Proc Indian Natn Sci Acad **86** No. 3 September 2020 pp. 1233-1238
© *Printed in India.* DOI: 10.16943/ptinsa/2019/49707

Research Paper

Use of Suitable Metal Matrix for Ion Current Enhancement During ^{10}Be AMS Measurement at IUAC, New Delhi

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(Received on 15 September 2018; Revised on 24 June 2019; Accepted on 25 June 2019)

An experiment was designed to find out suitable metal matrix for higher, stable and long-running BeO$^-$ beam current during ^{10}Be AMS measurements at Inter University Accelerator Centre (IUAC), New Delhi. Samples were prepared either by mixing BeO with metal matrix, or by co-precipitating *Be*-hydroxide and matrix of metal cation. The metals used were *Nb*, *Ag*, *Cu* and *Re,* and the effect of which were being studied. This systematic investigation shows the *Be* mixed with fine *Nb* powder gives rapid ionization and higher current than other mixtures, which is also in concordance with earlier studies at other AMS labs. However, *Be-Cu* co-precipitated sample also provides higher and stable beam current compared to Be-Ag co-precipitates.

Keywords: AMS; ^{10}Be; Beam Current; Powder Mixing; Co-Precipitation Mixing

Introduction

The abundance of cosmogenic radionuclides, such as, ^{10}Be, ^{26}Al in the natural samples like ice cores, seawater, quartz, soil, sediments and meteorites is often low and the sample quantities are usually limited. Accelerator Mass Spectrometry (AMS) has proved to be an excellent technique for measurement of such scanty cosmogenic radionuclides present in these samples. Our group is involved in the systematic study of glacier retreat in the upper Alakananda basin, Garhwal Himalaya as well as Schirmacher oasis, East Antarctica using cosmogenic radionuclides (^{10}Be and ^{26}Al) surface exposure dating. During the measurement of *in situ* ^{10}Be, the statistics are poor due to lower ion current especially in the samples having short exposure history. Natural samples have to pass through a series of chemical processes to extract *Be* prior to the AMS measurement.The final step of the chemical procedure is to convert *Be* to a suitable chemical compound, usually oxide for AMS measurement. For ^{10}Be measurement, prepared BeO is pressed into cathode tube and BeO$^-$ is extracted from the ion source. Negative ion is required to be extracted from the ion source of an AMS system. Sputtering of target material is carried out with Cs$^+$ ions. *Cs* also forms a monolayer on the target surface and when the sputtered atoms pass through *Cs* monolayer, they take electrons from *Cs* (*Cs* is most electropositive stable element). An extraction system extract out the negative ions of target material from the ion source. Preference of BeO$^-$ ions over *Be*$^-$ during ^{10}Be measurement is due to low electron affinity of *Be* and very low efficiency for formation of *Be*$^-$ ions (Klein *et al.,* 1982; Tuniz *et al.,* 1998). BeO alone cannot be ionized efficiently to achieve sufficient current therefore, BeO is generally mixed with metal powders such as *Nb* or *Ag* or *Cu* to enhance the electrical and thermal conductance and ionization potential (Fink *et al.*, 2000; Stone *et al.*,

