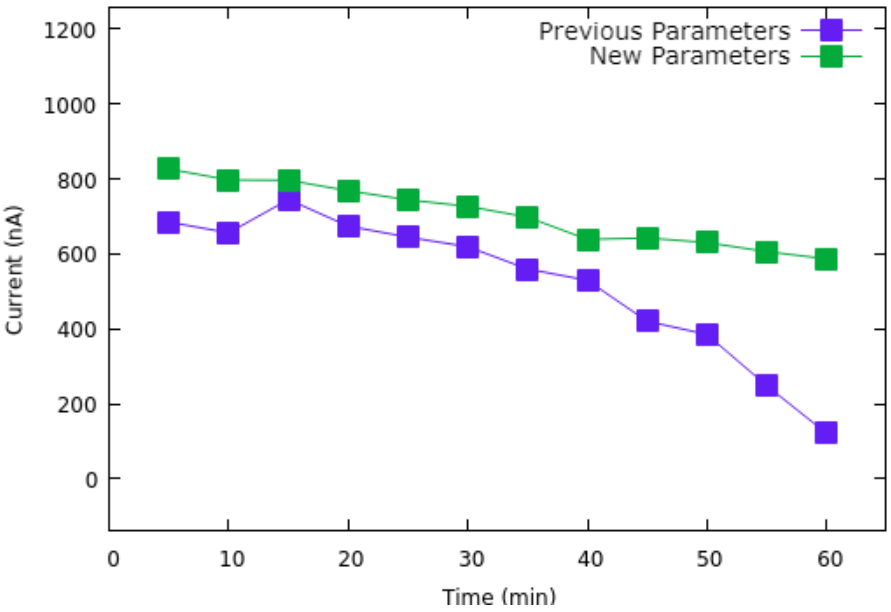

Figure 7. Comparison of Results with Nb and Ag.

4. Conclusion

The initial protocol (pH=9, calcination temperature at 1000°C and Nb mixture 1:4) showed great efficiency when obtaining high currents for ^{10}Be extraction, however, it was also found that changing from Nb to Ag carrier metal at 1:5 ratio achieved more significant beam currents and lower uncertainties in ^{10}Be concentration measurements. This change, when applied to natural samples, maintains the improvement observed in the blanks. For its use, a cost-benefit study with respect to Nb is recommended.

References

[1] S. Padilla, J.M. López-Gutiérrez, D.M.R. Sampath, T. Boski, J.M. Nieto, M. García-León, Determination of denudation rates by the measurement of meteoric 10Be in Guadiana river sediment samples (Spain) by low-energy AMS, J Environ Radioact. 189 (2018) 227–235. https://doi.org/10.1016/j.jenvrad.2018.04.016.

[2] G.M. Raisbeck, F. Yiou, Depositional rate and seasonal variation in 10Be precipitation, Nature. 282 (1979) 279–280.

[3] I. Graham, R. Ditchburn, B. Barry, Atmospheric deposition of 7Be and 10Be in New Zealand rain (1996-98), Geochim Cosmochim Acta. 67 (2003) 361–373. https://doi.org/10.1016/S0016-7037(02)01092-X.

[4] K.J. Kim, Y. Choi, Y.Y. Yoon, Monitoring 7Be and tritium in rainwater in Daejeon, Korea and its significance, Applied Radiation and Isotopes. 109 (2016) 470–473. https://doi.org/10.1016/j.apradiso.2015.11.094.