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2004; Hunt *et al.*, 2006; Berggren *et al.*, 2010; Kumar *et al.*, 2011). Mixing of these metal matrixes can be carried out by two methods; a) powder – powder mixing, i.e., mixing metal powder after converting natural sample into BeO powder form, b) co-precipitate mixing, i.e., mixing metal prior to precipitation of hydroxide (Stone *et al.*, 2004). Various experiments have been reported for enhancing BeO ion current using different ratios of metal matrix (Fink *et al.*, 2000; Stone *et al.*, 2004; Hunt *et al.*, 2006; Berggren *et al.*, 2010; Kumar *et al.*, 2011; Raisbeck *et al.*, 1987) by both powder mixing and co-precipitation mixing method (Table 1). As ion source design, ion source parameters, type of matrix and oxide:matrix ratios varies at different AMS laboratories, therefore, ion yield from sample differ at different facilities. Effect of matrix on beam current is evident from the literature, therefore it is important to select suitable metal matrix, its ratio and procedure of mixing to yield higher and longer-lasting beam current at respective AMS facility. We have also carried out this study to understand the behavior of our ion source with different metal matrix, its ratio and procedure of mixing to yield higher and long lasting beam current. The ion source parameters used in this experiment were optimum but not jacked upto their full potential, and therefore, the currents are lower in comparison to the other AMS laboratories. During AMS measurement, the ^{10}Be/^{9}Be ratio of natural samples depends on the ^{10}Be concentration in the material and the amount of ^{9}Be carrier added during the sample preparation. Reduction of the ^{9}Be carrier in the sample will increase the ^{10}Be/^{9}Be ratio as well as analytical precision (Stone *et al.*, 2004), but it will reduce the sample size to be analysed. Therefore, it is necessary to establish a safe and simple procedure to handle a lesser amount of sample during AMS measurement, without reducing the ion source yield and current stabilization. This study is intended to find a suitable metal matrix and its ratio (by comparing BeO$^-$ currents under same ion source conditions) for routine ^{10}Be measurement on natural samples at Inter University Accelerator Centre (IUAC), New Delhi.

For powder-powder mixing method, metal matrixes *Nb*, *Ag*, *Cu* and *Re* were added with BeO. In case of co-precipitation method, *Be* was precipitated with *Ag* and *Cu*. Selections of metal matrices are primarily based on the reported data from different AMS facilities. However, additional *Re* metal powder was chosen here due to its high work function, higher melting points and enhance ionization efficiency of other elements during thermal ionization mass spectrometry (Studier *et al.,* 1962; Mannion *et al.,* 2017). The outcome of this study will be useful in quick and precise ^{10}Be AMS measurement of the natural samples.

The IUAC-AMS facility is based on 15UD Pelletron accelerator along with a MC-SNICS (Multi-Cathode Source of Negative Ions by *Cs* Sputtering), gas and foil stripper, an offset Faraday cup after analyser magnet and a dedicated AMS beam line composed of Wien filter, Quadrupole magnet, a gas cell absorber followed by a multi anode gas ionization chamber (Kumar *et al.*, 2011). The results of the experiments reported in the present study were performed using the injection system of AMS facility (Fig. 1), which is composed of MC-SNICS, dipole magnet followed by Faraday cup.

Methodology

For these experiments 1000 ppm *Be* stock solution was prepared from NIST SRM 3105a standard solution. Known volume of this solution was transferred by pipette into a clean centrifuge tube for *Be* hydroxide precipitation. Since this *Be* solution was acidic, drop wise NH_4OH was added to adjust pH ~8 – 9 to allow precipitation of $Be(OH)_2$. Precipitates were separated by centrifugation (at 3000 rpm for 10 min) and washed repeatedly 3- 4 times with high purity de-ionized Milli-Q® grade water.These precipitates were transferred to a quartz vial and converted to BeO after step heating up to 900ºC in a muffle furnace. The prepared BeO was grounded to fine powder using stainless steel rod prior to mechanically mixing with the different metal matrix. Four different metal powders 1) Niobium (Nb) assay value 99.8% of size 1 to 5 µm, 2) Nb, >5 µm size, 3) Silver (Ag) assay value 99.9% of size 0.02 to 0.04 µm, 4) Copper (Cu) assay value 99.9% of size 0.02 to 0.04 µm and 5) Rhenium (Re) assay value 99.99% of size ~44 µm, were used for powder mixing. The metal powders were volumetrically taken and mixed with BeO thoroughly in a quartz vial using a stainless steel rod. BeO to metal matrix ratio was kept at 1:2. After uniform dispersion of BeO in the metal matrix, aliquots of mixers were filled (3/4th of the hole) into different aluminum cathode tubes, having a cylindrical hole bored into a funnel shaped cavity in one end.

Table 1: Beam current obtained by variety of metal matrix and mixer at different AMS facility. Ratios are w/w unless specified. * mean current of BeO in metal matrix

BeO: matrix	Ratio	Powder Mixing		Co-precipitated		Laboratory	Reference
		Current (µA)	Time (min)	Current (µA)	Time (min)		
BeO pure		3	5			University of Pennsylvania, USA	Middleton, 1984
		11	40				
		5	180 (Stopped)				
BeO:Ag	1:5	10.5	5				
		7.5	40				
		5	Over 10h				
Be:Ag	1:20			2.8		ETH/PSI, Zurich	Stone *et al.*, 2004
Be:Cu		1				VERA, Vienna	Steier *et al.*, 2004
BeO:Nb	1:1 (equimolar)	18.8 (mean)*	Over 24h			LLNL - CAMS, USA	Hunt *et al.,* 2006
BeO:Ag	1:1 (equimolar)	6.7 (mean)*					
BeO:Nb	1: 1.1,	9.6				Uppsala Tandem laboratory	Berggren *et al.,* 2010
	1: 5.4	8.97					
	1: 10	9.76					
	1 : 1 to 56			8.22 to 0.92			
BeO:Ag	1: 1.1,	6.25					
	1: 5.2	5.2					
	1: 10	6.01					
	1: 1 to 13.3			5.84 to 3.94			
BeO:Nb	1:3 (v/v)	1.1				IUAC, New Delhi	Kumar *et al.*, 2011

Co-precipitation mixing of beryllium was carried out with silver and copper. Granular $AgNO_3$ (Merck®, assay > 99.9%) and $Cu(NO_3)_2{\cdot}3H_2O$ (Merck®, assay > 99%) was used for preparing 1000 ppm stock solution. Volumetrically these solutions were mixed with the *Be* 1000 ppm stock solutions, prepared earlier, at two different ratios (at 1:1, 1:2) in separate centrifuge tubes. The pH then raised to ~8-9 by adding drops of 10 % (w/w) Na_2CO_3 and NH_4OH solution for silver and copper mixed solution, respectively (Stone *et al.*, 2004). Beryllium hydroxide with *Ag* and *Cu* hydroxides were precipitated and collected by centrifugation, washed with Milli-Q® grade water and transferred into quartz vials. These co-precipitated mixtures were heated at 100°C, 400°C and finally at 900°C to convert BeO plus conductive *Ag* and *Cu* metal matrix. The small pellets were grounded to fine powder and loaded in to the cathode tubes.

All the samples were placed in the MC-SNICS cathode wheel and analyzed under optimized parameters of ion source described in Kumar *et al.* 2011. Parameters were kept constant throughout the experiment; however, there may be some intermittent fluctuations in the parameters. Magnetic field for injector magnet was set for mass 25 ($^{9}Be^{16}O$). The current was measured at Faraday cup (FC-02) placed after the injector magnet. Hence, the reported current is for mass 25. Current was also measured at another Faraday cup (FC-01) placed between ion source and injector magnet (Fig. 1), but the results are not reported here as it shows the total current produced in the ion source and unanalyzed.

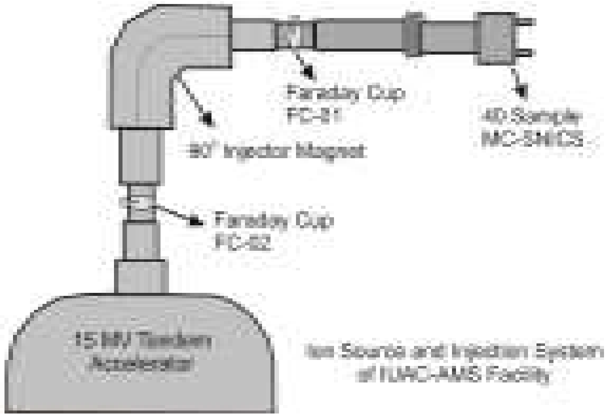

Fig. 1: Schematic of ion source and injection system of IUAC – AMS facility, New Delhi

Results and Discussion

During this experiment, we have tried to select the suitable metal matrix and ratio to get maximum current in less time. As discussed in the methodology, the mechanical mixing of BeO powder with metal matrix and co-precipitated samples with different ratios were analysed on the same day. Depending upon the initial current and current stability, the run durations were different for different mixtures (Tables 2 and 3). The reported beam current for different mixtures is at given run duration after it got stabilized for a minute. Currents observed at FC-02 are reported in the Tables 2 and 3 with type of matrix used for the mixing, BeO to metal ratio and time duration.