[5] C. Tiessen, D. Bemmerer, G. Rugel, R. Querfeld, A. Scharf, G. Steinhauser, S. Merchel, Accelerator mass spectrometry (AMS) for beryllium-7 measurements in smallest rainwater samples, J Radioanal Nucl Chem. 319 (2019) 965–973. https://doi.org/10.1007/s10967-018-6371-6.
[6] C.G. Méndez-García, S. Padilla, G. Rojas-López, R. García, C. Solís, E. Chávez, A. Huerta, K. De los Ríos, Atmospheric deposition of 10Be in Altzomoni rainfall, Nucl Instrum Methods Phys Res B. 536 (2023) 60–66. https://doi.org/10.1016/j.nimb.2022.12.020.
[7] L.R. McHargue, A.J.T. Jull, A. Cohen, Measurement of 10Be from Lake Malawi (Africa) drill core sediments and implications for geochronology, Palaeogeogr Palaeoclimatol Palaeoecol. 303 (2011) 110–119. https://doi.org/10.1016/j.palaeo.2010.02.012.
[8] M. Frank, B. Schwarz, S. Baumann, P.W. Kubik, M. Suter, A. Mangini, A 200 kyr record of cosmogenic radionuclide production rate and geomagnetic field intensity from 10Be in globally stacked deep-sea sediments, Earth Planet Sci Lett. 149 (1997) 121–129. https://doi.org/10.1016/s0012-821x(97)00070-8.
[9] B.S. Amin, D. Lal, B.L.K. Somayajulu, Chronology of marine sediments using the 10Be method: intercomparison with other methods, Geochim Cosmochim Acta. 39 (1975) 1187–1192. https://doi.org/10.1016/0016-7037(75)90060-5.
[10] J.A. Abreu, J. Beer, F. Steinhilber, M. Christl, P.W. Kubik, 10Be in ice cores and 14C in tree rings: Separation of production and climate effects, Space Sci Rev. 176 (2013) 343–349. https://doi.org/10.1007/s11214-011-9864-y.
[11] J. Jouzel, G. Raisbeck, J.P. Benoist, F. Yiou, C. Lorius, D. Raynaud, J.R. Petit, N.I. Barkov, Y.S. Korotkevitch, V.M. Kotlyakov, A comparison of deep Antarctic ice cores and their implications for climate between 65,000 and 15,000 years ago, Quat Res. 31 (1989) 135–150. https://doi.org/10.1016/0033-5894(89)90003-3.
[12] C.G. Méndez-García, G. Rojas-López, S. Padilla, C. Solís, E. Chávez, L. Acosta, A. Huerta, The impact of stable 27Al in 26Al/10Be meteoric ratio in PM2.5 from an urban area, J Environ Radioact. 246 (2022) 106832. https://doi.org/https://doi.org/10.1016/j.jenvrad.2022.106832.
[13] C.G. Méndez-García, S. Padilla, C. Solís, K. De los Ríos, E. Chávez, R. García, L. Acosta, A. Huerta, Meteoric 10Be concentrations in the center of Mexico, J Radioanal Nucl Chem. 322 (2019) 1455–1460. https://doi.org/10.1007/s10967-019-06841-x.
[14] S. Padilla Domínguez, Medidas de 10Be y 26Al en espectrometría de masas con acelerador de baja energía en el Centro Nacional de Aceleradores, (2015). http://hdl.handle.net/11441/32023 (accessed May 10, 2017).
[15] K. De Los Rios, C. Méndez-Garcia, S. Padilla, C. Solis, E. Chávez, A. Huerta, L. Acosta, Characterization of the LEMA isotope separator to measure concentrations of 10Be from atmospheric filters, J Phys Conf Ser. 1078 (2018). https://doi.org/10.1088/1742-6596/1078/1/012009.
[16] S. Padilla, J.M. López-Gutiérrez, G. Manjón, R. García-Tenorio, J.A. Galván, M. García-León, Meteoric 10Be in aerosol filters in the city of Seville, J Environ Radioact. 196 (2019) 15–21. https://doi.org/10.1016/j.jenvrad.2018.10.009.
[17] C. Solís, E. Chávez-Lomelí, M.E. Ortiz, A. Huerta, E. Andrade, E. Barrios, A new AMS facility in Mexico, Nucl Instrum Methods Phys Res B. 331 (2014) 233–237. https://doi.org/10.1016/j.nimb.2014.02.015.
[18] K. Nishiizumi, M. Imamura, M.W. Caffee, J.R. Southon, R.C. Finkel, J. McAninch, Absolute calibration of 10Be AMS standards, Nucl Instrum Methods Phys Res B. 258 (2007) 403–413. https://doi.org/10.1016/j.nimb.2007.01.297.
[19] E.C. Calvo, F.J. Santos, J.M. López-Gutiérrez, S. Padilla, M. García-León, J. Heinemeier, C. Schnabel, G. Scognamiglio, Status report of the 1 MV AMS facility at the Centro Nacional de Aceleradores, Nucl Instrum Methods Phys Res B. 361 (2015) 13–19. https://doi.org/10.1016/j.nimb.2015.02.022.
[20] G. Scognamiglio, Optimization of 10Be and 26Al detection with low-energy accelerator mass

spectrometry, University of Seville, 2017