Among all the mechanical powder mixed samples, BeO mixed with *Nb* fine powder (1 to 5µm) at 1:2 ratio gave rise to maximum current and stability compared to other prepared samples (Fig. 2). The initial current for this mixture was 1.62µA and which increased to maximum current of 1.71µA after five minute of ionization. The coarse grain *Nb* powder (>5 µm) mixed sample had lower initial current and reached 1.35µA after three minutes of ionization. This indicates that the finer grain metal matrix produces higher ionization current than the coarser metal matrix. This could be due to the better dispersion of finer powder within the sample, which provided interconnected network (conductive) of metal matrix (Stone *et al.*, 2004). For coarser metal matrix, dispersion will be poor hence, BeO beam current is low. The sample prepared with *Ag* metal powder (0.02 to 0.04 µm) shows continuous increase in current with time and reaches its maximum current of 1.08 µA after 12 minute. For *Cu* (0.02 to 0.04 µm) powder mixture yielded maximum current of 0.85 µA after 2 minutes, whereas, for *Re* (~44 µm) maximum current of 0.52 µA was obtained after 3 minutes of ionization (Fig. 2).

Table 2: Measured current for various metal matrixes at different ratios for powder-powder mixing method

Powder mixing (Be: Metal Ratio = 1:2) method	Time (min)	Current (µA)
Be:Nb (*Nb* powder size 1 to 5 µm)	1	1.62
	3	1.67
	4	1.7
	5	**1.71**
Be:Nb (*Nb* powder size > 5 µm)	1	1.3
	3	1.35
Be:Ag (*Ag* powder size 0.02 to 0.04 µm)	1	0.34
	6	0.79
	9	0.9
	12	1.08
	14	1.2
Be:Cu (*Cu* powder size 0.02 to 0.04 µm)	1	0.7
	3	0.85
Be:Re (*Re* powder size ~ 44 µm)	1	0.46
	3	0.52

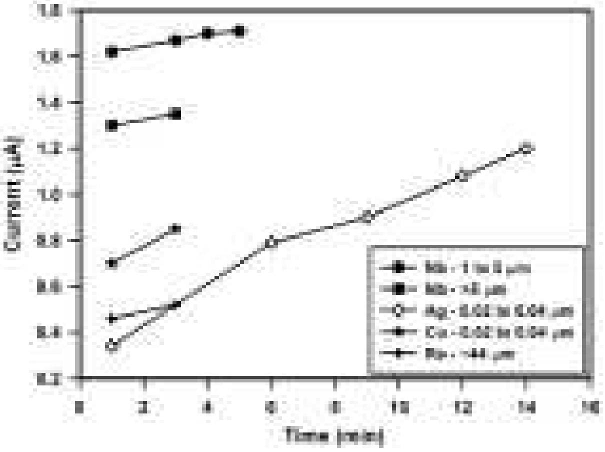

Fig. 2: Beam current for powder mixing samples at different run duration. The BeO to metal matrix ratio is 1:2

Table 3: Measured current for various metal matrixes at different ratios for co-precipitated mixing method

Co-precipitation method

Mixture	Ratio	Time (min)	Current (µA)
Be:Cu	1 : 1	1	0.47
		3	0.79
		4	0.93
		5	1.23
		7	1.52
		8	**1.6**
Be:Cu	1 : 2	1	0.3
		4	0.87
		5	1
		9	1.36
		11	1.4
Be:Ag	1 : 1	1	0.01
		3	0.05
		13	0.58
Be:Ag	1 : 2	1	0.37
		3	0.73
		4	0.97
		6	1.12
		9	1.27

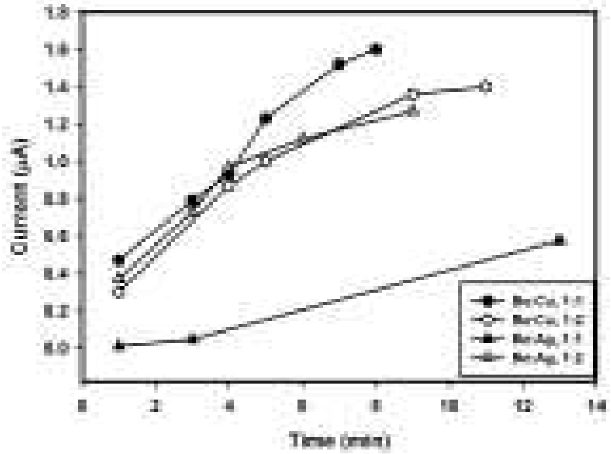

Fig. 3: Beam current for co-precipitated mixing samples at different run duration

Samples prepared from co-precipitation of *Cu* and *Ag* with *Be* were measured for different run duration (Table 2). Maximum current of 1.6 µA was observed from *Be* co-precipitated with *Cu* in 1:1 ratio after eight minutes of ionization and got stabilized. Whereas, increasing *Cu* content in the co-precipitation by two folds, the ionization of the sample decreased. Sample prepared with Be:Cu in 1:2 ratio showed maximum current of 1.4 µA after eleven minutes of ionization (Fig. 3). *Ag* metal matrix in the co-precipitated *Be* samples shows lower current than the *Cu* matrix co-precipitated samples. It is observed that higher the *Ag* concentration in the co-precipitated samples, higher the ion current. Current measured in the Be:*Ag* sample mixed in 1:2 ratio showed maximum current of 1.27µA and got stabilized after nine minutes of ionization. Whereas, sample containing 1:1 ratio of *Be* to *Ag*, gives 0.57µA current after thirteen minutes of ionization (Fig. 3). Lesser amount of *Ag* in the mixture may not be sufficient to encompass the BeO (Stone *et al.*, 2004) and reduces the interconnectivity; therefore, beam current is low.

Co-precipitated *Be*-*Ag* mixture in 1:2 ratio gave stable current in lesser time as compared to powder mixture of same ratio. Whereas, *Be*-*Cu* mixture showed better ionization current and stability compared to *Be*-*Ag* mixture in both the mixing method. All the *Be*:*Ag*/*Cu* mixture requires nearly five minutes or more to produce 1 µA current. Here, *Be*-*Nb* powder mixture showed higher beam current and quick stabilization in lesser time compared to other mixtures. Further experiments will be carried out with co-precipitated *Be*-*Nb* mixture to compare with the *Nb* powder mixed samples.

Among various physiochemical properties of metal such as work function, thermal conductance, heat of vaporization, electron affinity, resistivity, only electron affinity displays a correlation with the current for both mixing methods. Lower the electron affinity of metal matrices higher the ion yield and similar relation is also reported by Haunt *et al.*, 2006, with different set of metal matrices. However, result of *Re* mixing does not follow the same trend based on its electron affinity as other metals like *Nb, Cu* and *Ag* shows. Thermal properties like heat of vaporization and thermal conductance of *Nb* and *Re* are comparable, whereas *Cu* and *Ag* are different. Ion yield from *Nb, Cu* and *Ag* mixture (excluding *Re*) shows negative trend with heat of vaporization and thermal conductance. Relation between ion yield with resistivity and work function of the metal is not clear from this experiment. In addition to the fundamental properties of metal matrices, other factors such as a) dispersion of metal matrices within the sample, b) depth and compactness of packing, c) suitable metal matrices and its ratio, d) method of mixing appears to be important to achieve higher and stable current during AMS measurement.

Conclusions

Result of the above systematic investigation confirms that the Be mixed (1:2, BeO to metal ratio) with the fine (1 to 5 µm) *Nb* powder provides highest and stable current (1.71µA) compared to other metal matrices and mixing methods. This is also in concordance with earlier studies at other AMS labs. *Re* powder mixture resulted lowest current and stability. Co-precipitated *Be*-*Cu* mixture (1:1, BeO to metal ratio) produces higher and stable beam current than *Ag* co-precipitated. Detailed study is in progress to find out the suitable ratio of BeO: metal powder for extended period of current stability and to check ^{10}B isobaric interference occurrence due to the co-precipitation mixing.

Acknowledgements

The authors sincerely acknowledge the AMS group of IUAC, New Delhi, IISER Kolkata and Central University of Punjab, Bathinda for providing facility and administrative support for conducting this work. Authors are also thankful to the anonymous reviewers for their critical comments, which have helped in improving the quality of manuscript.

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